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Section

MATERIALS SCIENCE AND ENGINEERING

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CERAMIC COATINGS AS THERMAL BARRIER FOR METALLIC SUBSTRATE

BY

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Abstract. For many applications at high temperatures metallic materials are no longer satisfying the mechanical properties stability. In order to protect them ceramic coating around 100 µm thick are used. Types of ceramic materials, methods and thicknesses are analyzed in this paper in to ensure the integrity of the mechanical and resistance properties at high and very high temperatures. Usage of ceramic materials as thermal barrier coatings can increase the applications number of usual metallic material or improve the super-alloys properties (for example for Inconel to increase field of application at high temperatures from 1000-1200 to 1500-1600°C using proper ceramic coatings). In order to cover the metallic materials different technologies, register important results in ceramic layers obtaining and adhesion.

Keywords: ceramic layer, thermal barrier, alumina, YSZ.

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1. Introduction

The field of advanced structural ceramic materials is widely recognized as an increasingly important field for scientists in materials, space technologies, mechanical and tribological engineering, biotechnologies, chemistry and medicine. Recent developments in understanding the fundamentals of materials science have enabled impressive progress in attempts to develop smart and very tough structural ceramic materials. Progress in the field of advanced structural ceramic materials clearly requires an in-depth understanding of several disciplines as well as the development of new design methodologies to achieve new and better properties in terms of physical performance, tribological performance, high temperature behavior and even in biological environments (Fauchais *et al.*, 2001).

In the last 30 years, thermal barrier coatings have become essential for increasing the life of gas turbines, because gas turbo engines used in aeronautics operate at very high temperatures. This coating has the role of insulating the components, protecting them at the same time from the phenomena of corrosion, erosion, thermal and mechanical stresses that appear on their surfaces under operating conditions. The use of these thermal barrier coatings allows the operating temperature to increase without increasing the temperature in the base material and can reduce the amount of air required for cooling while maintaining the turbine's operating temperature. At the same time, it improves the durability and reliability of the turbine components (Shaw *et al.*, 2000).

Thermal barrier coatings (TBCs) used on turbine blades consist of a two-layer system. The first deposited layer is a relatively thin one, called an intermediate layer, and the second sprayed layer is called a thermal barrier type layer. The intermediate layer is usually made of MCrAlY metal alloy. The purpose of this layer is to protect the substrate from oxidation and corrosion and also to improve the adhesion between the substrate and the insulating layer. Usually, the standard material used in the aeronautical industry as a thermal insulator is zirconium oxide stabilized with yttrium oxide. But due to the excessive temperature to which the sprayed parts are subjected, it leads to the formation of a thin layer of thermal oxide (TGO) resulting from the oxidation of the intermediate layer. Plasma jet spraying represents one of the most important achievements in the field of surface engineering, a field in which remarkable progress has been made in recent years. The temperature variation produces high stresses in the materials from which the parts are made, stresses that can ultimately lead to their plastic deformation, to the exfoliation of the protective layers, to the damage of the components of sub-assemblies and assemblies. Zirconium oxide has a very low rigidity, this is due to the presence of microcracks and high porosity. This leads to the appearance of small tensions in the layer and to the prevention of its exfoliation. In addition, the porosity of the layer reduces the thermal conductivity, which is desirable (Jordan *et al.*, 2001).

In this paper the possibility of using ceramic coatings as thermal barrier of metallic materials is analyzed and different arguments were given concerning this subject.

2. Considerations on ceramic coatings as thermal barrier coatings

Thermal barrier coatings (TBC), as the name suggests, provide protection to materials against exposure to high temperatures. Because operating at higher temperatures increases the energy conversion efficiency of a system, engineering applications prefer energy conversion in a highly efficient environment. However, as the operating temperature increases, the material properties degrade and the material loses its strength and can no longer withstand external stresses. Therefore, a TBC material is deposited on a substrate (such as the material of a turbine blade), which restricts the thermal exposure of the base material. Now the material base will no longer directly bear the high operating temperature and will have much lower working temperatures (> 200–300°C) than that of the ambient environment and thus retain its mechanical properties. At the same time, the substrate is also protected from other aspects such as (1) oxidation from the environment, (2) corrosion from the flowing fluid and ambient gases, and (3) wear from the cooling fluid that has a high rate of displacement and which contains various forms of dirt.

TBCs must have low weight and low thermal conductivity and they should withstand large stress variations due to heating and cooling, as well as thermal shock. They must be chemically compatible with the underlying metal and the thermally grown oxide (TGO) and should operate in an oxidizing environment. TBCs must provide thermal insulation to the underlying superalloy engine parts. They must have strain compliance in order to minimize the thermal expansion mismatch stresses with the superalloy parts. Additionally, they must reflect much of the radiant heat from the hot gas and thereby, preventing it from reaching the superalloy substrate. Further, TBCs must provide thermal protection to the substrate for prolonged service times and thermal cycles without failure (Kabacoff, 2002).

TBCs often use yttria-stabilized zirconia (YSZ) deposition on their surface due to the following qualities of YSZ materials:

1. High melting point
2. Lower density
3. Lower thermal conductivity coefficient
4. Similar coefficient of thermal expansion
5. Good resistance to corrosion and oxidation
6. Good wear resistance

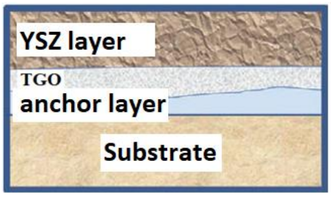

Fig. 1 – Scheme of coatings with materials used as a thermal barrier (Jadhav *et al.*, 2005).

TBC typically consists of four layers: (1) the metal substrate, (2) a metal bonding layer, (3) a thermally grown oxide (TGO), and (4) a ceramic cap layer, typically YSZ, as shown in Fig. 1. The incorporation of nano-YSZ particle sizes can have a valuable effect on fracture toughness (Fig. 2). The nanostructured YSZ ceramic material enables the elimination of cracks because the crack propagation energy can be released in the solid-state sintered nanocluster regions (Chen and Ding, 2002; Kulkarni *et al.*, 2003).

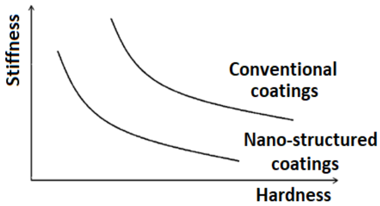

Fig. 2 – Comparative chart of hardening with nano-coatings versus conventional coatings (Gang *et al.*, 2003).

Prior to 1975, pure zirconia (ZrO2) was of very limited interest as a structural or engineering ceramic, and its use was restricted to refractory applications (Zhu *et al.*, 2001). This is attributed to the displacive tetragonal (t) to monoclinic (m) phase transformation, which occurs at ~950°C on cooling in pure ZrO2 and is accompanied by a shear strain of ~0.16 and a volume expansion of ~4%. The change of shape with the transformed volume can result in catastrophic fracture and hence structural unreliability of fabricated components. However, ZrO2 has other intrinsic physical and chemical properties, including high hardness, good wear resistance, low coefficient of friction, chemical inertness, ionic conductivity, low thermal conductivity and high melting point, which make it attractive as an engineering material. The focus of continued effort is to understand and improve its mechanical behavior (He *et al.*, 2001; Karthikeyan *et al.*, 1997). The dramatic increase in its industrial applicability has been brought about by the discovery that the t → m phase transformation can be controlled by suitable materials processing to become the source of transformation plasticity and transformation toughening in tailored, two-phase microstructures (Jadhav *et al.*, 2005).

Because of its low TEC compared to YSZ and relatively high thermal conductivity, Al2O3 did not prove to be a suitable material for the more sophisticated TBC applications (Hong *et al.*, 2005; Eigen *et al.*, 2005; Viswanathan *et al.*, 2006). The unstable phases like γ- and δ-Al2O3 make up the majority of the plasma-sprayed α-Al2O3 coating. Thermal cycling will cause these unstable phases to convert into stable -Al2O3, which is followed by a significant volume change ($\gamma \rightarrow \alpha$, ~15%) that causes microcracks to form in the coating (Tului *et al.*, 2006; Greuner *et al.*, 2005; Agarwal *et al.*, 2003; Devi, 2004). Only partially stabilize the α-Al2O3 by doping transition metal oxides into Al2O3, such as Cr2O3, Fe2O3, or TiO2. Al2O3 by itself is not a good TBC candidate, but when combined with YSZ, it can increase the substrate's toughness, hardness, and bond strength without significantly changing the substrate's Young's modulus (Goswami *et al.*, 2001). Thermal cycle lifetime of an 8YSZ-Al2O3 gradient coating is significantly longer than that of an 8YSZ coating (Liang *et al.*, 2005).

3. Conclusions

Ceramic materials represent a proper solution for thermal barriers coatings increasing the work temperature resistance of metallic materials at least with 150-200 °C. The deposition methods of the coatings provide proper adhesion properties for mechanical solicitations of the metallic elements. Corrosion protection is also enhanced using ceramic layers (chemically inert). Among oxidic or non-oxidic ceramic materials YSZ present very attractive properties as thermal barrier coating and atmospheric plasma deposition a proper technology to grow ceramic layers.

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ACOPERIRI CERAMICE CA BARIERĂ TERMICĂ PENTRU SUBSTRATURI METALICE

(Rezumat)

Pentru multe aplicații la temperaturi ridicate, materialele metalice nu mai satisfac stabilitatea proprietăților mecanice. Pentru a le proteja, se utilizează un strat ceramic de aproximativ 100 µm grosime. Tipurile de materiale ceramice, metodele și grosimile sunt analizate în această lucrare pentru a asigura integritatea proprietăților mecanice și de rezistență la temperaturi ridicate și foarte ridicate. Utilizarea materialelor ceramice ca acoperiri de barieră termică poate crește numărul de aplicații ale materialelor metalice obișnuite sau poate îmbunătăți proprietățile superaliajelor (de exemplu, în cazul Inconel, pentru a crește domeniul de aplicare la temperaturi ridicate de la 1000-1200 la 1500-1600°C, folosind acoperiri ceramice adecvate). În vederea acoperirii diferitelor tehnologii cu materiale metalice, se înregistrează rezultate importante în obținerea și aderența straturilor ceramice.

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ASPECTS REGARDING THE CHARACTERIZATION OF THE CORROSION-WEAR SYSTEMS OF THE MECHANICAL ACTUATION ELEMENTS USED FOR THE CIRCULATION OF WASTEWATER

BY

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Abstract. The paper includes a theoretical documentary study regarding the working conditions in which domestic industrial wastewater pumps operate.

The necessary properties of the materials from which the pump rotor and casing are made are mentioned in order to be able to resist erosive corrosion due to the presence of acids in the composition of the liquid, decomposed organic substances, bacteria and fungi and other chemically aggressive elements with the sewage water circulation systems.

Key words: wastewater, cavitation, submersible pump.

1. Introduction

In the last two centuries, the heavy industry and consumer goods, as well as animal husbandry, have experienced an exponential development. This contributed fully to the drying up of the drinking water reserve of the entire planet, so that the subsequent evolution of society is implicitly linked to a policy of

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cleaning and purifying wastewater so that it can be reintroduced into the natural circuit without the danger of destroying the water balance surface and depth.

a) b) c) d)

Fig. 1 – Treatment plants for industrial and domestic wastewater and their operating elements: a) wastewater treatment plant - spatial view; b) Piatra Neamț industrial water treatment plant; c) action elements; d) baths for chemical cleaning of wastewater.

In the framework of the water regeneration system used industrially and by each household user, we have, in addition to wastewater transport pipes, a biological or chemical purification basins, and a whole chain of mechanical aggregates that act for water circulation, see Fig. 1.

These aggregates also include the submersible water pumps used, which are generally high-power centrifugal pumps, which work in conditions of intense corrosive wear because the water contains strong organic and inorganic corrosive agents as well as suspensions and abrasive particles of various sizes and shapes.

Wastewater varies in composition depending on the collection area, which can be industrial, from animal breeding facilities or from domestic users containing sewage waste that includes pathogenic bacteria, fungi, organic and inorganic particles, emulsions, dissolved gases, etc. having a pH that varies between 6 and 9 (acidic pH). The most corrosive is sulfuric acid, which is found in high concentration in wastewater either as a result of production processes or as an element obtained from the reactions of decomposed organic substances (Karassik, 2001; Pracht, 2016).

To fulfill its purpose during operation, a submersible wastewater pump must withstand various mechanical and chemical stresses, such as:

- the cavitational effect due to the flow of residual water with turbulence is particularly strong and presents a danger for the integrity of the pump subassembly;

- the abrasive erosive action due to the chaotic and turbulent movement of metallic or other solid particles that hit the walls of the pumps with different forces, under variable contact angles, themselves differing in shape and size Fig. 2;

a) b)

Fig. 2 – Severe degradation of a submersible pump impeller and housing due to the combined action of mechanical abrasion and acid corrosion of the transported liquid medium: a) rotor; b) the casing.

- the thermal and mechanical action, because the pumps work outside, in winter they must withstand temperatures of up to -35°C (temperatures below 0°, when a pump is operating, create a danger of freezing the water inside the discharge chamber and on the pipes transport, microcracks appearing due to the 9% increase in the volume of frozen water) and in the summer up to 50°C; pumps that work in an immersed state must withstand the speed and force of the water containing abrasive particles;

- the acidic pH of the water which increases the content of active ions and the chemical reactivity of the liquid;

- corrosion, caused both by resulting products of industrial processes (such as degreasing acids reaching the exhaust system) and by sulfuric acid and sulfur dioxide dissolved in water that is produced as a result of the decomposition of organic origin substances;

- the increased corrosion caused by the presence of dissolved oxygen in the transported liquid, which changes the acidity of the water;

- corrosion accentuated by the fact that the non-laminar flow of the liquid flow removes the protective boundary layer on the pump's metal and the transport pipes, and the high content of chlorine and oxygen accelerates the process of chemical aggression, Fig. 3, especially for low-alloy steels and cast iron the grays (Metwally, 2008; Rothwell, 2000);

- non-uniformities in operation due to the variable viscosity of the residual water and the presence of different sizes particles in suspension;
- the action of aerobic and anaerobic bacteria on the metal from which the pump is made;
- the chemical attack of hydrogen sulfide (H_2S), which is product of sulfur-reducing bacteria from wastewater which flow into the sewer.

In addition to factors such as pH, temperature, and organic strength of the wastewater, flow rate and the impact of specific compounds in the liquid on sulfide reactions and bacterial growth must be incorporated.

a) b)

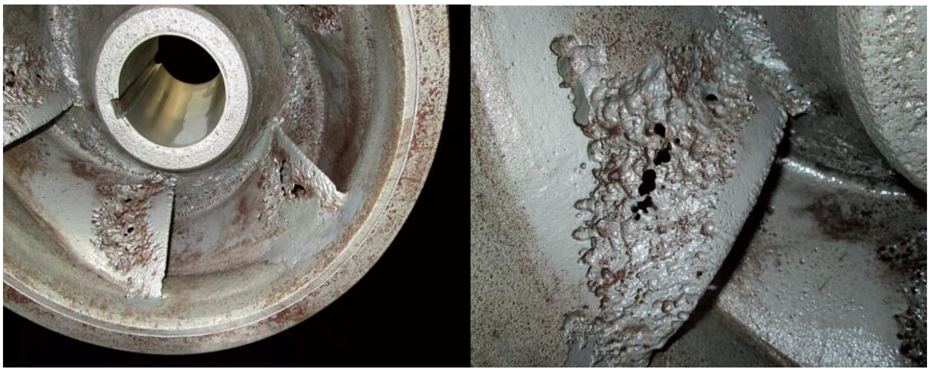
Fig. 3 – Material defects due to corrosion
a) the rotor of a wastewater pump corroded due to the presence of sand in the transfer liquid; b) intercrystalline corrosion of cast iron casing favored by the presence of solid suspensions.

The materials from which the wastewater pumps are built must be compatible with the pumped solution, so that the wear and corrosion of the materials that form the inner chambers and the transport elements are within tolerable limits. Since the pump is the heart of the filtration system, Fig. 4, it must have the ability to deliver and maintain the desired flow and pressure as dirt accumulates on the filter media (Morrow, 2010; Schweitzer, 2010).

Fig. 4 – Submersible wastewater pump.

The presence of the cavitation phenomenon in the pump is related to the large level difference between the position of the pump and the surface of the liquid (mainly in submersible pumps). Acoustic cavitation is the phenomenon of breaking and immediate restoration of a liquid under the action of sufficiently high tensions or rapid and sudden pressure variations.

Under the action of pressure changes, the average distance between the liquid particles varies until the energy necessary to break the liquid is reached. The break occurs when the acoustic pressure is of the opposite direction and cancels the pressure corresponding to the cohesive forces between the liquid particles. It was found that under the action of ultrasonic waves, the cavitation bubble increases its volume by filling with air or vapors resulting from evaporation that were in that place at the time of its formation.



a) b)

Fig. 5 – Types of wear:
a) cavitational wear in the pump rotors b) detail.

Fig. 6 – Defect due to pitting corrosion.

The appearance of the cavitation phenomenon also generates malfunctions in the pump and manifests itself when the pressure of the pump inlet is too low, causing the vaporization of the liquid inside its main body (Guo, 2016), Fig. 5, (Savin, 2017).

During pumping, the drop in liquid pressure leads to its sudden vaporization. The vaporization shows the formation of bubbles of different sizes that move quickly along the blades of the rotors. When vapor bubbles enter a region where the local pressure is greater than the saturation pressure, they suddenly burst open, creating a shock wave that over time can cause significant damage to the pump impeller or casing, Fig. 6.

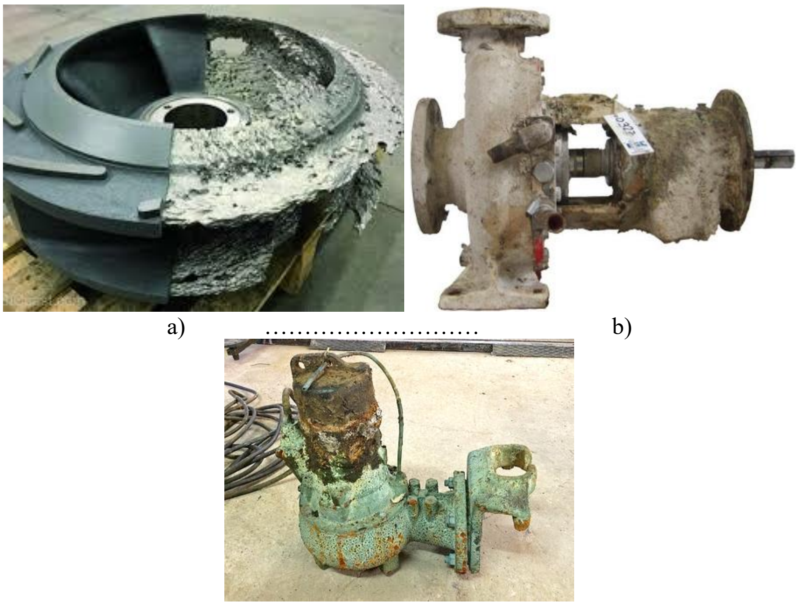
The period of operation and correct maintenance of a machine, installation, equipment, mechanism is determined by the speed with which the parts that compose it wear out. The phenomena of wear, fatigue and corrosion are the most aggressive factors that lead to the removal of the operating parameters of the installations. From this situation emerges the special importance given to the research of the physico-chemical phenomena that take place in the superficial layers in close connection with the technologies of obtaining these layers.

The present article presents a synthesis and a review of the corrosion and erosion conditions that must be faced by the materials used to make the rotors of the submersible domestic and industrial wastewater pumps in the sewage circuit in the treatment plants.

2. Corrosion of wastewater pumps

The notion of corrosion includes all chemical and electrochemical processes that result in the spontaneous and continuous degradation of the surfaces of metals and alloys. Most metals are found in nature in the form of combinations, most often in the form of oxides. This fact proves that for these metals, the metallic state is unstable from a thermodynamic point of view, in the presence of chemical and electrochemical agents, they tend to corrode, restoring the conditions from which they came.

Fig. 7 – Strongly corroded pump rotor used in sewage treatment plants.



a) ……………………… b)

c)

Fig. 8 – Corroded pumps: a) rotor with evidence of corrosion; b) corroded pump body; c) corroded pump.

Corrosion of casings, rotors and mechanical joining elements takes place in various forms, ranging from uniform attacks on the entire surface to localized attacks in certain areas that can lead to total destruction. The chemical and physical conditions of the environment determine both the type and rate of corrosion attacks. The working conditions are of particular importance and on the effects on the mechanical elements as well as on the liquid that is pushed through the pipes and that will also carry the type of corrosion products that are formed and also has an influence on the control measures that must be taken (Pump Handbook, 2004). Some degradation processes, such as erosion under the action of particle movement, cavitation, fatigue and adhesive wear are considered purely physical mechanisms and are not generally considered as chemical corrosion (Mahbuboor, 2012). Degradation processes such as general corrosion, pitting corrosion, galvanic corrosion, crevice corrosion, selective corrosion and intergranular corrosion are considered to be purely chemical in nature. Other degradation processes such as corrosive erosion, stress corrosion cracking involve mechanisms that contain both mechanical and chemical aspects.

A centrifugal pump degrades both under the action of the corrosive effect of the environment in which it works, and under the action of erosion achieved by the movement and dynamics of suspensions and solid particles in the wastewater and the action of moving parts. The physico-chemical phenomena that contribute to the degradation of the elements in the pump act both during the pump's operating period and during standby mode.

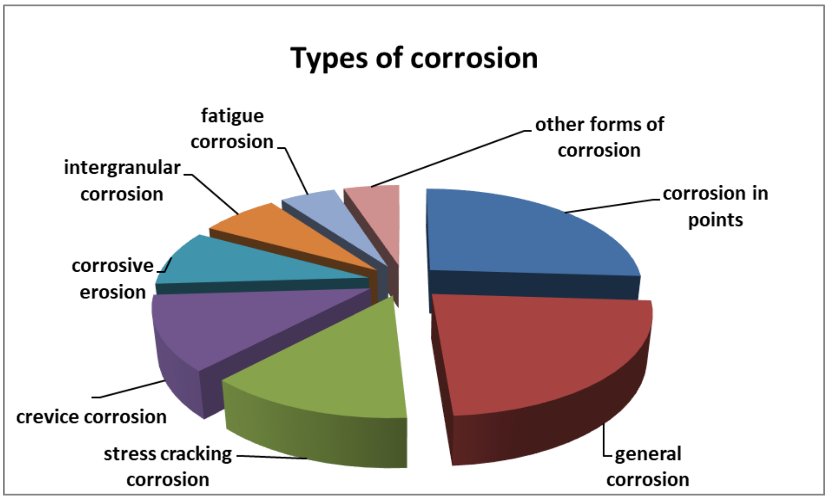


Fig. 9 – Corrosion forms encountered when corroding the constructive elements of wastewater pumps.

Due to the working conditions, the centrifugal pumps bear combined wear and corrosion attacks so that the degradation intensifies much more strongly when they work combined. Understanding the corrosion and erosion observed in centrifugal pumps involves aspects of mechanical, metallurgical and electrochemical engineering.

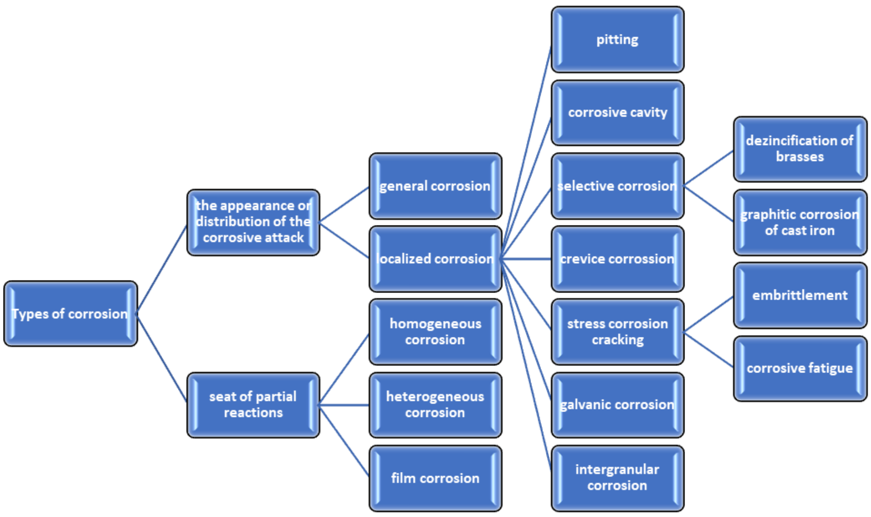


Fig. 10 – Types of corrosion.

Fig. 11 – The most usual types of corrosion.

Certain forms of corrosion are macroscopic and easily identifiable by visual examination, while others are microscopic, with identification possible by destructive metallographic examination. Corrosion in centrifugal pumps can be general in nature, affecting all wetted surfaces, or it can be localized, affecting only a small part of a single component. Often these localized forms of corrosion are the cause of corrosion-related pump failure. Localized corrosion is not easily identifiable during visual inspection and may be limited to a very small area making the probability of discovery very low if the examiner is not very experienced (Gall, 2013). Wastewater pumps mainly show the following types of corrosion, depending on the characteristics of the environment (temperature, pH, suspensions, entrained solid bodies, etc.) shown in the Fig. 10.

3. Conclusions

Taking into account everything that has been analyzed so far, we can conclude that the metal materials from which the wastewater pump is made must withstand:

- repeated mechanical demands,
- to work well without syncope in a wide range of temperatures between -50°C and +50°C,
- to transport the liquid with the same efficiency regardless of viscosity and non-uniformity,
- to resist erosion attacks due to mechanical particles entrained in the wastewater flow,

- to resist chemical corrosion due to the presence of hydrogen sulphide, bacteria and fungi present in wastewater.

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ASPECTE PRIVIND CARACTERIZAREA SISTEMELOR DE COROZIUNE-UZURĂ ALE ELEMENTELOR DE ACȚIONARE MECANICĂ UTILIZATE PENTRU CIRCULAȚIA APEI UZATE

(Rezumat)

Lucrarea prezintă un studiu documentar teoretic privind condițiile de lucru în care funcționează pompele menajere de apă uzată industrială.

Sunt menţionate proprietăţile necesare ale materialelor din care sunt realizate rotorul şi carcasa pompei pentru a putea rezista la coroziunea erozivă datorită prezenţei acizilor în compoziţia lichidului, substanţe organice descompuse, bacterii şi ciuperci şi alte substanţe chimice agresive, elemente cu sistemele de circulaţie a apei de canalizare.

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ŞTIINŢA ŞI INGINERIA MATERIALELOR

STUDY OF PROPERTIES OF ASPHALT CONCRETE USING MODIFIED BITUMEN WITH COMMERCIAL RECYCLED PLASTIC MR8

BY

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Abstract. The problem of materials recycling is one of the important problems discussed when sustainability is put into discussion. Because they are considered "dirty" some reclaimed plastics can not be recycled and remain waste. Using these materials in the technology of obtaining asphalt concrete is one of the solutions that can be at hand if some wants to reuse this kind of materials. The most important problem in this case is to find the optimum quantity of plastic that can be introduced in the composition, as bitumen modifier, to obtain some better properties or, at least not affecting negatively the properties of the resulted asphalt concrete. The present paper presents the results obtained studying the stability and flowing of an asphalt concrete BA 16 using Marshal cylinders, using the product MR8 as replacement for bitumen. At 8% MR8 in the composition, the properties of asphalt concrete remain at reasonable values comparing with the values using the classic recipe. The excess of MR8 as bitumen replacement starts at values greater than 15% reclaimed plastic added into the modified bitumen.

Keywords: plastic recycling, bitumen replacement, stability, flowing, Marshall cylinder.

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1. Introduction

The problem of materials recycling is one of the important problems discussed when sustainability is put into discussion. Plastic recycling has an important part in this matter because it is considered to be not biodegradable in normal conditions.

For example polyethylene terephthalate (PET) used for making drinking water bottles, "in post consumer" stage have sometimes, labels attached using glue and to use it in recycling technologies it must be cleaned carefully (Nwogu *et al*., 2019). This approach is water and energy consumer and the recovery technology can not ensure this kind of conditions in an easy manner and with small costs.

Other plastic items such as carry bags, sacks, milk pouches, bin lining, cosmetic and detergent bottles can not be cleaned enough to become recyclable. These materials can be considered waste in terms of recycling but there is another way of using some of them.

In India, for example, the government has introduced guidelines on use of some plastic waste in road construction (//rdso.indianrailways.gov.in/works/uploads/File/WKS-G-16.pdf).

According to this document Low Density Polyethylene (LDPE) from carry bags, sacks, milk pouches, bin lining, cosmetic and detergent bottles, High Density Polyethylene (HDPE) from carry bags, bottle caps, house hold articles, PET from drinking water bottles, and Polyurethane shall only be used in pavement construction. (//rdso.indianrailways.gov.in/works/uploads/File/WKS-G-16.pdf)

"Dirty" plastics reclaimed from garbage can not be recycled and safe disposal of these materials can be difficult. The problems generated by them vary from contaminating the material used as construction filler and reentering in the environment through wind or by water erosion, provoking the choke of the drains and drainage channels or can be eaten by grazing animals causing illness and death (//rdso.indianrailways.gov.in/works/uploads/File/WKS-G-16.pdf).

Using these materials in the technology of obtaining asphalt concrete is one of the solutions that can be at hand if some wants to get rid of this kind of waste.

On the other hand the desire to develop sustainable infrastructure, including pavement structures and materials, is ever increasing in recent times (Sustainable Asphalt Pavements, USA, 2019). When considering sustainability opportunities, it is important to take into account the effect on the durability and expected life of the pavement, as well as the reduction in financial or environmental cost of the more sustainable solution (Jamshidi and White, 2019; White, 2020).

When someone wants to use recycled plastic as replacement material for bitumen, in the asphalt concrete recipe, for example, the constraints are easy to understand: not damaging the properties of the final product and if it is possible, to enhance some of them. This approach obviously needs to find the optimum quantity of plastic that can be introduced as bitumen replacement. For example the results of the study of the combination of polyethylene terephthalate (PET) 50% + polystyrene (PS) 50% show that reclaimed plastic waste can replace 2% of the asphalt weight (Mahmuda *et al*., 2019) if used for making asphalt concrete wearing course and the product meets the asphalt modified requirements based on the Asphalt Pavement specification (Bina, 2010).

Reviewing a large number of studies (Brasileiro *et al*., 2019) concluded there are still uncertainties and gaps in the current knowledge about the use of the reclaimed polymer for asphalt modification.

This paper presents the results obtained using a commercial product made from a certain blend of reclaimed plastics, called MR8, made by MacRebur.ltd added in the asphalt concrete recipe.

2. Materials

The asphalt preparation can be done in continuous or discontinuous plants. The process consists mainly in preparing the aggregates by combining different sizes of rock particles, sand included, drying the composition, heating it at high temperatures followed by weigh batching. At this point the composition is mixed together adding into a mixer the proper quantity of filler and bitumen. Figure 1 shows the sketch of a discontinuous asphalt preparation plant that contains also the possibility of adding reclaimed plastics into the asphalt binder.

There are two possible way of proceeding – the dry process and the wet process.

In the wet process reclaimed polymers (RP) are added directly to the bitumen before mixing with aggregates (in Fig. 1, when lines “a”, “b”, and “d” are opened, keeping “c” and “e” closed). The polymers and bitumen are mixed at high temperatures for a given time in order to promote physical and chemical interactions. In the dry process, RP and bitumen can either be added to the aggregates at the same time (in Fig. 1 when lines “c” and “e” are the ones opened, and “a”, “b”, and “d” are closed) or the polymers can be added to the aggregate first as if it were another aggregate (Brasileiro *et al*., 2019).

An observation can be made here, the time of mixing needs to be larger in the dry process to enable polymer to “melt and cover” the hot aggregates and this diminish the productivity of the continuous asphalt plant, potentially affecting the economic efficiency.

One other observation to be considered is the uniformity of properties of the asphalt concrete i.e. the maintaining the recipe during preparation. Using natural raw materials there are slight differences that can be accepted but adding reclaimed plastics can be rather tricky. Obviously there is a need of controlling the quality of RP used in asphalt production and there is a need to do it at industrial scale.

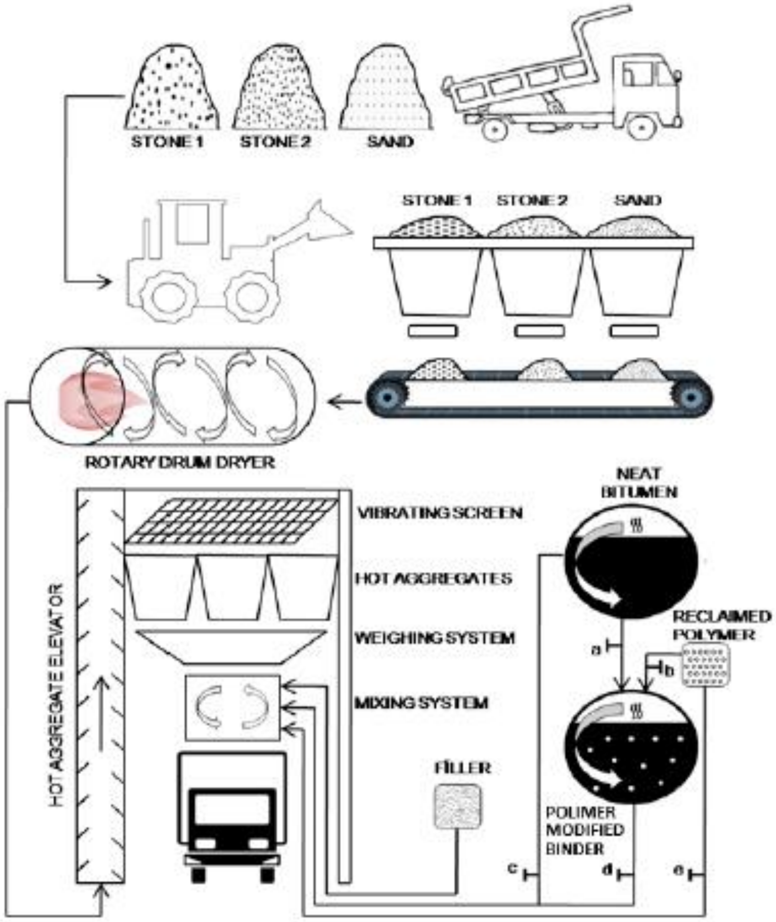

Fig. 1 – Sketch of the wet and dry process in a discontinuous asphalt plant (Brasileiro *et al*., 2019).

In Lockerbie, Scotland, U.K. there is a company called MacRebur.ltd which goal is to solve this issue, Fig. 2. The products made by MacRebur.ltd are made from non–recyclable reclaimed plastics considered waste and destined for landfill and incineration.

The product MR8 studied in this paper is “a blend of polymers designed for the extension of the bituminous binder for asphalt used in road surfaces. The manufacturer presents it as “ideally suited for car parks, driveways and local roads where sustainability and economics are the primary drivers” (https://macrebur.com/the-product).

This product modifies the natural bitumen and replaces a part of it in the asphalt recipe.

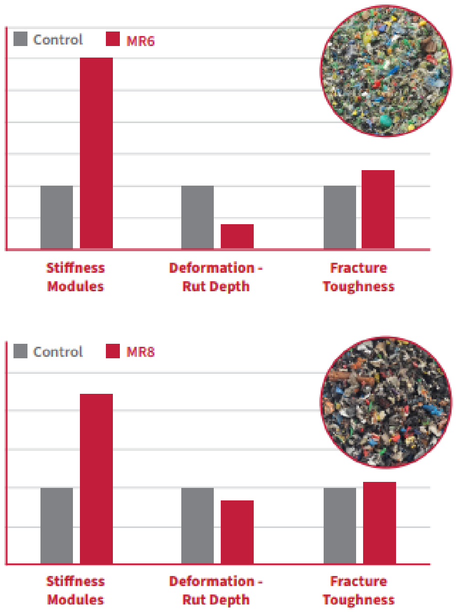

Fig. 2 – Commercial presentation of Mac Rebur products used in asphalt concrete recipe (https://macrebur.com/pdfs/product/MacReburProductSheet_v3.pdf).

The goal of the study is to determine the proper quantity of MR8 to be added in the hot bitumen (wet process) for obtaining the best properties of the asphalt made from natural aggregates obtained from a certain source from the Republic of Moldova. We consider this approach interesting because the natural aggregates used for asphalt obtaining are different in what concern the chemical composition, shape, granulometry and more over, their preparation depends of the technological endowment of the producer. In these conditions the effects of a new component in the recipe, MR8 has to be controlled first in laboratory conditions and after that on large scale to ensure the best properties for the asphalt concrete. The asphalt concrete studied is BA 16 used for parkings, driveways and local roads. The choice for this kind of asphalt was dictated by the producer of the MR8 that recommends the use of it as bitumen modifier or replacement for this kind of situations.

3. Experimental method

In order to perform laboratory tests on asphalt concrete using MR8 as bitumen modifier there were prepared samples according SM SR EN 12697-27 by dehydration.

We have used for testing Bitumen type BR 50/70 suitable for polymer modification. The modifier MR8 was inserted in a supplementary mixing process of hot bitumen and the quantities used in the experiment ranged from 8% to 35%. The properties of asphalt mixtures obtained using modified bitumen were compared with those of an usual concrete asphalt BA 16 made by the classic recipe using 5.7% bitumen BR 50/70.

There were tested 9 different recipes for modified bitumen in the attempt of identification of the optimum polymer content in the asphalt mixture able to enhance properties and also to establish the turning point when the modifier added is in excess.

For obtaining the control specimen the material was sampled “from the track” and prepared according SM SR EN 12697-27 and the sub samples for each test were prepared according SM SR EN 932-2.

The samples with modified bitumen were made separately using a smaller mixer and the same aggregate dosage as for the control specimen.

3.1. Testing equipment

The testing equipment was a Marshall Stability tester. The automatic apparatus can be used for determining the maximum load and the values of flowing of bituminous mixtures according to the standards EN 12697-34; 12697-23 and 12967 -12.

Fig. 3 – Photograph of the Marshal Stability tester (https://www.multilab.ro /asfalt/ aparat_Marshall_50KN.html).

The testing parameters can be established using the incorporated software. The testing program has the ability of continuously actuating the load and the displacement until the test is finished. The data are registered using the incorporated DataLoger acquisition system and the graphical output can be saved as MS Excell sheet and printed (https://www.multilab.ro).

4. Results

The results obtained on the Marshall cylinders for the 9 samples are given in the Table 1, 2, 3 and 4.

Sample I is the control sample of asphalt concrete BA 16, obtained in the classic technology.

Sample II is made using the same aggregate composition and has 8% MR8 in the bitumen.

Table 1
Asphalt concrete properties obtained using 8% and 10% content of MR8 in the bitumen as replacement

Characteristics on the Marshall cylinder	MU	Obtained values			Admissible values CP D.02.25
		I	II	III	
MR content in bitumen quantity (5.7% bitumen)	%	0	8	10	
Stability (S) at 60°C	KN	12.2	11.6	10.4	6.5...13.0
Flowing index (I)	mm	2.5	1.9	1.8	1.5...4.0
S/I Ratio	KN/mm	4.9	6.1	5.7	min. 1.6
Apparent density	Kg/m^3	2.49	2.49	2.49	-
Water absorption in volume	%	1.5	-	1.61	1.5...5.0

Table 2
Asphalt concrete properties obtained using 12% and 15% content of MR8 in the bitumen as replacement

Characteristics on the Marshall cylinder	MU	Obtained values			Admissible values CP D.02.25
		I	IV	V	
MR content in bitumen quantity (5.7% bitumen)	%	0	12	15	
Stability (S) la 60°C	KN	12.2	10.4	8.9	6.5...13.0
Flowing index (I)	mm	2.5	1.6	1.9	1.5...4.0
S/I Ratio	KN/mm	4.9	6.4	4.8	min. 1.6
Apparent density	Kg/m^3	2.49	2.49	2.49	-
Water absorption compared with the sample volume	%	1.5	-	-	1.5...5.0

Sample III is made using the same aggregate composition and has a content of 10 % MR8 in the modified bitumen composition.

Samples IV and V are made using 12% and respectively 15% MR8, as replacement of bitumen.

Sample VI, VII, VIII and IX have respectively 20%, 25%, 30% and 35% MR8 as replacement for bitumen.

The values obtained at the Marshall test can be compared in each table with the one shown in the first column, values represented the control sample.

Table 3

Asphalt concrete properties obtained using 20% and 25% content of MR8 in the bitumen as replacement

Characteristics on the Marshall cylinder	**MU**	**Obtained values**			**Admissible values CP D.02.25**
		I	**VI**	**VII**	
MR content in bitumen quantity (5.7% bitumen)	%	0	20	25	
Stability (S) la 60°C	KN	12.2	16.5	16.2	6.5...13.0
Flowing index (I)	mm	2.5	2.0	2.2	1.5...4.0
S/I Ratio	KN/mm	4.9	8.5	9.8	min. 1.6
Apparent density	Kg/m^3	2.49	2.47	2.46	-
Water absorption compared with the sample volume	%	1.5	0.7	1.9	1.5...5.0

Table 4

Asphalt concrete properties obtained using 30% and 35% content of MR8 in the bitumen as replacement

Characteristics on the Marshall cylinder	**MU**	**Obtained values**			**Admissible values CP D.02.25**
		I	**VIII**	**IX**	
MR content in bitumen quantity (5.7% bitumen)	%	0	30	35	
Stability (S) la 60°C	KN	12.2	16.9	15.0	6.5...13.0
Flowing index (I)	mm	2.5	2.4	1.4	1.5...4.0
S/I Ratio	KN/mm	4.9	10.2	10.9	min. 1.6
Apparent density	Kg/m^3	2.49	2.43	2.40	-
Water absorption compared with the sample volume	%	1.5	2.7	4.4	1.5...5.0

The results obtained are shown in Fig. 4 for an easier comparison.

The first sample represents an asphalt concrete BA 16 type destined for parkings, local roads and drives, made using neat bitumen. The values of the characteristics of it are considered the reference base for comparison, all of them being in the range of admissible standard values.

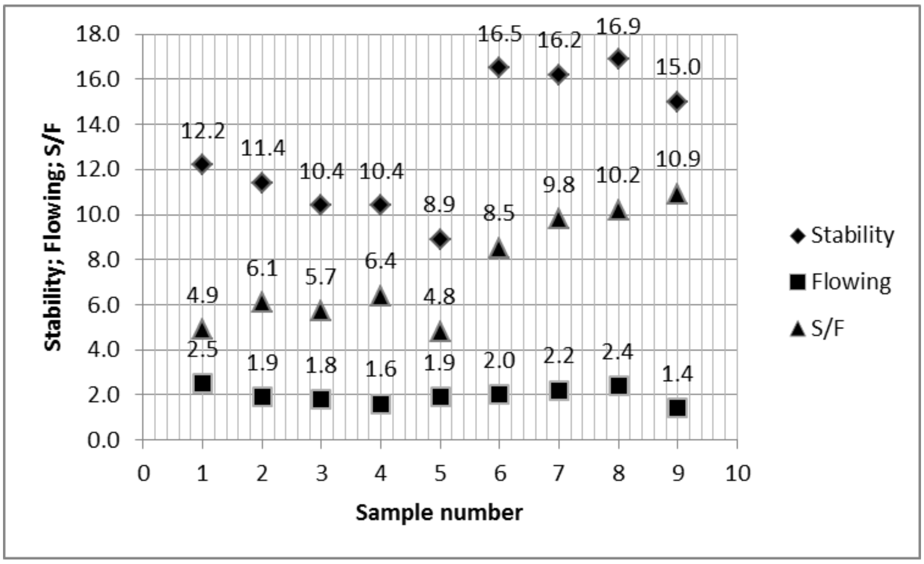

Fig. 4 – Values obtained for the stability, flowing and stability/flowing ratio for the asphalt concrete samples studied.

The second sample, using 8% of MR8 in the composition of the bitumen compared with the shows less value for stability and for flowing and the ratio between them is greater than the limit point 1.6; all the values are admissible and do not affect negatively the product. A slight improvement can be seen in flowing and a significant improvement in S/F ratio. The less stability is not so important for the category of road at which the material is destined to be used.

For 10% MR8 in the composition of the bitumen, the third sample, one can see a less value for stability and for flowing and the ratio between them is greater than the limit point 1.6; all the values are admissible and do not affect negatively the product. A slight improvement can be seen in flowing and an improvement in S/F ratio. The less stability is even greater than for sample 2 but not so important for the category of road at which the material is destined to be used.

For the forth sample, MR8 12% in the bitumen the stability remains at the same value as sample 3 and the flowing goes down to 1.6 that is a turning point, both values S and F are in the admissible limits. The ration between S/F has the highest value 6.4 also a turning point.

The fifth sample, 15% MR8 shows a decrease of stability about 25% compared with the reference value. The flowing enhances and the ration S/F is less then the reference. However, all the values for this composition are in the admissible range.

The sample 7, 8 and 9 corresponding to 20%, 25% and 30% show inadmissible value for the stability over the standard limit that is 13. For sample 7 and 8 the flowing is still in the range of admissible values.

The only composition that does not meet the flowing admissible value is sample 9.

4. Conclusions

After testing 8 different compositions of asphalt concrete made with MR8 added in the bitumen using the Marshall cylinder method we concluded that the replacement material do not affect negatively the product up to 15% concentration, all values regarding the stability and flowing being admissible.

Adding 8% MR8 in the bitumen lead to a stability of 93% compared with the reference considered in the test and 24% plus at flowing value. We consider it the most recommended value.

Adding 10% or 12% MR8 in the bitumen as lead to 85% stability compared with the reference considered in the test and 16% respectively 30% plus at flowing value.

More that 15% of MR8 added in the bitumen for making the asphalt concrete BA 16 using the same aggregate composition affects negatively the admissible values for asphalt concrete stability.

More research has to be done to establish the water absorption and water stability values for determining in a more comprehensive way the effect of MR8 as replacement of bitumen in BA 16 asphalt concrete.

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STUDIUL PROPRIETĂȚILOR BETONULUI ASFALTIC UTILIZÂND BITUM MODIFICAT CU PLASTIC RECICLAT MR8

(Rezumat)

Problema reciclării materialelor este una dintre problemele importante când se pune în discuție sustenabilitatea. Deoarece sunt considerate "murdare" unele materiale plastice recuperate nu pot fi reciclate și rămân deșeuri. Utilizarea acestor materiale în tehnologia de obținere a betoanelor asfaltice este una dintre soluțiile care poate fi la îndemână pentru a refolosi totuși aceste materiale. Cea mai importantă problemă în acest caz este găsirea cantității optime de plastic care poate fi introdusă în compoziție, pentru a modifica bitumul, pentru obținerea unor proprietăți mai bune sau cel puțin pentru a nu afecta negativ proprietățile betonului asfaltic ruzultat. Lucrarea de față prezintă rezultatele obținute la studiul stabilității și fluajului unui beton asfaltic BA 16 utilizând cilindri Marshall, folosind produsul MR8 ca înlocuitor de bitum. La 8% MR8 în compoziție proprietățile betonului asfaltic rămân la valori rezonabile prin comparație cu rețeta clasică. Excesul de MR8 ca înlocuitor de bitum începe de la valori de peste 15% plastic reciclat introdus în bitumul modificat.

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BIODEGRADABLE ZINC-BASED ALLOYS WITH HIGH POTENTIAL FOR MEDICAL APPLICATIONS

BY

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Abstract. A biodegradable Zn-based alloy have been developed for the purpose of being used for possible applications such as advanced orthopedic implant. This type of implants can be an alternative to conventional implants to avoid a second surgery and reduce or even eliminate the problems with biocompatibility. In this article, the current research status summarizes the biodegradable materials based on Zn. Briefly discuss the biological function of Zn, the design standards of orthopedic implantation, and the corrosion behavior of biodegradable materials. Many new types of biodegradable zinc-based alloys are evaluated based on biological disassembly, biocompatibility and mechanical performance assessment. Zn-based materials play an important role in the growth of skeletal metabolism and new cells, and shows a degradation without excessive hydrogen release. Over the years, great efforts have been made to achieve excellent mechanical performance of such alloys. Adding different components to pure Zn, such as Mg, Ca, Mn, or Li, can improve the mechanical properties of Zn alloy.

Keywords: biocompatibility, alloy, mechanical properties, biodegradable, implant.

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1. Introduction

Orthopedic devices for implant are used to repair fractures or replace broken bones. Metallic devices used to repair fractures, can cause side effects such as osteoporosis and slow bone healing (Li *et al*., 2022; Xing *et al*., 2022). Other problems associated with conventional fasteners include allergic reactions, corrosion, ion release, fatigue failure, hydrogen release, and the necessity of a second surgery (Unune *et al*., 2022; Wang *et al*., 2022). Biodegradable materials have been developed to solve the problems associated with non-degradable devices (Paiva *et al*., 2022; Pothupitiya *et al*., 2022). Magnesium and zinc based materials are suitable biomaterials for the development of biodegradable devices because present a good degradation rate.

Excessive release of magnesium-based degradation products limits its use for biomedical applications (Jana *et al*., 2022). In contrast to Mg-based materials, biodegradable Zn alloys show average degradation rates. Their biodegradation products are completely biodegradable without releasing hydrogen. If we compare with Mg alloys, Zn alloys show lower corrosion rates (Di *et al*., 2022). Many zinc-based alloys have been used by incorporating bioactive substances or by adapting material processing methods in order to improve biodegradation rates and mechanical properties.

These alloys have great potential to be developed as advanced orthopedic implants with scope to replace conventional implants. Several challenges such as biodegradation behaviour and mechanical properties must overcome to qualify them for medical applications (Hussain *et al*., 2023). In recent years, many papers on Zn-based biodegradable materials have been published. Yuan *et al*. (2022) summarizes a surface modification method for Zn-based biodegradable materials. Li *et al*. (2020) presents challenges and opportunities for the development of Zn-based biodegradable materials.

Shi *et al*. (2020) discuss about the effects of secondary phase and alloying elements on the mechanical properties of Zn-based alloys. Huang *et al*. (2022) discusses the effect of alloying elements on the softening phenomenon of Zn-based biodegradable materials. Che *et al*. (2022) investigated the development of biodegradable metal-based membranes for bone regeneration applications. This article introduced the current state of some research based on biodegradable zinc alloy. Many zinc-based biodegradable materials studied in recent years have been evaluated in terms of biodegradability, biocompatibility, and mechanical properties.

2. Production by casting of zinc-based alloys

Zinc-based alloys are manufactured by casting, as this allows easy adjustment of the alloy composition and the widest possible variety. Casting allows us to produce complex shapes, but casted products can have defects such as shrinkage cavities, voids and cracks, and the dimensional accuracy of castings is poor compared to machined parts. Obtaining alloys by casting involves melting raw materials and pouring him into moulds, where solidifies it. Melting takes place in a furnace (with resistance or induction) at temperatures between 450 - 700°C, depending on the composition of the alloy (Fig. 1). A controlled environment is required during casting to prevent oxidation reactions and to control gas dissolution to avoid porosity. The molten material is poured into a suitable graphite mould with the desired shape and dimension for solidification (Gong *et al*., 2015; Yue *et al*., 2017; Ehsan *et al*., 2016). After cooling, the steel ingot obtained is taken out, mechanically turned, cut, and ground to obtain a sample for further investigations.

a) b) c) d)

Fig. 1 – Alloys obtaining.
a) Induction furnace, b) Raw material, c) Casting moult, d) Ingot.

3. Alloying of zinc-based biodegradable

Mg is an excellent alloying element, and Zn-Mg binary alloy can be formed by casting. Compared with pure Zn, Zn-Mg binary casting alloys were found to have greatly improved microhardness, tensile strength and elongation. In addition to the reported biodegradable Zn-Mg alloys, the essential nutrients Ca, Sr, Sn, Fe have also been investigated. Other elements Y, Li, Mn that are used as alloying elements for biomedical applications can also be considered as potential alloying elements when developing new biodegradable zinc alloys. Mostad *et al*. (2015) developed a series of Zn-Mg alloys with different Mg mass fractions (0.15%, 0.5%, 1%, 1.5%, 2%, 3%,4%, 5%). The mechanical properties of zinc-magnesium-based alloys developed in recent years are shown in Table 1.

Table 1
Mechanical properties of Zn-Mg based alloys

Composition [wt.%]	TYS [MPa]	UTS [MPa]	EL [%]	Ref.
Zn-0.1Mg	72	81	0.6	(Liu *et al.*, 2019)
Zn-0.5Mg	92	108	0.8	(*Liu et al.*, 2019)
Zn-1Mg	113	137	0.9	(Tong *et al.*, 2020)
Zn-1.5Mg	120	151	1.3	(Liu *et al.*, 2016)
Zn-2Mg	117	162	4.1	(Yang *et al.*, 2018 a)
Zn-3Mg	64	84	1.3	(Dambatta *et al.*, 2017)
Zn-4Mg	132	166	3.1	(Yang *et al.*, 2018a)

4. Short presentation of physical and mechanical properties of bone, main non-biodegradable and biodegradable materials

Table 2 shows some physical and mechanical properties of previously known non-biodegradable and biodegradable materials and properties of natural bone tissue. Pure zinc has the smallest σ_{UTS}, σ_{TYS} and ε among all metallic biomaterials. The development of zinc alloys with improved σ_{UTS} (tensile strength), σ_{TYS} (tensile strength) and ε (elongation) is one of the main prospects as candidate materials for potential medical applications.

Table 2
Psychical and mechanical properties of non-biodegradable and biodegradable metallic materials

Material	ρ (g/cm^3)	σ_{UTS} (MPa)	σ_{TYS} (MPa)	E (GPa)	ε (%)	Ref.
Cortical bone	1.8-2.0	35-283	106-114	5-23	1.07-2.1	(White *et al.*, 2008; Black and Hastings, 1998)
Trabecular bone	1.0-1.4	1.5-38	1-12	0.01-1.6	2.20-8.5	(White *et al.*, 2008; Giesen *et al.*, 2001)
316L stainless steel	8.0	450-650	200-300	190	30-40	(Black and Hastings, 1998)
Co-Cr alloy	9.2	860	310	210	20	(Chen *et al.*, 2018)
Ti-6Al-4V	4.4	895-1025	825-869	110-114	6-10	(Niinomi, 1998)
Pure Mg	1.7-2.0	90-190	65-100	41-45	2-10	(Agarwal *et al.*, 2016)
Pure Fe	7.8	180-210	120-150	211.4	40	(Schinhammer *et al.*, 2010; Mani *et al.*, 2007)
Pure Zn	7.14	18-140	10-110	1.2-2.1	0.3-36	(Levy *et al.*, 2017; Čapek *et al.*, 2018)

The mechanical properties of zinc alloys can be improved by adjusting their microstructure through alloying and special fabrication techniques, followed by multiple post-treatments (Venezuela *et al*., 2019; Zhao *et al*., 2017a; Sikora-Jasinska *et al*., 2017; Zhao *et al*., 2017b).

5. Applications of zinc based biodegradable alloys

Zn-based biodegradable alloys have great potential to become a new class of biodegradable devices, but there are still some problems to be overcome for the successful clinical design of Zn-based biodegradable alloys. As a rising star, Zn-based biodegradable alloys are promising in medical applications due to their various optional fabrication and processing methods, tuneable mechanical properties, reasonable degradation behaviour, and good biocompatibility. Great interest and potential. Zinc-based alloys are used in a variety of medical applications such as wound closure devices (biodegradable staples, clips, plugs, microcracks and rivets), orthopedic fasteners (fixation plates, screws and porous scaffolds), cardiovascular stents and bone implants (Table 3).

Table 3
Medical applications of Zinc-based alloys

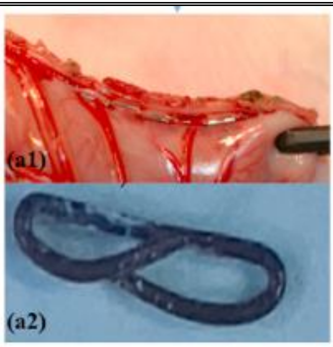
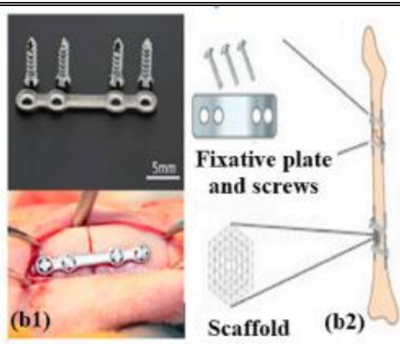
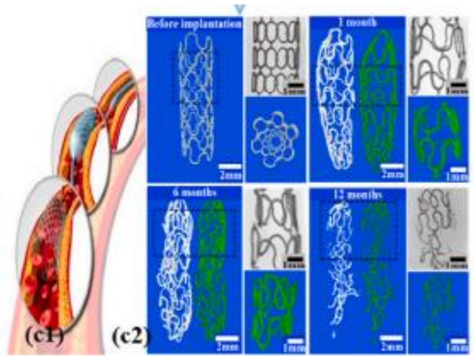
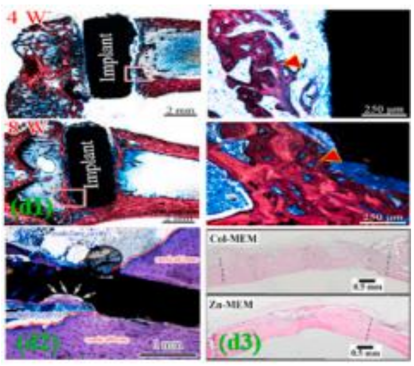
Wound closure devices	**Orthopedic fixation device**
	
(a1) staple line made from Zn based alloy (Muley *et al*., 2016) (a2) macroscopic view of Zn alloy staples (Amano *et al*., 2020)	(b1) Zn alloy plate and screws, and fixed mandibular bone fractures (Wang *et al*., 2019) (b2) Zn-based alloy fixative plates, screws, and porous scaffolds (Su *et al*., 2019)

Table 3
Continuation

Cardiovascular stents	**Bone implants**
	
(c1) stent implantation into a coronary vessel (Mostaed *et al*., 2018) (c2) 2D and 3D micro-CT images of Zn stents (Yang *et al*., 2017)	(d1) Characterization of hard tissue sections of Zn-5HA composite implantation sites at 4 and 8 weeks. Red triangles indicate newly formed bone (Yang *et al*., 2018b) (d2) Observation of different parts of the implant after 6 months (Bian *et al*., 2018) (d3) Image showing the maturation of newly formed bone in the Zn-MEM group compared to the not yet mineralized bone matrix in the Col-MEM group (Chou *et al*., 2016).

6. Conclusions

The demand for clinical orthopaedic implants for age-related bone diseases is increasing. Adding alloying elements such as Mg, Ca, Mn and Zn based materials can meet the required design criteria. Microstructural refinement can be achieved using post-processing deformation techniques. Due to their desirable mechanical properties and degradability, zinc-based biodegradable materials have the potential to become orthopaedic implants for treating difficult bone diseases. This paper revealed the biological functions of Zn, design criteria for materials in orthopaedic implants, and the performance of Zn-based biodegradable alloys.

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ALIAJE BIODEGRADABILE PE BAZĂ DE ZINC CU POTENȚIAL MARE PENTRU APLICAȚII MEDICALE

(Rezumat)

Aliajele biodegradabile pe bază de Zn au fost dezvoltate cu scopul de a fi utilizate pentru posibile aplicații, cum ar fi implanturile ortopedice avansate. Acest tip de implant poate fi o alternativă la implanturile convenționale pentru a evita o a doua intervenție chirurgicală și pentru a reduce sau chiar a elimina problemele de biocompatibilitate. În acest articol este prezentat stadiul actual al cercetărilor materialelor biodegradabile pe bază de Zn. În principal, s-a urmărit funcția biologică a Zn-ului, standardele de proiectare ale implantării ortopedice și comportamentul la coroziune al materialelor biodegradabile. Multe tipuri noi de aliaje biodegradabile pe bază de zinc sunt evaluate pe baza biocompatibilității și a evaluării performanței mecanice. Materialele pe bază de Zn joacă un rol important în creșterea metabolismului scheletic și a celulelor noi și prezintă o degradare fără eliberare excesivă de hidrogen. De-a lungul anilor, s-au făcut eforturi mari pentru ca astfel de aliaje să capete performanțe mecanice excelente. Adăugarea diferitelor componente la Zn pur, cum ar fi Mg, Ca, Mn sau Li, poate îmbunătăți proprietățile mecanice ale aliajului de Zn.

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PREPARATION METHOD OF ECOFRIENDLY GEOPOLYMER BRICKS REINFORCED WITH RECYCLED GLASS FIBERS

BY

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Abstract. Fiber-reinforced geopolymers have the ability to successfully replace Ordinary Portland Cement-based products while meeting the current requirement to reduce CO_2 emissions associated with the building materials sector. In addition, by introducing different types of recycled fibers in their composition, the intrinsic brittleness of the geopolymer matrix can be eliminated, while providing a sustainable solution to reduce waste generation and landfill. In this study, the methodology and schematic representations of an industrial manufacturing technology are presented. With this technology, innovative bricks as well as other types of prefabricated products made of geopolymer composites reinforced with recycled glass fibers can be obtained. Furthermore, the proposed geopolymers are cured at room temperature and use coal ash as raw material. Also, the aim of introducing recycled glass fibers is to improve the bending strength of the obtained precast and to eliminate the main limitation associated with the brittleness of these products.

Keywords: recycled glass fibers, geopolymer composite, microstructural analysis, coal ash, eco-friendly.

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1. Introduction

Nowadays, the most common building element is concrete (Gebremariam *et al*., 2021). Annually, over 32 billion tons of concrete are produced worldwide, and a significant increase is foreseen (Amran *et al*., 2022). Concrete is an oxide material made of a mix of aggregates, cement, water, and different types of reinforcements. Considering the environmental effect of using this material, ordinary Portland Cement (OPC) consumption is the one with the highest concern because OPC production alone is considered responsible for the emission of up to 9% of the total amount of gases affecting the atmosphere (He *et al*., 2019). Next to the environmental disadvantages, concrete also shows high brittleness, and its use is strongly dependent on its reinforcements (Zhang S. *et al*., 2021). Cement manufacturing contributes to climate change by consuming a lot of energy, especially during calcination, and emitting high amounts of CO_2 into the environment. The kiln temperature takes place at around 1500°C for cement manufacturing in order to calcine the limestone (Habert, 2013). To produce the necessary heat, large volumes of anthropogenic fossil fuels are consumed, resulting in CO_2 emissions and the consumption of non-regenerable virgin raw materials. The quantity of CO_2 created in the raw mix by limestone calcination is greater than the amount of CO_2 produced during burning; up to 1.3 tons of CO_2 emissions per ton of calcinated lime have been reported (Shan *et al*., 2016). Currently, there is a worldwide concern and preoccupation with finding alternatives that can contribute to the reduction or removal of the harmful consequences of cement manufacturing. Furthermore, numerous governments have lately vowed and established objectives for carbon neutrality. This target cannot be achieved only by improving the energy efficiency of different manufacturing technologies; recycling previously generated waste and developing only recyclable-by-design materials are also necessary. Moreover, this transition must occur while conserving the natural environment.

In the construction industry, one promising method seems to be the recycling of demolition waste or any other building material that can be considered end-of-life (Alani *et al*., 2022; Elchalakani and Elgaali, 2012). Moreover, the use of recycled waste materials in specified amounts to replace components such as cement and aggregates in the manufacturing of cement-based concrete provides essential support for energy savings and environmental preservation. A greener alternative to OPC-based materials was found in geopolymer technology, but still, some of the intrinsic limitations (brittleness) couldn’t be removed (Steinerova *et al*., 2017). Geopolymers are also mixing materials whose properties are strongly influenced by the characteristics of the raw materials and also by the manufacturing parameters, i.e., mixing parameters, curing time, temperature, etc. (Aziz *et al*., 2019). Considering their similar properties to those based on OPC, most of the fibers that can be used to reinforce concrete structures are compatible with geopolymer matrix (Ranjbar and Zhang, 2020). To further reduce the negative environmental impact, different types of fibers, especially secondary byproducts, can be incorporated into the mixture, and the matrix itself can be synthesized using recycled wastes that have a high content of Al and Si oxides (Burduhos-Nergis *et al*., 2022; Hao *et al*., 2022). In (Das and Rout, 2023), the authors conducted a comprehensive state-of-the-art study on the possible utilization of fly ash as a substitute for virgin, non-regenerable, alumino-silicate sources. Many other studies have been conducted on the use of iron, steel, aluminum, copper, zinc, and similar mine tailings in the creation of green concrete by partially substituting the virgin aggregates with this recyclable mineral (Burduhos-Nergis *et al*., 2022; Taylor *et al*., 2015; Vizureanu *et al*., 2021). The utilization of mine tailings in concrete manufacturing is viewed as promising for decreasing waste and safeguarding natural resources. It has been discovered that not all mine tailings are suitable for incorporation; some of them, especially those reaching in sulfides, when used in powder, sawdust, or dissolved form, have a larger porosity due to gas generation and the consequent expansion. Concrete strength degrades as a result of the porosity caused by gas development. However, there are still many aluminosilicate minerals that aren't currently integrated into any manufacturing technology, which could reduce landfilling at a relevant rate (recycling rate higher than production rate).

Sustainable development is becoming increasingly popular due to the dumping of hazardous solid waste from industry, such as fly ash (FA), slag, and red mud (RM). It is estimated that the global yearly output of FA is between 71 million and 1 billion metric tons, resulting in a severe threat to the environment (Kheimi *et al*., 2022). This includes air, soil, and water pollution caused by the leakage of different dangerous substances. Waste from mining and processing sulfidic ores to create Cu, Zn, Pb, Ni, and other essential metals is the largest extractive waste in Europe. The improper handling of waste can cause environmental problems, such as acid mine drainage, which is the discharge of acidic water from mine sites. As the transition to a green, circular civilization moves forward, these by-products will provide essential raw materials for other industries. In Europe, approximately 600 metric tons are generated annually, with an estimated 28 000 metric tons in tailing storage facilities, dry piles, or backfilled mines (*Mine Tailings to Treasure: Providing Society with Sustainable Resources | NEMO Project | Results in Brief | H2020 | CORDIS | European Commission*, n.d.). In China, only the red mud emissions exceeded 3.5 million metric tons, while its utilization rate was only 5.24% (Zhang L. and Schwärzel, 2017). The massive accumulation of mine tailings takes up land resources, even causing severe ecological problems such as surface water pollution, groundwater pollution, and soil alkalinization. Moreover, when it comes to municipal household waste, most of it is still disposed of in landfills or incinerated (almost 50% at the European level). There is no doubt that this waste will cause soil pollution, water pollution, and air pollution.

The application of geopolymer materials can effectively solve waste landfilling and all environmental problems caused by this poor management of mineral by-products. Fire resistance, chemical corrosion resistance, great mechanical strength, and exceptional durability are all benefits of geopolymers. Geopolymeric materials have been considered alternatives for ordinary Portland cement (in all its applications) since the early 1980s, owing to their reduced carbon dioxide emissions and performance benefits. Moreover, previous publications show the successful application of geopolymers as coating materials with excellent properties such as high strength, artificial aging resistance, high temperature resistance, and good processing performance, which can be used as coatings for lightweight polystyrene wall, roof, and partition tiles. Therefore, this study aims to propose and describe some methods of obtaining innovative bricks and other types of precasts from geopolymer composites. Moreover, to overcome the intrinsic limitation of geopolymers, i.e., brittleness, recycled glass fibers are presented as a potential reinforcement, while the products are cured at room temperature for energy efficiency.

2. Geopolymers obtaining

Geopolymers, being inorganic polymeric materials, are classified as an alkali-activated material subtype. Geopolymers are a subset of alkali-activated materials that contain more Al than Ca based on their Ca and Al concentrations. Furthermore, geopolymers may be produced using acid activators; therefore, the phrase “geopolymers are alkali-activated materials” is incorrect. Geopolymers can use natural and waste materials as primary raw materials in alkaline or acidic activation reactions. Therefore, the formation of geopolymers takes place after mixing a solid material rich in Al and Si oxides with an alkaline or acid solution suitable to dissolve the structure of the minerals from the aluminosilicate source. The formation reaction is known as “geopolymerization”. Geopolymerization is a chemical process that can take place at room temperature or at high temperatures, resulting in an amorphous phase and a three-dimensional silico-aluminate network structure (Burduhos Nergis *et al*., 2018). It can be divided into three main steps: dissolution of aluminosilicate materials in concentrated alkaline or acid solution; transfer; solidification or gelation of materials; condensation reaction of alumina and silica hydroxyl; and hardening of the gel phase. As the gel phase hardens, it condenses to form a three-dimensional silicoaluminate network (Joseph, 2008).

According to literature (Burduhos Nergis *et al*., 2020), for alkali-activated geopolymers, a mixture of Na_2SiO_3 and NaOH (in a ratio of 3/2 Na_2SiO_3 to NaOH) and a concentration of 10 M NaOH led to the highest dissolution rate of Si^{4+} and Al^{3+} ions in aluminosilicate materials compared to the lower concentration of NaOH, which resulted in a higher degree of geopolymerization. For acid geopolymers, it was observed that an Al/P molar ratio of 1 would possess optimal properties. Curing temperature is essential for geopolymerization, as it accelerates the dissolution of raw materials and creates a faster formation of the amorphous phase peak in XRD models (Cong and Cheng, 2021).

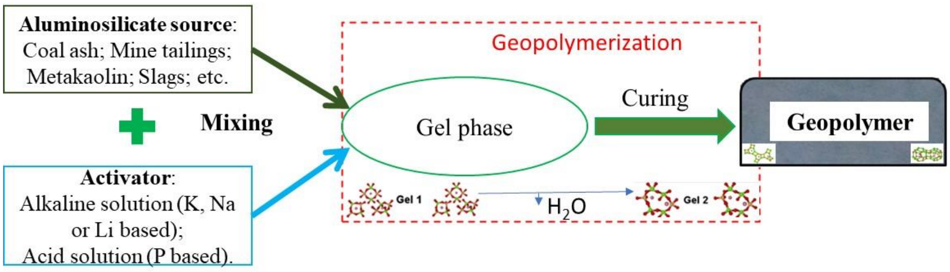

Fig. 1 – Schematic representation of geopolymers obtaining.

According to previous studies (Shehata *et al*., 2021; Zhang P. *et al*., 2020), the geopolymers can be created starting with one or two components. In the case of one-component geopolymers, the activator and the aluminosilicate source are both in dried form. Therefore, the mixing stage is necessary only for the water addition that will make the activator dissolute and start the catalytic effect. This method shows some advantages related to the safety concerns associated with the storage and manipulation of activators in liquid form; however, during the dissolution of alkaline activators, an exothermic reaction will take place that can affect the workability of the mixture and the durability of the mixing equipment. In the case of two-component geopolymers, the activator is prepared 24 hours before mixing, so the exothermic effect is removed, and mixed with the solid component in the first stage of manufacturing (as presented in Fig. 1). Therefore, in this case, during mixing, the amount of heat released will be insignificant enough to not affect the performance of the mixer.

3. Manufacturing precasts using geopolymers

Geopolymers are an emerging class of inorganic materials based on aluminum and silicon oxides that are chemically balanced by alkaline metals such as Li^+, K^+ or Na^+. At the basis of their production is the geopolymerization reaction, which consists of the ability of alkaline or acid solutions (activators) to dissolve particles of silicon and aluminum oxide-rich material. The technology developed in this study concerns the realization of a geopolymeric material and the process to obtain precast products with a lower CO_2 footprint than Portland cement-based products. Thus, by developing a geopolymer based on thermal power plant ash and reinforced with recycled glass fibers, the aim is to obtain an "environmentally friendly" product with properties comparable to those of Portland cement-based concrete. Furthermore, the technological flow for obtaining the material will be developed in accordance with the requirements of the construction sector. In order to determine the equipment required for the production line, the following characteristics (parameters, manufacturing steps) are established.

3.1. Parameters influencing the properties of geopolymer products

In this study, it will be considered a geopolymer composed of two main components: the base material (the solid component) and the alkali activator (the liquid component). The major component is the base material, which must be rich in silicon and aluminum and can be a natural mineral (clays, kaolin) or an industrial waste (thermal power plant ash, red mud, slag). There are several factors influencing the decision to design a material to obtain a geopolymer, which are closely related to the cost or availability of the raw material source as well as the scope of the resulting geopolymer (for example, metakaolin will be much more appropriate for water filtration applications than any other aluminosilicate source since it will result in intrinsic porosity with heavy metal retention or absorption capacity) (Vizureanu and Burduhos Nergis, 2020).

Since the characteristics and properties of geopolymers depend on a multitude of factors, it is essential to determine the optimal parameters specific to the raw material, activation solution, drying stage, and mixing stage. Table 1 summarizes the optimum parameters for obtaining precast alkali activated and reinforced with recycled glass fibers, as determined by preliminary studies.

Table 1

Optimum parameters of obtaining precasts with recycled glass fibers

	Parameter	Optimum value
Solid component	*Particle size distribution*	*≤80 µm*
	Humidity	*≈0*
	Chemical composition (Si + Al oxides)	*≥75 wt.%*
	Aggregates amount (0-4 mm)	*50 wt.%*
Liquid component	*Liquid to solid ratio*	*0.75*
	Na_2SiO_3 to NaOH ratio	*1.5*
	NaOH concentration	*10M*
Drying stage	*Curing temperature*	*22*
	Curing time	*Sealed 24h*
Mixing stage	*Mixing time*	*5 min.*
	Mixing parameters (velocity, mixer type)	*EN 196-1*
Fiber content	*Fiber content*	*2 wt.%*
	Fiber length	*60 mm*

Geopolymers containing several constituents in the solid component must be mixed in the dry state before introducing the activation solution. The main purpose of dry mixing is to increase the homogeneity of the final structure. At the same time, activating the geopolymer with a multicomponent solution involves mixing them before introducing the activator into the solid component.

3.2. Technological flow of obtaining geopolymers precast

Based on laboratory analyses and in accordance with NE 012-99, the targeted geopolymers exhibit similar characteristics to Portland cement-based materials of class C8/10 (used for casting leveling layers in foundations), as they have a compressive strength greater than 10 MPa at 28 days. Also, their flexural strength was significantly improved by introducing recycled glass fiber into the composition. Considering that the obtained materials can be used in all applications compatible with the technical characteristics of the C8/10 class, a versatile production line has been established for the manufacture of several variants of precast: pavers, kerbs, concrete blocks for masonry, foundations, pillars, floor slabs, chimneys, gutters, road gully covers, etc. The schematic process of obtaining the proposed products is presented in Fig. 2.

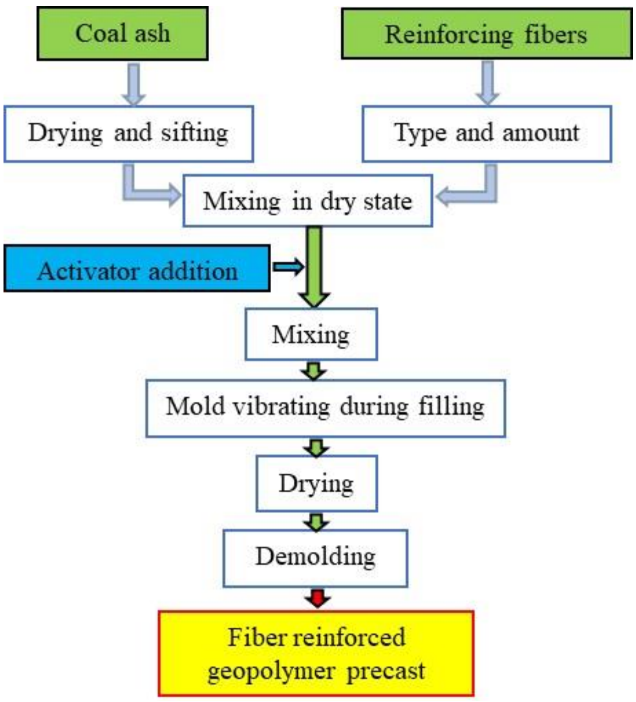

Fig. 2 – Schematic representation of geopolymer precast manufacturing.

Following is the equipment necessary to obtain geopolymer precast based on the schematic diagram presented in Fig. 2.

Coal ash and reinforcing fiber storage station

In the first stage, the raw material taken from the storage ponds will be transported to the storage station and stored in bunkers. The storage bunkers will ensure a constant volume of material for the drying station by means of conveyor belts. For this station, two pieces of equipment are necessary: storage bunkers with the necessary capacity (established depending on the productivity of the following stations) and conveyor belts to assure the transport of the raw materials to the mixer area. Also, the bunkers will be fed by means of conveyor belts (which will move the material from the hopper to the bunker) or by direct loading with specific means (wheelbarrow, bulldozer, etc.).

Coal ash and reinforcing fiber drying station

Water in the thermal power plant ash can bring about changes in the alkalinity of the activator, which can decrease its dissolving capacity. In order to eliminate this disturbing factor (humidity), a drying step was introduced after the thermal power plant ash was collected. Therefore, for this stage, two pieces of equipment are necessary: a continuous belt-type dryer with automated variation and a hot air generator (Fig. 3).

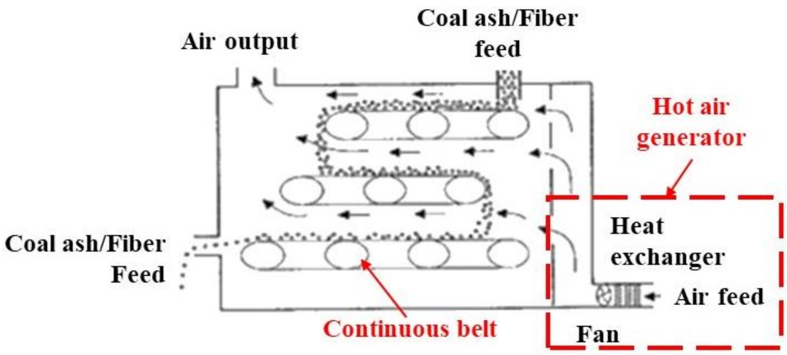

Fig. 3 – Schematic representation of drying station.

The coal ash drying stage is carried out in controlled heating enclosures, and the optimum drying period can be determined experimentally by automatically checking the moisture content of the mixture.

The main purpose of drying the raw material is to bring the solid component within controllable parameters (humidity ≈ 0) in order to eliminate the effect of excess water on the mechanical characteristics of the precast products.

Coal ash processing station

Considering that the coal ash is deposited in dump sites, it can be found only as a mixture of fly ash and bottom ash. Even though the fly ash is composed of mostly very fine particles, the bottom ash has a significant amount of large impurities that come from coal (unburned coal, gravel, stones, etc.). Moreover, during landfilling, different impurities from nearby areas can reach the dump and the storage area. Since the particle size distribution of the raw materials is a parameter with great influence on the properties of the final product, the coal ash must be processed to remove any large impurities. The equipment necessary for this station is: crushers with mechanized feed; a particle size separation line with by-pass; an airlock with bi-directional pneumatic drive; a sieve conveyor with discharge into silo for thermal power plant ash (Fig. 4).

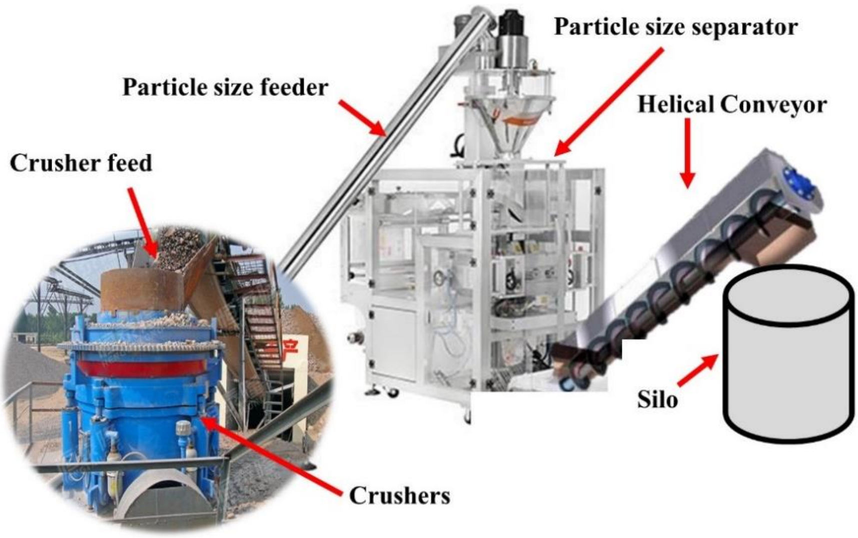

Fig. 4 – Schematic representation of coal ash processing station.

Grinding and particle size separation of the raw material are mainly aimed at increasing the reactivity of the mixture and improving the compactness of the precast. In general, mixtures formed from smaller particle sizes will have higher reactivity and superior mechanical properties.

Component mixing station

In this stage, each component is weighted and introduced into the mixture depending on the selected amount. Moreover, this stage also includes the dissolution and preparation of the activator. The mixing station consists of the following equipment: conveyor belts that bring the established amounts of each component from silos to the mixer; an activator preparation section that consists of tanks for each component of the activator (water, sodium silicate, and sodium hydroxide), dosing units, and pumps for discharge; and a mixer for homogenizing components with pneumatic discharge. The schematic representation of the mixing station is presented in Fig. 5.

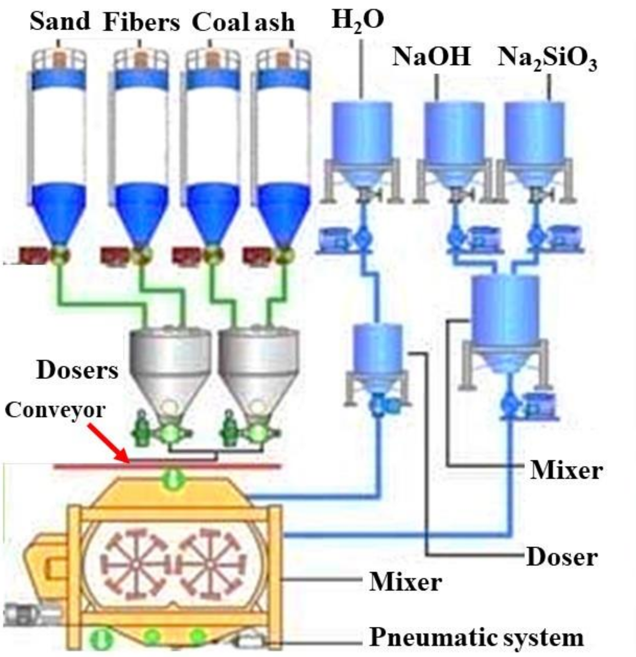

Fig. 5 – Schematic representation of mixing station.

Further, the pneumatic system will be used to fill different types of dies in order to obtain bricks, covers, panels, and any type of precast that can be manufactured from C8/10 conventional concrete.

4. Conclusions

In order to obtain geopolymer precasts, such as pavers, curbs, concrete blocks for masonry, foundations, pillars, covers, gutters for the roadway, bricks, etc., it is necessary to build a production line composed of four stations. In the first station, the raw materials will be stored. In the second and third stations, the raw materials will be processed by drying and sifting. In the fourth station, the liquid component will be prepared and mixed with the solid component. Further, the geopolymer mixture will be introduced into dies with the desired form and stored at room temperature until delivery.

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METODĂ DE OBȚINERE DE PREFABRICATE GEOPOLIMERICE ARMATE CU FIBRE DE STICLĂ RECICLATE

(Rezumat)

Geopolimerii ranforsați cu fibre au capacitatea de a înlocui cu succes produsele pe bază de Ciment Portland Obișnuit, îndeplinind în același timp cerința actuală de reducere a emisiilor de CO_2 asociate sectorului materialelor de construcții. În plus, prin introducerea de diferite tipuri de fibre reciclate în compoziția acestora, se poate elimina fragilitatea intrinsecă a matricii geopolimerice, oferind, în același timp, o soluție durabilă pentru reducerea generării și depozitării unor deșeuri. În acest studiu, sunt prezentate metodologia și reprezentările schematice ale unei tehnologii de fabricație industrială. Prin această tehnologie se pot obține cărămizi inovatoare, precum şi alte tipuri de prefabricate din compozite geopolimerice armate cu fibre de sticlă reciclate. Mai mult, geopolimerii propuşi sunt întăriți la temperatura camerei şi utilizează cenușă de cărbune ca materie primă. De asemenea, scopul introducerii fibrelor de sticlă reciclată este de a îmbunătăți rezistența la încovoiere a prefabricatelor obținute și de a elimina principala limitare asociată cu fragilitatea acestor produse.

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ANALYSIS OF CHEMICAL REACTIONS OCCURRING ON CONTACT BETWEEN A BIODEGRADABLE Fe-Mn ALLOY AND AN ELECTROLYTE SOLUTION

BY

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Abstract. Biomedical engineering has been developed very rapidly recently by improving tissue healing techniques, so that the field of implants is essential to the scientific world, especially in terms of biodegradable materials. In this sense, a series of new properties and ways to improve them are pursued. Most publications concern an excellent biocompatibility, mechanical stability and control over the degradation process to obtain better results in response to tissue healing. Scientists can relate to excellent results obtained from in vitro research, to achieve positive results in the sense of in vivo experiments. In this paper the authors relate to promising studies from the literature based on Fe-Mn-Si alloys in which encouraging results were obtained to further study these types of alloys as biodegradable materials with shape memory effect, an important property in the case of some types of medical applications where it could facilitate the more efficient healing process.

Keywords: biodegradable materials, degradation, shape memory effect.

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1. Introduction

The concept of degradable biomaterials is that some implants may only require their temporary presence to support the healing process of diseased tissue and to degrade once the lesion is healed. Figure 1 illustrates an example of a temporary implant (stent) that is implanted to open a narrowed artery.

Implants of this type have in common the same concept, but with applications in different parts of the body with different specific functions. For example, temporary cardiovascular implants like stents (Fig. 1), should be able to open a narrowed artery and keep it open until the blood vessel is remodelled, to degrade and be replaced with the newly formed tissues of the vessels. Temporary orthopaedic implants would aim to support, for example, a fractured bone, hold it tight until a favourable bone joint is formed, then degrade and be replaced with new bone tissue (Datta *et al.*, 2011; Wegener *et al.*, 2011).

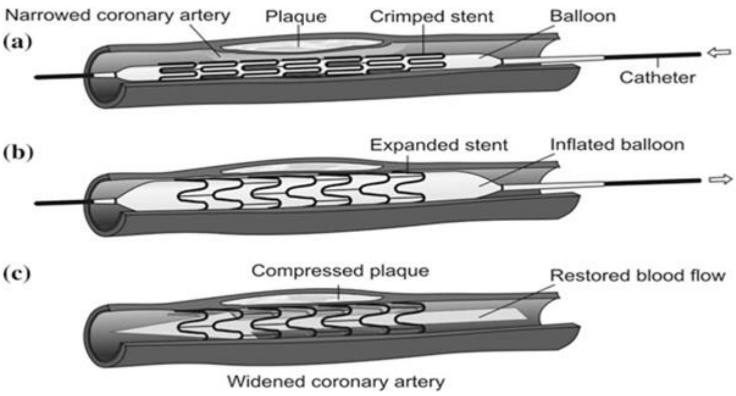

Fig. 1 – Illustration of a coronary stent during: a) delivery in an artery narrowed by a catheter, b) expansion to open the artery, c) restoration of blood flow (Hermawan and Mantovani, 2009).

Biodegradable coronary stents should strike a compromise between mechanical integrity and degradation (Hermawan *et al.*, 2010). Degradation should occur very slowly to maintain the optimal mechanical integrity of the stent until the remodelling process is completed, for which a period of 6 to 12 months is expected (El-Omar *et al.*, 2001; Schomig *et al.*, 1994). As mechanical integrity decreases, degradation progresses and the rate of degradation should be sufficient to prevent an intolerable accumulation of degradation residues around the implantation site and systemic organs. A total acceptable period for a stent to be fully degraded should be between 12 and 24 months after implantation (Serruys *et al.*, 2006), although this is not yet supported by sufficient data and real evidence of the in vivo degradation process, including for orthopaedic implants.

Most publications on biodegradable metals deal with the development of materials, the improvement of properties and the study of degradation (Schinhammer *et al.*, 2010; Moravej *et al.*, 2010a; Liu and Zeng, 2011). There is still limited research to turn biodegradable metals into implants or prototypes. Experimental developed implants include a coronary stent of Fe-Mn alloy (Hermawan and Mantovani, 2011), WZ21 Mg gastrointestinal alloy (Hänzi *et al.*, 2011), and Mg micro-clip for laryngeal micro-surgery (Chng *et al.*, 2012).

2. Fe-Mn as biodegradable alloys

Iron is critical to a large number of enzymes and proteins in the human body that contain Fe. It is critical to the breakdown of lipids, proteins, and DNA damage due to its reactivity to oxygen molecules that could produce reactive species through the Fenton reaction (Mueller *et al.*, 2006). Another equally important role is in transport, reduction of ribonucleotides and dinitrogen, storage and activation of molecular oxygen, etc. (Fontcave and Pierre, 1993).

Pure iron can benefit the proliferation of human endothelial cells if the cells have been metabolically inhibited only with elution medium at a concentration higher than 50μg / ml, regardless of the incubation time (Zhu *et al.*, 2009). An in vitro study reported that excess Fe ions reduced the growth rate of smooth muscle cells, which was seen to be a positive aspect in preventing restenosis in stent application (Mueller *et al.*, 2006). In vivo implantation of pure Fe stents in the descending aorta in rabbits from New Zealand showed favourable results, but if thromboembolic complications, significant neointimal proliferation, and systemic toxicity, no inflammatory response was found until 18 months (Peuster *et al.*, 2001).

Following some debates and toxicological analyses of the materials regarding the potential alloying elements for Fe, the suitable candidate was Mn, which can transform Fe into nonmagnetic, due to the austenite formation (Dargusch *et al.*, 2019). Manganese is an essential element of the body of all mammals. Its excess has not been reported to be toxic to the cardiovascular system due to the extensive plasma protein binding process that counteracts the effect of Mn toxicity (Moravej *et al.*, 2010b). Specialist studies have shown the mechanism of Fe-Mn alloy degradation during dynamic degradation tests in Hank's modified solution (Hermawan, 2012), (Fig. 2).

The initial corrosion reaction occurred between the metal and the liquid medium as soon as the sample was immersed. The oxidation occurred randomly in the places on the most anodic outer surface, such as grain boundaries or at the interface between different phases, equations (2.1.1) and (2.1.2). The corresponding cathodic reaction (water reduction) subsequently consumed the released electrons, equation (2.1.3) (Hermawan and Mantovani, 2009). Subsequently, the layers of insoluble hydroxides (metal oxides) were formed from free metal ions, which reacted with hydroxide ions (OH^-) following equations (2.2.4) and (2.2.5). Following visual observations, these hydroxides appeared as a red-brown (Fe_2O_3) layer on the top and a black (Fe_3O_4 and FeO) layer on the bottom. Chloride ions from the solution penetrated the metal substrate to compensate for the growth of metal ions under the hydroxide layer (Hermawan, 2012). The formed metal chloride was then hydrolysed into hydroxide and free acid, equation (2.3.6), lowering the pH value in the pitting pits while the mass solution remained neutral.

(2.1) Initial corrosion reaction:	(2.1.1) $Fe \rightarrow Fe^{2+} + 2e^-$
	(2.1.2) $Mn \rightarrow Mn^{2+} + 2e^-$
	(2.1.3) $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$
(2.2.) Formation of hydroxide layers:	(2.2.4) $2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2$ or $2FeO.2H_2O$
	(2.2.5) $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ or $2Fe_2O_3.6H_2O$
(2.3) Pitting formation:	(2.3.6) $Fe^{2+} + 2Cl^- \rightarrow FeCl_2 + H_2O \rightarrow Fe(OH)_2 + HCl$
(2.4) Ca / P layer formation:	Precipitation from solution

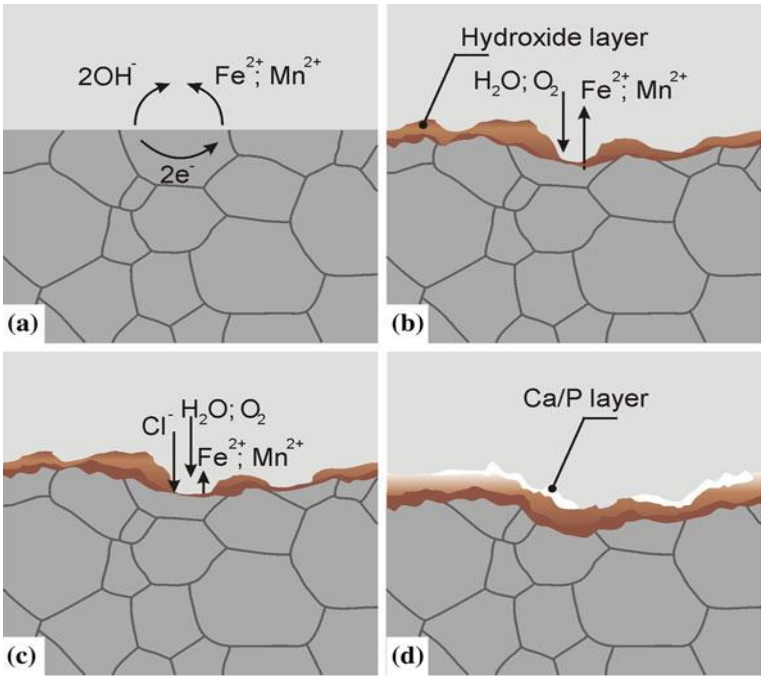

Fig. 2 – Illustration for the degradation mechanism of Fe-Mn alloys:
a) initial reaction, b) formation of the hydroxide layer, c) formation of pitting pits,
d) formation of the Ca / P layer (Hermawan and Mantovani, 2009).

3. Fe-Mn-Si as shape memory alloys

Shape memory alloys are characterized by two unique behaviour, thermally or mechanically activated: the shape memory effect and the pseudoelastic effect. This behaviour, due to the particularly crystalline structure of the alloys, ensure the recovery of the original shape even after large deformations and the maintenance of a constant applied force in correspondence with significant dislocations. These properties, to which is added a good resistance to corrosion and bending, the compatibility with magnetic and biological resonance, explain the high diffusion, in the last 20 years, of SMA in the production of biomedical devices, especially for mini-invasive techniques.

The use of Fe - Mn - Si alloys as shape memory alloys for joints has had favourable results in the past (Wada *et al.*, 2008). Also, it is mainly used in alloys for biomedical metallic materials and due to this fact, Fe-Mn-Si alloys could be studied as biodegradable metals (Zhang *et al.*, 2010). In the study by Liu *et al.* (2011), Fe30Mn6Si alloy was characterised on microstructure, mechanical properties and shape memory effect, in vitro biocompatibility, corrosion rate in Hank's solution, cytotoxicity and haemolysis. It was used for this iron (99.9%), silicon (99.999%) and manganese (99.7%), melted in a vacuum induction furnace, argon atmosphere for the manufacture of Fe30Mn and Fe30Mn6Si alloys. Part of the Fe30Mn6Si alloy was cut, treated at 850°C for 1 hour with water cooling to improve the shape memory effect (Liu *et al.*, 2011).

The results showed that the strength of the Fe30Mn6Si alloy was higher than the other types of samples. In terms of elongation, the Fe30Mn6Si alloy showed a decrease with the addition of Si to the Fe30Mn alloy, but was found to be higher than that of pure iron. The shape memory effect of the Fe30MnSi alloy was clearly shown and the recovery ratio approximately 53.7% (Liu *et al.*, 2011).

The performed analysis revealed that the Fe30Mn and Fe30Mn6Si alloys are formed from ε-martensite and γ-austenite type phases, and the pure iron from the α-ferrite single phase (Liu *et al.*, 2011). The latter is known to be more resistant to corrosion than the ε-martensite and γ-austenite phases (Lin *et al.*, 2002).

It has been shown that Fe30Mn and Fe30Mn6Si have a higher corrosion rate than pure iron. An increase in the γ-austenite content was observed with the addition of Si. The electrical resistivity of ε-martensitic is higher than that of the γ-austenitic state for Fe-based shape memory alloys (Charfi *et al.*, 2009). From here, it can be explained the higher corrosion rate of the Fe30Mn6Si alloy from electrochemical measurements.

Regarding cytotoxicity and hemolysis, it was found that at a higher concentration of released ions, the rate of degradation increases and thus reaches lower viability. Fe30MnSi showed low biocompatibility in this regard.

The study showed that cell viability showed an increase after the next day until day 4, which is promising in terms of cellular application (Liu *et al*., 2011).

4. Conclusions

The study by Liu *et al*. (2011) concluded that Fe30Mn6Si alloy is a suitable biodegradable metal as a material with shape memory function. It consists of the martensite and austenite phases at room temperature and has superior mechanical properties to pure iron, showing a good corrosion rate. Reduced cell viability was due to the release of ions at a higher concentration, but the subsequent increase in viability on the second day was a promising result. It is important to mention that Fe30Mn6Si is non-hemolytic, as well as the percentage of hemolysis being below 2%.

As a perspective, following the encouraging preliminary results found in the literature, the possibility of future studies should be considered for analyzing the behaviour of alloys such as Fe-Mn-Si as intelligent materials with shape memory effect and at the same time studied from the perspective of biodegradable materials.

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ANALIZA REACŢIILOR CHIMICE CARE AU LOC LA CONTACTUL DINTRE ALIAJUL BIODEGRADABIL Fe-Mn ŞI O SOLUŢIE DE ELECTROLIT

(Rezumat)

Ingineria biomedicală s-a dezvoltat foarte rapid în ultimii ani prin îmbunătățirea tehnicilor de vindecare a țesuturilor, astfel încât domeniul implanturilor prezintă un mare interes pentru lumea științifică, în special în ceea ce privește materialele biodegradabile. În acest sens, se urmăresc o serie de noi proprietăți și modalități de îmbunătățire a acestora. Majoritatea publicațiilor se referă la o biocompatibilitate foarte bună, stabilitate mecanică și control asupra procesului de degradare pentru a obține rezultate mai bune ca răspuns la vindecarea țesuturilor. Oamenii de știință se pot raporta la rezultatele foarte bune obținute în urma cercetărilor in vitro, pentru a obține rezultate pozitive în sensul experimentelor in vivo. În această lucrare, autorii se referă la studii promițătoare din literatura de specialitate bazate pe aliaje Fe-Mn-Si, în care s-au obținut rezultate încurajatoare pentru a studia în continuare aceste tipuri de aliaje ca materiale biodegradabile cu efect de memorie a formei, o proprietate importantă în cazul anumitor tipuri de aplicații medicale, unde ar putea facilita un proces de vindecare mai eficient.

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APPAREL CONSUMER'S COMPREHENSION TOWARDS SUSTAINABILITY

BY

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Abstract. The fashion industry is already well known for its damaging environmental impact. Over the years, those negative influences have gained momentum, and the consequences lie ahead, in terms of climate change and even human health damage. Since outcomes have become increasingly more visible to the naked eye, concerns about developing methods to prevent and diminish the harm that the apparel industry is capable of doing started to take form at the European Commission level.

Shaping the consumer's behaviour, based on the ideal traits that researchers establish, is not sufficient, and is even unattainable at first.

This study is based on a public survey, addressed to apparel consumers. The aim is to identify, not only the concrete level of knowledge that consumers have about fashion sustainability, but also the main reasons behind the purchasing process. Nonetheless, valuable pieces of information were thus obtained, concerning post-consumer apparel waste, from a consumer's perspective.

Keywords: apparel industry, consumer's awareness, environmental impact, post-consumer apparel waste, sustainable behaviour.

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1. Introduction

The fashion industry is one of the pillars that actively and constantly generate sources of environmental pollution. The reason behind mass production is customer demand. The reason behind customer demand is, often cases, poor product quality. Being aware of the impact that their activity has on ecosystems, and human health, as well as how textile production contributes to the consumption of natural resources, the manufacturing companies have developed new approaches toward attaining more sustainable production processes. Given the European Circular Economy Action Plan (European Commission, 2020), stakeholders, mills, designers, and textile experts, are encouraged to pursue the paradigm change that the apparel industry requires. The manufacturers of materials responded to the initiative, by making available textiles that have a lower impact on the environment, thus offering the possibility to opt for sustainable materials. In this sense, this concept has become increasingly implemented among clothing brands, which in turn have shown an interest in including ecological or biodegradable materials in the developed collections (Gradowska and Wołosowicz, 2022; Khandual and Pradhan, 2018; Nayak *et al.*, 2020).

However, as manufacturers have understood the importance to be given to the harmful effects that clothing has on the environment, it is important to emphasize that the value chain is bidirectional, consisting of the synergy between manufacturers and buyers. Since more and more garment items available on the market will be commercialized under the "sustainable" label, it's important to understand how receptive fashion consumers will be to the updated character of the clothing pieces (McNeill and Moore, 2015).

This study aims to attain a clear picture that depicts the real level of information that Romanian apparel consumers have towards sustainability in fashion, as well as identifying the reasons that linger behind their purchasing behaviours.

In order to develop the most effective pollution management in the textile industry, as well as to enable the integration of sustainable practices into the value chain of a garment, action must be taken among buyers as well.
(Lenne and Vandenbosch, 2017; Georgsson and Johansson, 2020) This ensures the metamorphosis of the apparel industry, at the highest level of efficiency. Within this study, the most preferred way of apparel disposal has been identified, along with the main criteria for clothing items to become pre-consumer textile waste.

2. The fashion consumer's level of comprehension

For this study, an online survey has been drafted. Romanian respondents, with ages between 14 and over 60 years old, were asked to fill out and answer the questions. The survey was available online between the 15th of January and the 6th of March, with a final sample size of 395 respondents.

The questions have been crafted in such a way that would ensure a smooth and gradual approach for the consumers. For instance, when aiming to identify the main sources of information that they can relate to, in regard to fashion sustainability, the first step was to identify if they have ever heard about the given topic before. Results show that Romanian apparel consumers have a sense of familiarity with fashion sustainability (Fig. 1), developed via media, either through written articles, documentaries, fashion shows, news, or other forms of information (Fig. 2).

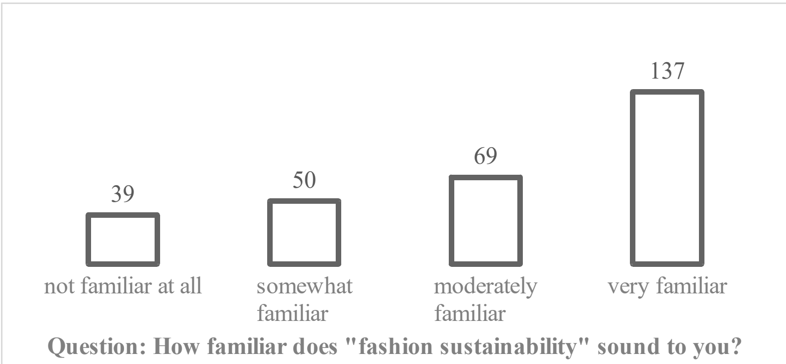

Fig. 1 – The consumer's level of familiarity towards fashion sustainability.

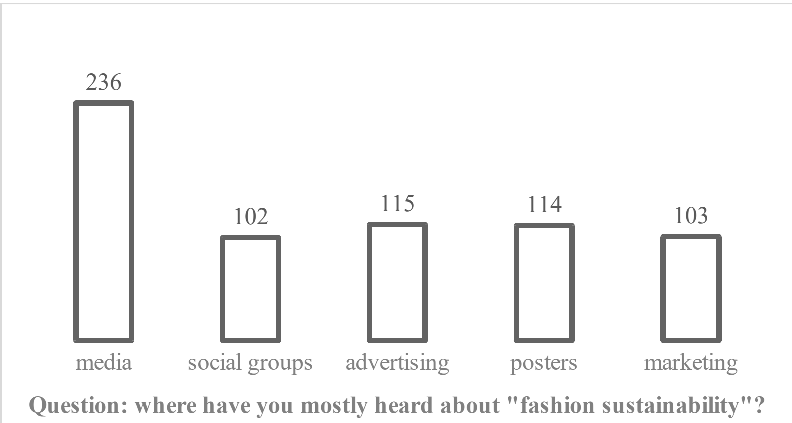

Fig. 2 – The most common sources of information regarding fashion sustainability.

The second layer that needed to be uncovered was the real – not just declared- level of understanding the respondents possess. In order to reach the needed results, the consumers were first asked if they know what apparel sustainability stands for. 80% of the sample claimed that they hold a certain level of information and understanding regarding this topic. The following question had a series of six answers, that represent the multi-faceted sides of apparel sustainability. The list also contained two wrong answers, which were meant to promote an accurate filter between the respondents who have previously stated to know what fashion sustainability is, without truly having a real understanding of this term. Once more, the gradual approach is emphasized, ensuring that the respondents hold the slightest notion of the topic they are being asked about. Thus, the results indicate that only 74% of consumers who first claimed to understand what this term stands for, were being accurate. The remaining 26% consider fashion sustainability to be either a trend or ridiculously overpriced clothing items (Table 1).

Table 1

Questions hierarchy to determine the real level of consumer's comprehension

Q: Do you know what "fashion sustainability" stands for?	Q: Choose the most accurate description for this term from the list below	Overall answers	Answers validity
Yes 80% of the total sample	*Apparel items made from recycled fabrics*	*48*	*Correct answers, 74%*
	Clothing items that are more durable than the ones already on the market	*55*	
	Garment products made from ecological/biodegradable fabrics	*45*	
	Clothes produced under fair labour	*7*	
	A trend	*25*	*Wrong answers, 26%*
	Overpriced garment pieces	*15*	

In other words, those consumers, due to misinformation, would present a certain amount of restraint when facing sustainable apparel pieces on the market - they wouldn't tend to invest in such items, because of their lack of understanding about it, thus operating out of a limited purchasing behaviour.

3. Purchasing and disposal practices

In terms of motivations and frequency, when it comes to apparel purchasing, findings show that Romanian consumers tend to invest in new pieces of clothing, mostly when the old and outdated items must be replaced (Fig. 3). Nonetheless, they also tend to buy new apparel when they must attend a formal event, where a dress code is in most cases a requirement. Thus, they tend to purchase, as the results depicted below show, several times a month, or even a week (Fig. 4). This detail alone is an indicator of the consuming frequency that the Romanians show when it comes to fashion, as well as their tendency to accumulate a fair amount of clothing items, which will ultimately lead to generating a fair amount of pre-consumer apparel waste.

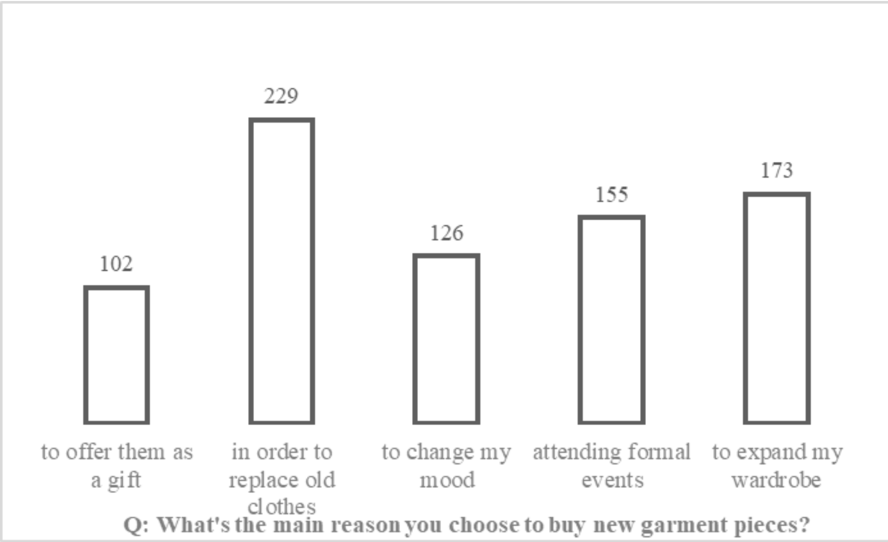

Fig. 3 – The main reasons behind apparel purchasing, from a consumer's perspective.

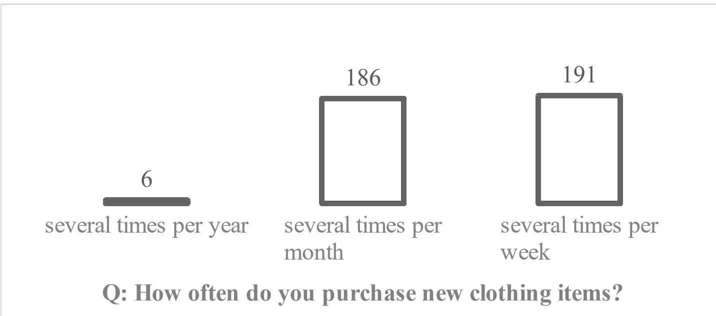

Fig. 4 – Purchasing frequency.

When it comes to waste management, 61% of respondents claimed that the most common method of discarding old clothing items is by donating them to those in need (Fig. 5). Nonetheless, Romanian consumers were able to give precise pieces of information in regard to the criteria by which they label their clothes as “old” and decide to discard them. According to the data, an apparel item is no longer wearable, by those who participated in the survey, when it has slight signs of damage, such as holes and stains, or when it no longer fits the dimensional requirements (Fig. 6).

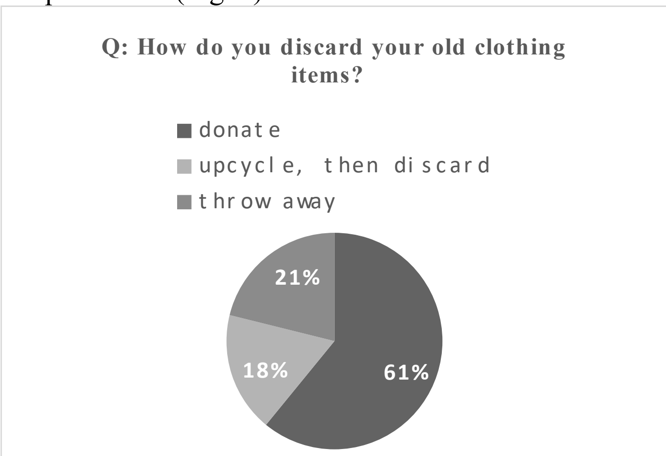

Fig. 5 – Disposal methods for post-consumer apparel waste.

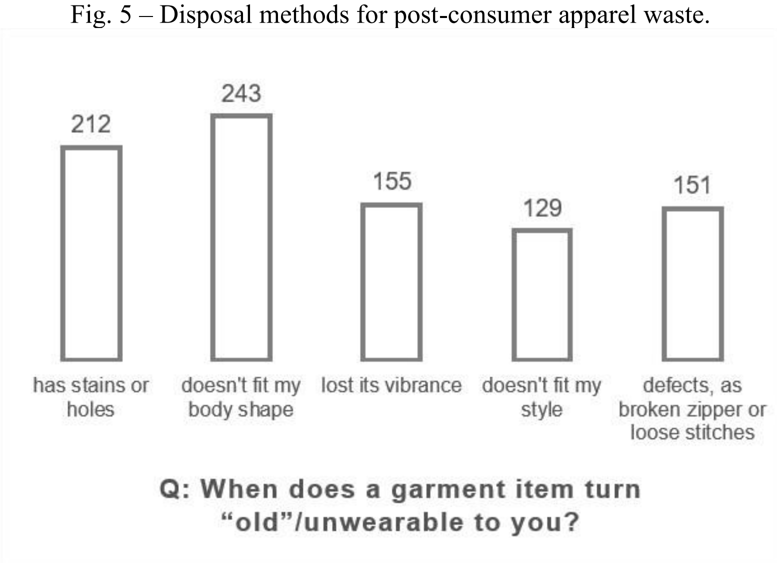

Fig. 6 – The reasons why consumers choose to discard garment items.

The reasons based on which the consumers choose to discard their old clothing items are legit, which emphasizes the fact that Romanian consumers care somewhat less about trends, but are rather interested in a clothing item's functionality. Romanian fashion consumers tend to donate their unwanted apparel pieces, and this indicates a tendency toward increasing the life cycle of a clothing items. Therefore, it is mandatory to highlight the consumer's demands based on a practical, even sustainable, mentality.

4. Conclusions

The findings show that the Romanian consumers have their purchasing behaviour equally developed on a basic need of replacing their outdated clothing items, and thus on a sense of renewing their wardrobe, which also goes hand in hand with a swift purchasing peace, as results indicate that they are prone to invest in new clothing items several times per week or month. Another detail which stands out, in terms of purchasing motivation, is the one that indicates that fashion consumers prefer to buy new apparel items when attending a formal event. We can conclude that they will wear the purchased item only several times, which emphasises, on one hand, the consumption trend among consumers, as well as their tendency to gather clothing pieces, in short periods of time.

Nonetheless, another important aspect revolves around the majority of the Romanian consumers who have proven to be well informed in terms of fashion sustainability, along with a significant amount of them who chose to dispose their unwanted or outdated clothing items by simply throwing them away. Apart from the contradiction between these two findings, a key-aspect lies in between: consumers have stated that the main source of information, in regards to the topic of this study, relies on the mass-media. Considering that, it becomes obvious that the Romanian consumers require a certain amount of education in terms of post-consumer apparel waste management. Given the circumstances, the solution relies on informing and instructing them via mass media. This can be accomplished, both by bringing their awareness on the hazardous effects that improper apparel disposal has over the environment, by using a proper terminology, which can be easily comprehended by any of them, as well as offering solutions that encourage apparel upcycling, designed in a way that is adapted to their household items, and thus can be accessible for the consumers to operate on.

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ÎNȚELEGEREA CONSUMATORILOR DE ÎMBRĂCĂMINTE FAȚĂ DE SUSTENABILITATEA ÎN MODĂ

(Rezumat)

Industria modei este bine cunoscută pentru impactul negativ pe care îl are asupra mediului. De-a lungul anilor, influențele nefavorbile au luat amploare, iar consecințele sunt traduse prin, schimbări climatice severe, precum și amenințări la adresa sănătății umane. Deoarece rezultatele au devenit din ce în ce mai vizibile, preocupările cu privire la dezvoltarea unor metode de prevenire și diminuare a prejudiciului adus asupra mediului de către industria produselor de îmbrăcăminte, au început să prindă formă la nivelul Comisiei Europene.

Modelarea comportamentului consumatorului, pe baza trăsăturilor ideale stabilite de cercetătorii și specialiștii în domeniu, nu este suficientă și necesită o analiză detaliată.

Acest studiu se bazează pe un sondaj public, adresat consumatorilor de îmbrăcăminte. Scopul este de a identifica, nu doar nivelul concret de cunoștințe pe care îl au consumatorii despre sustenabilitatea modei, ci și principalele motive din spatele procesului de cumpărare. Cu toate acestea, au fost astfel obținute informații valoroase, referitoare la deșeurile de îmbrăcăminte post-consum, din perspectiva consumatorului.

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STUDY ON CLAYS AND THEIR USE AS ANTIMICROBIAL AGENTS IN THE COSMETOTEXTILE INDUSTRY

BY

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Abstract. This article addresses the potential use of natural clays as antimicrobial agents in the field of cosmetotextiles, a unique product category that combines the fields of cosmetics and textiles. Cosmetotextiles are produced through a microencapsulation process in which microcapsules are applied directly to textile fibers. Natural clays have been used for centuries for medicinal purposes, and their potential use as antimicrobials has gained interest in recent years due to the growing popularity of natural remedies. Despite the long history of using clay for medicinal purposes, the exact mechanism behind its antibacterial properties is still not fully understood. However, research has shown that clays intended for pharmaceutical and cosmetic products are safe and non-irritating materials. With this in mind, the use of clays in pharmaceuticals and cosmetics has increased in recent years, with many manufacturers turning to natural remedies and alternative sources of ingredients. The objective of this paper is to provide a comprehensive review of various types of clays and cosmetotextiles to identify potential "clay-textile" pairs for future research. The ultimate goal is to find an improved "clay-textile" pair that is highly effective as an antimicrobial agent in cosmetic textiles. The selected "clay-textile" pairs will be characterized according to their specific end-use requirements. In summary, this paper aims to shed light on the potential use of natural clays as antimicrobial agents in cosmetotextiles. It is hoped that the

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use of natural clays in cosmetotextiles can be further optimized through further research for the benefit of industry and consumers.

Keywords: Clay, antibacterial agents, textiles, dispersion, cosmetotextile.

1. Introduction

Clays are abundant and inexpensive natural resources that are very versatile. These materials are characterized by their flexibility when wet and strength when dry and are composed mainly of fine silicate and mineral particles (Standard Test Methods for Liquid Limit, 2010). The study of clays as fine-grained rocks or soil constituents is critical to understanding global biological and ecological processes. Clays, with their physical and chemical properties, are an integral part of our daily lives and have numerous applications. Therefore, understanding the properties and behavior of clays is fundamental to realizing their potential and using them effectively. From construction and agriculture to pharmaceuticals and cosmetics, the applications of clays are diverse and far-reaching. Through extensive research, we can unlock the full potential of clays and contribute to a sustainable future (Standard Practice for Classification of Soils for Engineering Purposes, 2011). Clay has been used by humans for a long time, from prehistoric times to the present day. Therefore, its influence can be observed in a variety of fields, including ceramics, building materials, health, and others (Vaccine Safety Review Committee, 2004).

For many years, scientists and researchers have been concerned with the criteria for the particle size of clay, but a consensus has not yet been reached. Nevertheless, it is undeniable that clay continues to be an incredibly important subject of study for a wide range of disciplines. From materials science and geology to medicine and agriculture, the diverse applications of clay have attracted the attention of experts in a variety of fields (Churchman *et al.*, 2006). Despite the conventional method of using particle size as the upper limit for distinguishing clay from mud, the International Association for the Study of Clays (AIPEA) / Clays Mineral Society (CMS) has a different view. It defines clay based on its plasticity and its ability to harden when dried, which are its main characteristics. Clay minerals are those minerals that impart plasticity to clay and harden upon firing or drying, regardless of their particle size or origin. This definition is not limited to phyllosilicates, but may also include non-phyllosilicate minerals, whether natural or synthetic. Clay minerals can be identified using techniques such as X-ray diffraction. It shows that plasticity depends not only on particle size or shape, but also on chemical composition, pH, degree of crystallinity, and physical state of the particles in the material (Guggenheim and Martin, 1995).

Cosmetotextiles, textiles impregnated with a durable cosmetic substrate that gradually releases over time to provide cosmetic and biological benefits such as slimming, refreshment, anti-aging, fitness, and health, have gained considerable attention in recent years. These innovative textiles fall into the category of cosmetotextiles as defined by the European Cosmetics Directive, which states that any textile containing a substance or preparation that is released over time to various parts of the human body, including the skin, and has specific functions such as perfuming, cleansing, changing appearance, protecting, maintaining good condition, or correcting body odors are considered cosmetotextiles (Mukesh *et al.*, 2011). Cosmetotextiles are textiles that have been treated with a durable cosmetic substrate that is released over time to perform cosmetic and biological functions. For a textile to be considered a cosmetotextile, the cosmetic ingredients grafted onto the textiles must be able to transfer to the wearer's skin in sufficient quantity to provide noticeable cosmetic and health benefits (Mukesh, 2021).

2. Clays and cosmetic textiles

Clays and Cosmetotextiles: Literature Findings

It is well known that clay minerals are formed by the process of chemical weathering of rocks over long periods of time (Environmental Characteristics of Clays and Clay Mineral Deposits, 2008).

In recent years, a wide range of clays have been used for medicinal purposes, especially for external applications such as mud therapy. Kaolin and smectite clays, which include bentonite, montmorillonite, and Fuller's earth, are among the most commonly used clays (Ferrell, 2008).

Clay has been used for its medicinal properties since ancient times, with the earliest records of its use dating back to Mesopotamian clay tablets circa 2500 BC. The ancient Egyptians also used clay for medicinal purposes (Harth, 2013). Medicinal clay was highly valued for its anti-inflammatory and antiseptic properties. In fact, it was so highly regarded that the physicians of the pharaohs used it for medicinal purposes, while it was also used to preserve mummies (Coulumbe, 2008).

Bentonite, one of the most commonly used healing clays today, has been used to treat a variety of health problems such as infections and digestive disorders. Bentonite is applied to the skin as a poultice and ingested, among other uses. However, it should be noted that while bentonite itself is not classified as a carcinogen, some bentonite deposits may contain varying amounts of crystalline silica, which is known to be carcinogenic to humans and can be inhaled. Therefore, it is important to ensure the purity and quality of bentonite before using it for medicinal purposes (Afriyie-Gyawu *et al.*, 2005). Palygorskite, also known as attapulgite, is a type of clay that is highly absorbent, similar to bentonite. It is abundant in southern Nevada and has been used in various anti-diarrheal medications because of its ability to bind acids and toxic substances in the stomach and digestive tract. However, the USFDA has found studies on its efficacy to be inadequate, and further studies are needed to establish its safety and effectiveness (Wagner *et al*., 1987). Kaolin is a widely used clay in various industries, including pharmaceuticals and cosmetics. It is commonly referred to as "white cosmetic clay" due to its light color and is known for its low absorption capacity compared to other clays used in the pharmaceutical industry (Gupta *et al*., 2011).

Blue clay is a popular remedy in traditional medicine for various ailments such as eczema, psoriasis, rheumatism and others. Among the various types of blue clay, Cambrian blue clay from the Leningrad region is considered the oldest on earth. Its properties are the subject of extensive research due to its potential use in various applications (Kryuchkova *et al*., 2020).

Researchers have investigated the possibility that an Oregon blue clay (Fig. 1) has antimicrobial properties against pathogenic bacteria such as Escherichia coli and Staphylococcus aureus, including antibiotic-resistant strains (Muyzer *et al*., 2016).

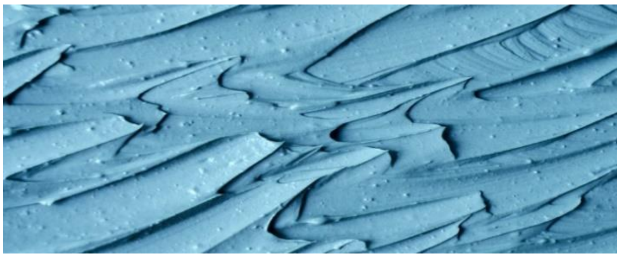

Fig. 1 – Blue clay from Oregon (https://www.outsourcing-pharma.com, 2018).

In Romania, blue clay was accidentally discovered during the exploitation of a yellow clay deposit for pottery. However, analyses have shown that blue clay has a high content of silicates and oxides, and its use has been found to have beneficial effects on the human body (https://www.argilaalbastraderaciu.ro).

Clays are known to be rich in trace minerals. Montmorillonite clays, for instance, can contain up to 75 different trace minerals. However, the specific amount of a certain trace mineral present in a particular clay can vary significantly depending on the location where it was sourced (Saary *et al.*, 2005).

Clays are typically divided into three or four groups, depending on the source. These categories include kaolinite, montmorillonite-smectite, iolite, and chlorite. However, in some source's chlorites are considered a separate group within the phyllosilicates. (Environmental Characteristics of Clays and Clay Mineral Deposits, 2008).

Clays are commonly used as excipients in drugs, and their main side effects are similar to those of neutral excipients. These effects include a reduction in the rate of absorption of antibiotics and hormones by coating the digestive tract. This can lead to increased toxicity of certain drugs, such as citrate salts, which can become toxic if not metabolized quickly enough. Mild side effects of clays include nausea, slowed absorption of nutrients from food, and constipation (Albert *et al*., 1978).

With the rapid advances in science and technology, textiles have found new applications in the cosmetic industry. Cosmetotextiles, which have emerged from the combination of cosmetics and textiles, are a new field of cosmetic textiles. The textile industry is optimistic that these products will open up new target groups and sustainable markets. Textiles are an important interface between people and their environment. However, achieving significant cosmetic effects with textiles presents a significant challenge (Achwal, 2003).

In addition to their primary function of protecting against environmental influences such as UV radiation and cold, textiles can also serve as a "second skin" However, for cosmetotextiles to be effective, they must be of high quality even before cosmetic products are applied. It is therefore important that these products meet industry standards such as Oeko-Tex® 100 and Oeko-Tex® 1000 (Mathis and Mehling, 2011).

In the field of cosmetotextiles, microencapsulation technology is a widely accepted method for regulating the release of active ingredients. However, there are alternative approaches for the production of cosmetotextiles (Gordon, 2002).

In the field of cosmetotextiles, various techniques are used to produce these unique textile products. Some cosmetotextiles are made by refining layers, while others are created by adding dopants to the fiber. Despite the numerous manufacturing techniques, there is no single classification for cosmetotextiles. To solve this problem, Mukesh Kumar Singh and his team have proposed a classification system based on the effects on the human body. This classification includes cosmetotextiles that are slimming, moisturizing, energizing, perfuming, refreshing and relaxing, revitalizing, UV-protective, and used to improve skin firmness and elasticity (Mukesh *et al*., 2011).

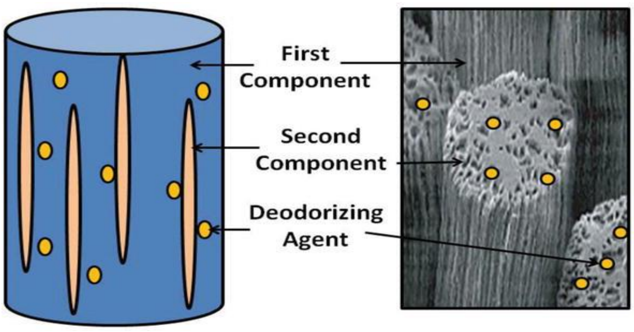

Fig. 2 − Concept of inherent deodorant textile fibre (Mukesh, 2021).

Developing functional and effective cosmetotextiles that deliver a desirable benefit to the wearer within a short period of time is a challenging task. The challenge lies in transferring a sufficient amount of cosmetic ingredients to the skin while minimizing loss during washing. Researchers have explored various strategies to address this issue. Traditionally, efforts were focused on retention during washing, while transfer was neglected (Mathis and Mehling, 2011).

Impact of Various Clay Types on the Textile Fabric Industry

Over the years, numerous studies have been conducted to investigate the effects of clays on textiles. Most of these studies focused on the decontamination of dyed water, which was achieved by various methods such as biological treatment, coagulation/flocculation, ozone treatment, chemical oxidation, photocatalytic processes, membrane processes, and adsorption. Among these methods, adsorption has emerged as the most commonly used due to its ease of use and efficiency in removing contaminants from low-concentration solutions. As researchers continue to explore innovative and cost-effective adsorbents, Tunisian clays from Tabarka and Fouchana have been identified as potential adsorbents for removing anionic dye (RR 120 - red dye) from textile industries' effluents. Nejib Abidi and his team discovered that the clay texture, rather than porosity, surface area, or cation exchange capacity, was the primary factor affecting the efficiency of dye removal from water (Abidia *et al.*, 2019). In their review of the use of clay and modified clay for dye adsorption, Abida Kausar and colleagues found that modified clay was more efficient compared to unmodified clay. Various techniques were used to characterize the clays before and after adsorption of dyes, but the authors noted that many studies lacked complete information on the characterization of the clay as an adsorbent. The authors suggest that further research is needed to investigate this area (Kausar *et al*., 2018).

Textiles are ideal breeding grounds for microorganisms, particularly when exposed to appropriate moisture and temperature in contact with the human body. As a result, there has been a surge of interest in the antimicrobial modification of textiles as hygiene concerns continue to rise. However, the use of many antimicrobial agents has been avoided due to their potential harmful effects, leading to the exploration of inorganic nanoparticles and their nanocomposites as a viable alternative. In a review written by Roya Dastjerdi *et al*. on the application of inorganic nano-structured materials in the modification of textiles, the focus was on the antimicrobial properties. One of the nano-structured materials studied was nano-clay and its modified species. Additionally, they referenced research works by Williams et al. that observed complete sterilization of E. coli by Agricure clay, Seckin *et al*. who extended a clay-poly (vinyl pyridine) matrix for the removal of bacterial cells from water, and Hu *et al.* who investigated the antibacterial effect of ion-exchanged montmorillonite with Cu ions (Dastjerdi and Montazer, 2010).

Carlos Rafael Silva de Oliveira and his team investigated the use of thermal stability of clays for finishing cotton fabrics using phosphate/clay minerals by direct coating technique. Their goal was to obtain a flame-retardant fabric (Silva de Oliveira *et al*., 2021).

Clays are commonly used in the cosmetic industry in combination with polymers such as polyvinyl alcohol (PVA) (Lu *et al*., 2020). To further explore the potential of clays in skin care, Nidhi Asthana and her team developed a peel-off mask formulation using green nanotechnology. The team used particles of green clay and aloe vera to create the gel using solution-cast technology, resulting in a thin film with high applicability. This new formulation offers promising opportunities for the development of innovative, environmentally friendly skin care products (Asthana *et al*., 2020).

In a study by Rehan et al. the interaction of chitosan with clay and Ag-NP was investigated to prepare nanocomposites of Cs/AgNP and Cs/AgNP/clay using the pad dry cure method. The resulting nanocomposites exhibited remarkable hydrophobicity, high strength, uniform morphology, enhanced thermal stability, successful deposition on the surface of cotton fabric, high water absorption, antimicrobial activity, flame retardant properties, controlled release of fragrance, and UV protection. These results suggest that nanocomposites can be an effective solution to improve the functional properties of textiles (Rehan *et al*., 2018).

3. Conclusions

As people around the world turn their attention to natural resources to protect the environment, clays have emerged as a promising solution due to their multiple healing properties and low cost. While there have been insufficient studies on the use of clays in cosmetotextiles, the potential of cosmetotextiles - clothing infused with cosmetics - offers exciting new possibilities for the future. The use of clays in textiles has the potential to revolutionize the way we think about clothing and skin care, and with ongoing research and development, we can expect to see the development of many new and valuable products in the coming years. As customer expectations continue to rise, more research will be conducted to determine the best “textile-clay pair” for maximum efficacy.

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STUDIU PRIVID ARGILELE ȘI UTILIZAREA ACESTORA CA AGENȚI ANTIMICROBIENI ÎN INDUSTRIA COSMETOTEXTILELOR

(Rezumat)

Argilele naturale au fost utilizate atât în medicina antică, cît și în cea modernă, însă mecanismul care face ca anumite argile să fie letale pentru agenții patogeni bacterieni, nu a fost încă identificat. Pe de altă parte, cosmetotextilele sau textilele cosmetice reprezintă o categorie de produse care combină domeniul cosmeticelor cu

industria textilelor de cele mai multe ori printr-un proces de microîncapsulare, prin fixarea microcapsulelor direct pe fibrele textile.

Utilizarea mineralelor argiloase în scopuri cosmetice și farmaceutice s-a dezvoltat în ultimii ani datorită succesului în ceea ce privește remediile naturiste. În plus, argilele destinate produselor farmaceutice și cosmetice s-au dovedit a fi materiale non-toxice și neiritante. Scopul lucrării de față este efectuarea unei clasificări a argilelor și cosmetotextilelor, pentru identificarea în perspectivă, a unor perechi „argilă-textil" îmbunătățite din punct de vedere funcțional, pe baza studiului literaturii de specialitate.

Cercetările proprii viitoare vor fi concentrate și pe caracterizarea perechilor de „argilă-textil" selectate conform criteriilor impuse de destinația concretă a acestora.

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BIOMATERIALS IN MEDICAL APPLICATIONS: A REVIEW

BY

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Abstract. Biomaterials have emerged as a pivotal field in modern medicine, revolutionizing the way we diagnose, treat, and restore the human body. With their unique ability to interact with biological systems, biomaterials have opened up new avenues for medical applications, ranging from regenerative medicine and tissue engineering to drug delivery systems and medical implants. This review aims to provide an overview of the diverse applications of biomaterials in the field of medicine, highlighting their significance, recent advancements, and future prospects.

Keywords: biomaterials, medical applications, future trends on biomaterials.

1. Introduction

Biomaterials can be defined as materials that are designed and engineered to interact with biological systems, either in a therapeutic or diagnostic capacity. These materials are typically used in medical and healthcare applications to replace or enhance natural functions within the body.

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Biomaterials are chosen for their biocompatibility, which refers to the ability of a material to perform its intended function without causing an adverse response in the biological system. They are used in various fields such as regenerative medicine, tissue engineering, drug delivery, medical implants, and diagnostic devices. Biomaterials can be composed of metals, polymers, ceramics, composites, natural materials, or a combination thereof, and are carefully selected and tailored to meet specific biological and mechanical requirements for their intended applications (Baltatu *et al*., 2021a; Baltatu *et al*., 2021b; Vallet-Regi *et al*., 2022; Chen *et al*., 2015).

Biomaterials play a pivotal role in modern medicine, revolutionizing the field of medical applications. These materials, ranging from polymers to metals, ceramics, and composites, have opened new avenues for therapeutic interventions, tissue engineering, and medical device development. In this mini review, we will explore the diverse range of biomaterials used in medical applications, highlighting their properties, applications, and the potential impact they have on improving patient outcomes (Ratner *et al*., 2004; Antoniac *et al*., 2022; Ratner and Zhang, 2020).

Biomaterials used for bone regeneration aim to provide a supportive environment for the growth and regeneration of new bone tissue. They can be classified into several categories based on their composition and properties. In Fig. 1 is presented the main classification of biomaterials for bone regeneration.

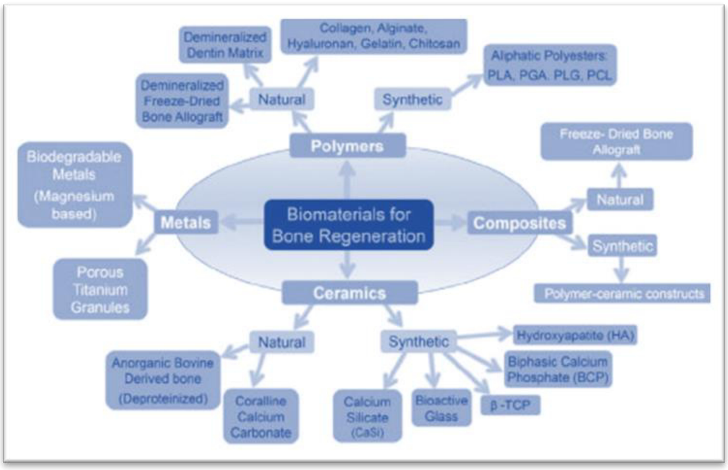

Fig. 1 – Biomaterials for bone regeneration.

It's important to note that the selection of biomaterials depends on factors such as the defect size, location, and patient-specific considerations. Researchers and clinicians carefully choose biomaterials that can provide an optimal environment for bone regeneration based on the specific requirements of each case.

Recent uses of biomaterials include 3D bioprinting for tissue engineering, bioresorbable stents for cardiovascular interventions, smart drug delivery systems with stimuli-responsive properties, and the development of neural interfaces and organ-on-a-chip systems for advanced medical research and treatment.

In this article, we delve into the fundamental aspects of biomaterials, exploring their selection criteria, biocompatibility, and the materials commonly used in medical applications. We discuss the role of biomaterials in tissue engineering, where they act as scaffolds for the regeneration of damaged tissues and organs. Furthermore, we explore their crucial role in the development of drug delivery systems, enabling targeted and controlled release of therapeutic agents.

The use of biomaterials in medical implants has been instrumental in improving the quality of life for countless individuals. We examine the applications of biomaterials in orthopedic and dental implants, cardiovascular devices, and prosthetics, shedding light on their ability to restore lost function and enhance patient well-being (Wang *et al*., 2015).

Additionally, this review touches upon the use of biomaterials in diagnostic tools and imaging techniques, such as contrast agents, biosensors, and monitoring devices, which enable accurate disease detection and monitoring (Chelariu *et al*., 2006; Kokubo and Yamaguchi, 2011).

Finally, we discuss the challenges and future prospects of biomaterials in medical applications, including the need for personalized medicine, advancements in biofabrication techniques, and the exploration of innovative biomaterials for emerging medical technologies.

In conclusion, this review underscores the pivotal role of biomaterials in revolutionizing medical applications. From regenerative medicine to drug delivery systems and medical implants, the versatility and biocompatibility of biomaterials have paved the way for groundbreaking advancements in healthcare. Understanding the current state of biomaterials and their potential future developments will undoubtedly contribute to further advancements in medical science, improving patient outcomes and ushering in a new era of personalized and effective medical care.

2. Classification

Biomaterials are a class of materials that interact with biological systems, ranging from cells and tissues to whole organisms. These materials are designed to be compatible with living systems and are utilized in various medical, pharmaceutical, and biotechnological applications. The choice of biomaterials depends on their intended use and the specific requirements of the application. Here are some common types of materials used for biomaterials:

Metals: Metals such as titanium, stainless steel, and cobalt-chromium alloys are frequently used in biomedical implants due to their excellent mechanical properties, durability, and biocompatibility. They are commonly used for orthopedic implants like joint replacements and dental implants.

Polymers: Polymers offer a wide range of properties and can be tailored to meet specific requirements. Examples of biocompatible polymers include polyethylene, polyurethane, poly(lactic-co-glycolic acid) (PLGA), and poly(ethylene glycol) (PEG). These polymers are used in applications such as drug delivery systems, tissue engineering scaffolds, and surgical sutures.

Ceramics: Bioceramics, such as alumina, zirconia, and hydroxyapatite, are used in medical and dental implants, as well as bone graft substitutes. Ceramics are known for their high biocompatibility, strength, and ability to bond with natural bone tissue.

Composites: Biomaterial composites combine the advantageous properties of different materials. For instance, carbon fiber-reinforced polymers offer high strength and are used in orthopedic applications, while bioactive glass-polymer composites provide both mechanical strength and bioactivity for bone regeneration.

Natural materials: Biomaterials derived from natural sources, such as collagen, chitosan, and silk, are utilized due to their biocompatibility and ability to mimic the extracellular matrix. These materials are often employed in tissue engineering, wound healing, and drug delivery applications.

Hydrogels: Hydrogels are three-dimensional networks of hydrophilic polymers that can absorb and retain large amounts of water. They have a soft and flexible nature that resembles biological tissues and are used in applications such as tissue engineering, drug delivery, and wound dressings.

Biological materials: Biomaterials can also include naturally occurring biological substances like extracellular matrix components, proteins, and peptides. These materials can be used to promote cell adhesion, guide tissue regeneration, and enhance the biocompatibility of implants.

Each class of biomaterials has its own advantages and considerations, and the choice of the best class depends on the specific application and requirements (Bita *et al*., 2016; Liu *et al*., 2021; Anderson *et al*., 2008; Wang *et al*., 2021; Istratov *et al*., 2021). In Table 1 is a comparison highlighting the characteristics of each class of biomaterials.

Table 1
Properties of the main classes of biomaterials

Class	Properties
Metals	**Strength and mechanical properties**: Metals, such as stainless steel and titanium alloys, exhibit excellent strength and mechanical properties, making them suitable for load-bearing applications. **Biocompatibility**: Many metal alloys have good biocompatibility and can integrate well with surrounding tissues. **Corrosion resistance**: Metals can have high corrosion resistance, ensuring long-term stability of implants. **Limitations**: Some metals may cause adverse reactions in certain individuals, and they may not be suitable for applications that require bioresorbability.
Ceramics	**Biocompatibility**: Ceramics, like zirconia ceramics and calcium phosphate, are biocompatible and can promote tissue integration. **Strength and stiffness**: Ceramics possess high strength and stiffness, making them suitable for load-bearing applications. **Wear resistance**: Ceramics have excellent wear resistance, which is beneficial for orthopedic and dental applications. **Brittle nature**: Ceramics are brittle and may be prone to fracture under certain conditions, limiting their use in high-impact applications.
Polymers	**Versatility**: Polymers offer a wide range of properties and can be tailored to specific applications. They can be flexible, biodegradable, and have tunable mechanical properties. **Biocompatibility**: Many polymers are biocompatible and can be designed to mimic the properties of natural tissues. **Ease of processing**: Polymers are generally easier to process and shape compared to metals and ceramics. **Lower strength**: Polymers may have lower strength and stiffness compared to metals and ceramics, limiting their use in high-load applications.
Natural materials	**Biocompatibility**: Natural biomaterials, such as collagen, hyaluronic acid, and fibrin, are biocompatible and often exhibit excellent integration with tissues. **Bioactivity**: Natural materials can possess inherent bioactivity, promoting cell adhesion, migration, and tissue regeneration. **Biodegradability**: Many natural materials are biodegradable, allowing for controlled degradation over time. **Variability and sourcing challenges**: Natural biomaterials may exhibit variability in composition, and their sourcing and processing can present challenges.

It is important to note that the selection of biomaterials involves considering factors such as biocompatibility, mechanical properties, degradation characteristics, sterilization methods, and regulatory requirements to ensure the materials are safe and effective for their intended applications.

3. Selection criteria for biomaterials

The selection criteria for biomaterials depend on the specific application and intended purpose. However, some common criteria considered when choosing biomaterials include:

Biocompatibility: The biomaterial should be compatible with the biological system it will interact with, minimizing adverse reactions and promoting integration with surrounding tissues.

Mechanical properties: The biomaterial should possess suitable mechanical properties that match the intended application. This includes considerations such as strength, flexibility, elasticity, and toughness.

Degradation rate: The degradation rate of the biomaterial should be carefully controlled to align with the healing or regenerative process. It should degrade at a rate that allows for tissue regeneration while maintaining its structural integrity during the healing period.

Stability: The biomaterial should exhibit long-term stability to ensure its functionality is maintained over time without significant degradation or changes in its properties.

Surface characteristics: The surface of the biomaterial can influence cell adhesion, proliferation, and interaction. Surface properties like roughness, topography, and chemical composition should be tailored to promote desired cellular responses.

Immunogenicity: The biomaterial should minimize immune responses and avoid triggering excessive inflammation or rejection reactions.

Sterilization and sterilizability: The biomaterial should be capable of being sterilized to prevent infections and ensure its safety for implantation or use in medical procedures. Different biomaterials may have varying compatibility with different sterilization methods.

Cost-effectiveness: The biomaterial's cost should be reasonable and justifiable for its intended application, considering factors such as manufacturing processes, availability, and scalability.

Regulatory compliance: The biomaterial should meet relevant regulatory requirements and standards to ensure its safety and efficacy in medical applications.

Biodegradability: In certain applications, such as temporary implants or drug delivery systems, biodegradability is desired to eliminate the need for removal procedures.

It's important to note that the specific criteria and their relative importance may vary depending on the intended application, patient-specific factors, and the stage of development or research (Weng *et al*., 2019; Shahani, 2006; Anderson *et al*., 2008; Thomsen and Ericson, 1991; Ackun-Farmmer *et al*., 2021).

To verify the selection criteria of biomaterials, several tests and evaluations are typically conducted. These tests help assess the material's suitability for the intended application and ensure it meets the required criteria. In Table 2 are presented some commonly performed tests.

Table 2
Test used for testing biomaterials

Class	Properties
Biocompatibility Testing	This involves evaluating the material's compatibility with biological systems. It includes tests such as cytotoxicity, genotoxicity, hemocompatibility, and sensitization assessments to determine if the material induces adverse effects on cells, tissues, blood, or the immune system.
Mechanical Testing	These tests evaluate the mechanical properties of biomaterials, including tensile strength, compressive strength, flexural strength, and elasticity. These tests assess whether the material can withstand the loads and stresses it will encounter in the specific application.
Degradation Testing	For biodegradable biomaterials, degradation testing is conducted to assess the material's degradation rate and by-products. This helps ensure the material degrades in a controlled manner without causing harmful effects to the surrounding tissues.
Surface Characterization	Surface properties, such as roughness, surface energy, and wettability, are evaluated to determine how the material interacts with biological systems, including cell adhesion, protein adsorption, and bacterial attachment.
Wear and Friction Testing	For biomaterials used in load-bearing applications, wear and friction tests assess their resistance to wear and evaluate their lubricity. This is crucial to ensure longevity and minimize the potential for adverse reactions or tissue damage.
Sterility Testing	This test confirms that the biomaterial is free from microbial contamination and suitable for use in sterile environments or in contact with sterile biological systems.
In vitro and *In vivo* Testing	*In vitro* testing involves evaluating the material's behavior in simulated physiological conditions, such as cell culture studies, to assess cell-material interactions. In vivo testing involves implanting the material in animal models to evaluate its performance, biocompatibility, and tissue response.
Preclinical and Clinical Trials	For biomaterials intended for human use, preclinical and clinical trials are conducted to assess safety, efficacy, and performance. These trials involve testing the material in animal models and human subjects under controlled conditions.

It's important to note that the specific tests conducted may vary depending on the nature of the biomaterial, its intended application, and regulatory requirements. These tests collectively provide valuable data to verify the selection criteria of biomaterials and ensure their suitability and safety for use in various biomedical applications (Ashtiani *et al*., 2021; Dhivya *et al*., 2015; Srivastav *et al*., 2011; Sidambe *et al*., 2014; Langer and Tirrell, 2004).

4. Status of biomaterials applications

According to a report from Fortune Business Insights, the global biomaterials market was estimated to be valued at around USD 155.05 billion in 2022 and is expected to grow at a compound annual growth rate (CAGR) of 15.52% from 2023 to 2030. However, please note that market sizes are subject to change over time due to various factors such as technological advancements, regulatory changes, and market dynamics (www. Fortunebussinessinsights.com).

Also, ReportsInsights Consulting Pvt. Ltd. has conducted a comprehensive research study on the biomaterials market, which examines various aspects including market size, value, supply chain, regulatory environment, and trends. The report focuses on key factors such as the increasing demand for cardiovascular devices and the importance of advanced biomaterials for efficient tissue replacement, driving the growth of the market. Furthermore, it provides a detailed analysis of market segmentation based on material type, application, and region. By studying these segments, the report uncovers emerging trends and potential opportunities for market players. Armed with this valuable information, manufacturers can enhance their competitive advantage by pursuing strategic collaborations, mergers, and acquisitions, as well as introducing innovative products to strengthen their position in the market (www.globenewswire.com).

The biomaterials market revenue is experiencing growth due to several factors, including increased funding and grants by government agencies worldwide for innovative therapeutic biomaterial development, expanded application in surgical devices, a rise in the prevalence of cardiac issues, and an upsurge in regenerative medicine research. Over the coming years, there is expected to be a notable increase in cosmetic surgery and tissue repair applications, which will contribute to the overall growth of the biomaterials market. Regenerative medicine heavily relies on novel biomaterials, aiming to produce in vitro models that accurately mimic in vivo applications, including the production of transplantable organs and organ models for drug development. The key objective is to develop organoids that closely resemble human organs in terms of functionality. To achieve this, the composition of biomaterials, their uniqueness, and their suitability for each specific organ are of utmost importance. In the field of drug development, the utilization of induced pluripotent stem cell (iPSC)-derived blood-brain barrier (BBB) organoid models, for example, can aid in the selection of drugs based on their ability to penetrate the BBB. This advancement can significantly accelerate the drug development process (www.reportsanddata.com).

The development of cardiac organoids, which aim to replicate the complexities of heart tissue, relies on biomaterials such as peptides linked to scaffolds. The future success of replacing cardiac scars depends on the use of biomaterials that promote tissue regeneration without triggering immune responses and subsequent transplant rejection.

Peripheral nerve and spinal cord injuries can cause significant pain and greatly impact individuals' lives. The primary causes of neurological deficits in these injuries are the disruption and degeneration of axons. Biomaterials offer new possibilities for improving these conditions. They can be designed as scaffolds that mimic the extracellular matrix of nerve tissue, promoting axonal regeneration when implanted. Additionally, biomaterial scaffolds can be utilized to deliver therapeutic agents directly to the damaged site (Virtanen, 2008; Prasad *et al*., 2017; Huang and Best, 2007).

Severe facial injuries, particularly those affecting the underlying bony structure, often require the use of implanted biomaterials and devices for repair. The market for such treatments has experienced revenue growth due to advancements in broad-spectrum antibiotics, a deeper understanding of bone and soft tissue healing, and the remarkable compatibility of well-vascularized facial tissues with alloplastic materials (Huang and Best, 2007; Wu *et al*., 2020; Manivasagam *et al*., 2010; Bobyn *et al*., 1999; Baltatu *et al*., 2022).

The biomaterials market (Fig. 2) encompasses a wide range of materials, including metals, ceramics, polymers, and composites, that are designed for use in medical and non-medical applications. The market is driven by factors such as the increasing prevalence of chronic diseases, growing demand for implantable medical devices, advancements in regenerative medicine and tissue engineering, and the rising geriatric population.

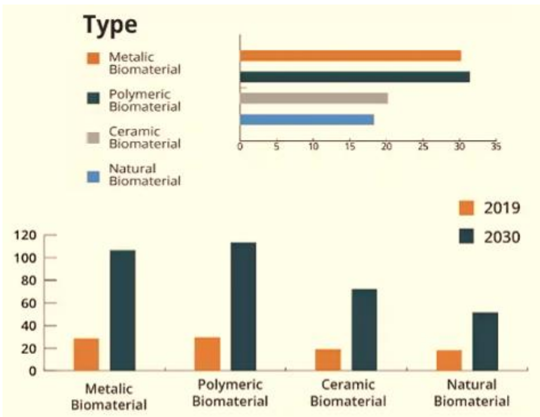

Fig. 2 – Biomaterials market (www.reportsanddata.com).

Within the biomaterials market, medical applications have been the dominant segment, accounting for a significant share. The demand for biomaterials in medical applications is driven by the increasing number of surgeries, rising awareness about the benefits of biomaterials, and advancements in healthcare infrastructure.

It's important to note that the biomaterials market is dynamic and continuously evolving. New materials and technologies are being developed, and the market size is likely to witness growth in the coming years. For the most up-to-date information on the biomaterials market size, I recommend referring to market research reports, industry analysis, and market intelligence sources specific to biomaterials.

5. Biomaterials in Medical Applications

Biomaterials play a pivotal role in various medical applications, revolutionizing the field of healthcare. These materials, carefully designed to interact with biological systems, are utilized in a wide range of medical devices, implants, and therapies. Biomaterials in medical applications offer unique properties such as biocompatibility, mechanical strength, controlled degradation, and bioactivity, enabling them to seamlessly integrate with the human body. They contribute to advancements in areas like orthopedics, cardiovascular devices, tissue engineering, drug delivery systems, and regenerative medicine. By harnessing the potential of biomaterials, medical professionals can improve patient outcomes, enhance quality of life, and pave the way for innovative treatments and interventions. With ongoing research and development, biomaterials continue to drive progress in medical science, unlocking new possibilities for healthcare solutions (Wang *et al.*, 2019; Janarthanan and Noh, 2021; Spataru *et al.*, 2021; Bastola *et al.*, 2020; Bhattacharyya *et al.*, 2021).

Orthopedics: Biomaterials have revolutionized orthopedic interventions, enabling the repair and regeneration of damaged bones and joints. Synthetic bone graft substitutes, composed of calcium phosphate ceramics or bioactive glasses, promote bone healing and integration. Metallic implants provide strength and stability for joint replacements and fracture fixation, improving patients' mobility and quality of life.

Cardiovascular Applications: Biomaterials have paved the way for life-saving cardiovascular interventions. Biocompatible and hemocompatible materials, such as biostable polymers and titanium alloys, are used in the fabrication of stents, heart valves, and artificial blood vessels. These devices restore blood flow, prevent clotting, and alleviate symptoms associated with cardiovascular diseases.

Tissue Engineering: Biomaterials play a crucial role in tissue engineering, aiming to regenerate damaged or lost tissues. Scaffold materials provide structural support for cell attachment, proliferation, and differentiation. Biodegradable polymers, such as poly(lactic-co-glycolic acid) (PLGA) and collagen, facilitate the growth of new tissues, while biocompatible hydrogels serve as injectable matrices for cell encapsulation and controlled drug release.

Biomaterials have transformed medical applications, offering unprecedented opportunities for therapeutic interventions, tissue engineering, and medical device development. The diverse range of biomaterials, including polymers, metals, ceramics, and composites, cater to specific requirements in various medical fields. These materials enable improved patient outcomes, ranging from enhanced mobility and reduced pain to tissue regeneration and organ replacement. As research and innovation continue, biomaterials will undoubtedly play a central role in shaping the future of medicine, driving advancements and innovations in healthcare.

6. Challenges

The utilization of biomaterials in medical applications brings forth numerous benefits, but it also poses certain challenges that need to be addressed. These challenges encompass aspects such as biocompatibility, mechanical performance, degradation, sterilization, and long-term safety. Achieving optimal biocompatibility, ensuring the biomaterial's compatibility with the host's tissues and minimizing adverse reactions, remains a key challenge. Additionally, balancing the mechanical properties of biomaterials to withstand physiological loads while avoiding excessive stiffness or brittleness is crucial. Controlling the degradation rate of biodegradable biomaterials to align with tissue healing and regeneration timelines presents another challenge. Furthermore, ensuring effective sterilization of biomaterials without compromising their structural integrity is vital. Lastly, ensuring the long-term safety and reliability of biomaterials throughout their lifespan in the body is an ongoing challenge that requires comprehensive testing and evaluation. Addressing these challenges is essential for advancing the field of biomaterials and maximizing their potential for medical applications. The main challenges are presented in Table 3.

Table 3
Test used for testing biomaterials

Aspects	Description
Biocompatibility	One of the primary challenges in biomaterials development is achieving optimal biocompatibility. While many biomaterials exhibit good biocompatibility, there can be variations in individual patient responses and potential immune reactions. Improving biocompatibility to minimize adverse reactions remains a crucial challenge.
Degradation Rate and Mechanical Properties	Biomaterials designed for temporary use, such as scaffolds, should degrade at a rate that allows new tissue formation but maintains sufficient mechanical stability during the healing process. Balancing degradation kinetics and mechanical properties is challenging, as materials that degrade too quickly may compromise structural integrity, while those that degrade too slowly can impede tissue regeneration.
Biomaterial-Host Interactions	Biomaterials interact with the host environment upon implantation. These interactions involve cellular responses, inflammation, and potential infection. Understanding and controlling these interactions to optimize tissue integration and minimize adverse effects are ongoing challenges.
Long-term Stability and Durability	Some biomaterials, such as implants or medical devices, require long-term stability and durability within the body. Ensuring the mechanical integrity and functional performance of these materials over extended periods can be challenging, especially when considering wear, corrosion, or fatigue in dynamic physiological environments.
Scalability and Manufacturing	Biomaterials must be scalable and manufacturable to meet clinical demands. Challenges exist in terms of producing biomaterials with consistent quality, reproducibility, and cost-effectiveness, especially when transitioning from laboratory research to large-scale production.

7. Future Prospects

The future prospects for biomaterials used in medical applications are incredibly promising, with advancements on the horizon that have the potential to revolutionize healthcare. Emerging technologies, such as 3D printing and nanotechnology, are paving the way for precise fabrication of biomaterials with tailored properties and intricate structures. This opens up new possibilities for personalized implants and tissue engineering. Additionally, the development of smart biomaterials that can respond to biological cues or external stimuli holds great potential for targeted drug delivery and enhanced therapeutic outcomes. The integration of bioactive molecules and growth factors into biomaterials is also anticipated to further stimulate tissue regeneration and repair. Moreover, the use of biomaterials in combination with stem cells and gene therapy offers exciting prospects for regenerative medicine and the development of novel therapies. As research and innovation continue to accelerate, biomaterials are poised to play a pivotal role in shaping the future of medical applications, ultimately improving patient care and transforming the healthcare landscape.

8. Conclusions

In conclusion, this review highlights the significant role of biomaterials in medical applications and their immense potential to revolutionize healthcare. Biomaterials offer unique properties such as biocompatibility, mechanical strength, controlled degradation, and bioactivity, making them indispensable in various medical devices, implants, and therapies. Despite challenges in achieving optimal biocompatibility, balancing mechanical properties, controlling degradation, sterilization, and ensuring long-term safety, ongoing research and advancements continue to address these hurdles. The future prospects for biomaterials in medical applications are highly promising, with emerging technologies like 3D printing, nanotechnology, smart biomaterials, and the integration of bioactive molecules, stem cells, and gene therapy opening up new frontiers. As biomaterials evolve, personalized treatments, tissue regeneration, targeted drug delivery, and innovative therapies are becoming increasingly attainable. With continuous research and innovation, biomaterials are poised to reshape the landscape of medical applications, ushering in a new era of improved patient care and transformative healthcare solutions.

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BIOMATERIALE ÎN APLICAȚII MEDICALE: TRECERE ÎN REVISTĂ

(Rezumat)

Biomaterialele au apărut ca un domeniu esențial în medicina modernă, revoluționând modul în care diagnosticăm, tratăm și restaurăm corpul uman. Cu capacitatea lor unică de a interacționa cu sistemele biologice, biomaterialele au deschis noi căi pentru aplicații medicale, variind de la medicina regenerativă și ingineria

țesuturilor până la sisteme de administrare a medicamentelor și implanturi medicale. Acest studiu își propune să ofere o privire de ansamblu asupra diverselor aplicații ale biomaterialelor în domeniul medicinei, evidențiind semnificația acestora, progresele recente și perspectivele de viitor.

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NUMERICAL STUDY ON PEG 400-BASED MATERIALS ENHANCED WITH OXIDE NANOPARTICLES

BY

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Abstract. Nanofluids are homogeneous mixtures of solids and liquids, with solid particles smaller than 100 nm uniformly and stably suspended in a fluid. Nanoparticles that have high thermal conductivity include metallic (Ag, Cu, Al, etc.) and non-metallic (TiO_2, Al_2O_3, ZnO, MgO, carbon nanotubes, etc.) particles and can be used as an additive for the preparation of nanofluids. There are several advantages in dispersing nanoparticles compared to millimeter-sized particles in working fluids, such as better nanoparticle stability in base fluids, lower viscosity, improved thermal conductivity and decreased corrosion. Thus, the preparation of nanofluids with good stability is the most crucial step in conducting experimental studies on their thermophysical properties and heat transfer. In this paper we have carried out a numerical study of the laminar flow of a fluid through a pipe, using the Ansys Fluent software. The simulation corresponds to the forced laminar flow and heat transfer for two oxides - PEG 400 nanofluids. To obtain nanofluids, MgO and TiO_2 nanoparticles in different mass concentrations were dispersed in the PEG 400 base liquid. The properties of nanofluids were determined experimentally (viscosity and specific heat) and theoretically (density and thermal conductivity). The numerical analysis was implemented for two Reynolds numbers, Re = 500 and Re = 1000. The velocity of the fluid entering the pipe is constant and was calculated based on the Reynolds number for each fluid. Concerns the results, the heat transfer

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performance of nanofluids was defined by the convective heat transfer coefficient. Numerical research that significantly contributes to the critical analysis of the new studied fluids. The general conclusion of the numerical studies was that it is absolutely necessary to first determine the thermophysical properties of the fluids and their variation with temperature, thus creating the premises for a correct numerical analysis.

Keywords: MgO, TiO_2, PEG 400, nanofluids, thermophysical properties.

1. Introduction

The idea of developing new fluids, with nanoparticles in suspension, appeared due to the exhaustion of all methods of heat transfer intensification. Initially, the idea of intensifying heat transfer was based on increasing the heat transfer surface, later, research was focused mainly on the heat transfer coefficient, which depends very much on the type of fluid (with reference to its thermophysical properties). Thus, the idea of fluid improvement and the development of new fluids with high thermal conductivity appeared. Studies on the determination of the thermophysical properties of nanofluids must be deepened, as there are no complete approaches in the literature, making it impossible to evaluate the behavior of these fluids in practical applications.

Dehaj and Mohiabadi (2019) performing an interesting study on MgO nanoparticle dissolved in a deionized water solution with polyethylene glycol (PEG-400) surfactant. The manufactured new fluids were study in terms of performance of nanofluids in heat pipe solar collector, and was found an higher efficiency of heat pipe solar collector at higher concentrations of the nanofluids. Another investigation of gamma-Al_2O_3, TiO_2, and CuO nanoparticle enhanced fluids was conducted by Hojjat *et al*. (2011). More precisely, authors studied the turbulent flow region at different concentrations of nanoparticles using correlations for the prediction of the Nusselt number, and concluded that the convective heat transfer coefficient and Nu number are significantly higher than of base fluid. Other authors (Aissa *et al*., 2023; Minea *et al*., 2021; Chavez *et al*., 2022; Rubbi *et al*., 2021) reviewed the results obtained in various research performed to evaluate the thermophysical properties of nanofluids and their capacity to improve the heat transfer occurring in industrial equipment's. Other researchers performed the numerical analyzes that took into account a laminar flow regime and different practical situations of heat flow application, for example: along the entire length of the tube (Chereches *et al*., 2017; Sekrani *et al*., 2019), in the middle of the tube (Chereches *et al*., 2019; Chereches *et al*., 2021) or only at the exit of the fluid from the tube (Chereches *et al*., 2020).

The general conclusion of the numerical studies was that it is absolutely necessary to determine in the first phase the thermophysical properties of the fluids and their variation with temperature, thus creating the premises for a correct numerical analysis. In this paper, the numerical analysis of PEG 400-based fluids, enriched with nanoparticles in suspension, will be presented in detail, which is accompanied by a detailed discussion of the results as well as a comparison with the base fluid.

2. Numerical approach and results

In this section are simulate a forced laminar flow in a pipe using Ansys Fluent (Ansys Inc. Workbench) for two oxides - PEG 400 nanofluids. The description of the case studied are fully explained in Chereches *et al.* (2021). The liquid enters the tube at a constant velocity (calculated based on the Reynolds Number (see Eq. (1)) value of each liquid) and constant temperature 298.15K. The simulation was performed for two Reynolds Number, Re at 500 and Re at 1000.

$$Re = \frac{w \cdot d}{\nu} \tag{1}$$

In Eq. (1), w is the average fluid velocity, (m/s); d is the characteristic length of the flow, (m); and υ is the kinematic viscosity of the fluid, (m^2/s). Chemicals properties, as per delivered by the provider for the base fluid and nanoparticles, are presented in the following tables (see Table 1 and Table 2):

Table 1

Main properties of polyethylene glycol PEG 400 at 298K

Chemical formula	C_2H_4O
Melting point	> 300°C
Molecular mass	380 – 420 g mol^{-1}
Density	1.125 g cm^{-3}
pH	4.5 – 7.0

Table 2

Main properties of MgO and TiO_2 nanoparticles

Nanoparticle	CAS Number	Dimensions	Density	Molar mass	Specific Heat Capacity
MgO	549649	50 nm	3.580 g/cm^3	40.32 g/mol	877 J Kg^{-1} K^{-1}
TiO_2	718467	21 nm	4.0 g/cm^3	79.87 g/mol	683 J Kg^{-1} K^{-1}

Sample concentrations were calculated using mass fractions, and conversions between mass and volume fractions are given in Table 3.

$$\frac{1}{\varphi_{vol}} = 1 + \frac{\rho_p}{\rho_{bf}}\left(\frac{1-\varphi_{wt}}{\varphi_{wt}}\right) \tag{2}$$

In Eq. (2), φ_{wt} is mass fraction, φ_{vol} is particle volume fraction, ρ is density, p is refers to particles and bf is refers to base fluid. The main thermophysical properties at 298.15 K for the fluids used in this research are presented in Table 4 and in Table 5 are show the numerical results for Re = 500 and Re = 1000. Since two types of nanofluids with the same concentration of nanoparticles and the same base fluid were used for the comparison, their properties are also described in Table 4. The nanoparticles used were ZnO and Al_2O_3, the studies being carried out by these authors (see Chereches *et al*., 2023).

Table 3
Samples code and concentration

Code fluids	Mass fraction	Volume fraction
PEG 400	0.000	0.000
PEG0.25_MgO	0.0025	0.00079
PEG0.5_MgO	0.0050	0.00158
PEG1_MgO	0.0100	0.00316
PEG1.5_MgO	0.0150	0.00476
PEG2.5_MgO	0.0250	0.00799
PEG0.25_TiO_2	0.0025	0.00070
PEG0.5_TiO_2	0.0050	0.00141
PEG1_TiO_2	0.0100	0.00283
PEG1.5_TiO_2	0.0150	0.00426
PEG2.5_TiO_2	0.0250	0.00716

Table 4
Thermophysical properties of the fluids at 298.15 K

Fluids	Specific heat, J/Kg K	Density, Kg/m^3	Thermal conductivity, W/ m K	Dynamic viscosity, N s/m^2	Kinematic viscosity, m^2 s	Velocity, m/s for Re = 500	Velocity, m/s for Re = 1000
PEG 400	*2325*	*1125*	*0.190*	*0.124*	*1.10E-04*	*0.937*	*1.875*
PEG 400 + 0.5% MgO	*2119*	*1128*	*0.190*	*0.0989*	*8.77E-05*	*0.746*	*1.491*
PEG 400 + 1.5% MgO	*1889*	*1136*	*0.195*	*0.107*	*9.42E-05*	*0.801*	*1.602*
PEG 400 + 0.5% TiO_2	*2245*	*1129*	*0.191*	*0.105*	*9.30E-05*	*0.791*	*1.582*
PEG 400 + 1.5% TiO_2	*2370*	*1137*	*0.194*	*0.115*	*1.01E-04*	*0.860*	*1.720*
**PEG 400 + 0.5% Al_2O_3*	*2472*	*1127*	*0.191*	*0.129*	*1.11E-04*	*0.973*	*1.947*
**PEG 400 + 0.5% ZnO*	*2359*	*1130*	*0.199*	*0.130*	*1.15E-04*	*0.979*	*1.957*

*Fluids used for comparison

Table 5

Numerical results for Re = 500 and Re = 1000

Fluids	Reynolds Number	Velocity	Nu at x=267	Nu at x=6045	Tm at x=267	Tm at x=6045	Tw at x=267	Tw at x=6045
PEG 400	500	0.937264	89.07	169.44	298.00	298.04	315.64	307.32
	1000	1.874528	106.78	377.65	298.00	298.01	312.71	302.17
PEG 400 + 0.5% MgO	500	0.745555	82.50	148.08	298.00	298.10	317.05	308.71
	1000	1.491111	103.83	293.50	298.00	298.02	313.13	303.37
PEG 400 + 1.5% MgO	500	0.800937	83.13	148.24	298.00	298.11	316.90	308.71
	1000	1.601873	105.35	289.06	298.00	298.02	312.92	303.45
PEG 400 + 0.5% TiO_2	500	0.790839	63.10	119.39	298.00	298.19	322.90	311.35
	1000	1.581678	84.32	163.47	298.00	298.03	316.64	307.65
PEG 400 + 1.5% TiO_2	500	0.860063	89.28	166.29	298.00	298.05	315.60	307.50
	1000	1.720125	108.19	361.12	298.00	298.01	312.52	302.36

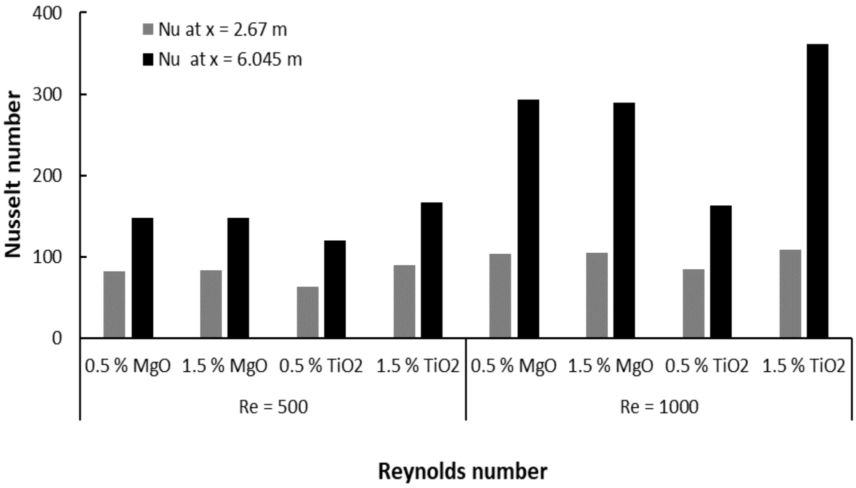

Fig. 1 – Nusselt number variation versus Reynolds number, at x = 2.67 m and x = 6.045 m.

As can be seen from Table 4, the nanofluids with ZnO and Al_2O_3, with a mass concentration of 0.5% have a higher specific heat and viscosity compared to the other nanofluids with the same concentration. Results for the Nu number at both distance are shown in Figs. 1 and 2, where it can see an increase of Nu number while the nanoparticles are added to base fluid and Re increase. The biggest increases were recorded for nanofluids with ZnO and Al_2O_3, almost twice as high compared to nanofluids with TiO_2 and MgO. In Fig. 3 are portrayed the data for the relative heat transfer coefficient for suspensions with MgO and TiO_2. Also, results show that adding 0.5% MgO to base fluid, the heat transfer is reduced (see Fig. 4). This phenomenon may appear due to the high increase in viscosity. If we take a look at Fig. 4, we can see that the higher heat transfer coefficient was obtain for nanofluids with moderate addition (0.5%) of nanoparticles of ZnO and Al_2O_3. This observation validates the influence of the base liquid and the possible synergy between base fluid and NP type on the heat transfer performance.

If considering the overall heat transfer performance of the entire geometry, the outlet wall temperature was evaluated as indicated in Fig. 5. The highest temperature is at the end of the heating area (see x=2.65 m) and the fact that the temperature drops at the exit shows an increase in heat transfer in the pipe, and in our case the best results were for the nanofluid with 0.5% wt TiO_2 at Re = 500.

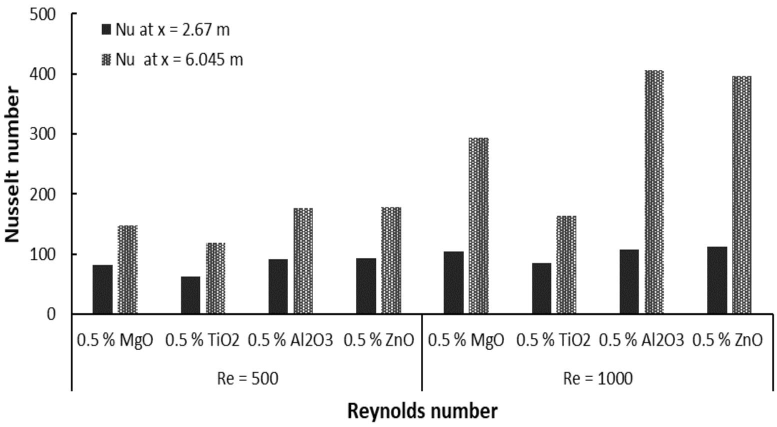

Fig. 2 − Nusselt number variation versus Reynolds number, at x = 2.67 m and x = 6.045 m.

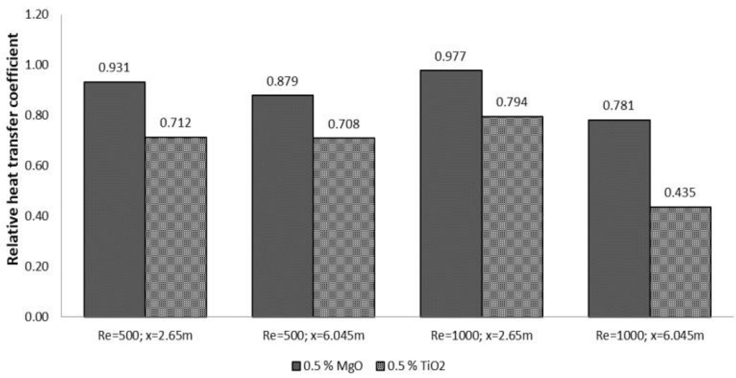

Fig. 3 – Relative heat transfer coefficient variation in comparison with base fluid, at x = 2.67 m and x = 6.045 m.

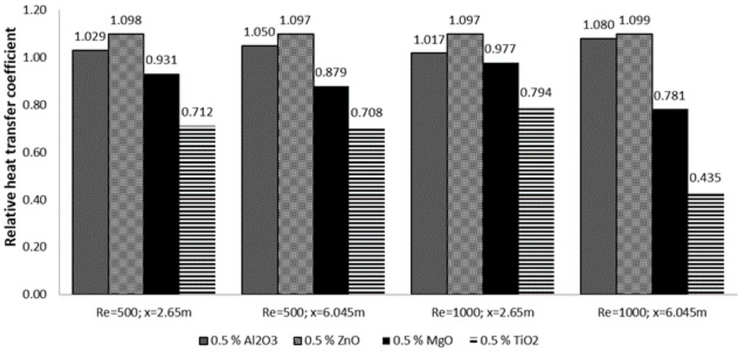

Fig. 4 – Relative heat transfer coefficient variation in comparison with base fluid, at x = 2.67 m and x = 6.045 m, for four different fluids.

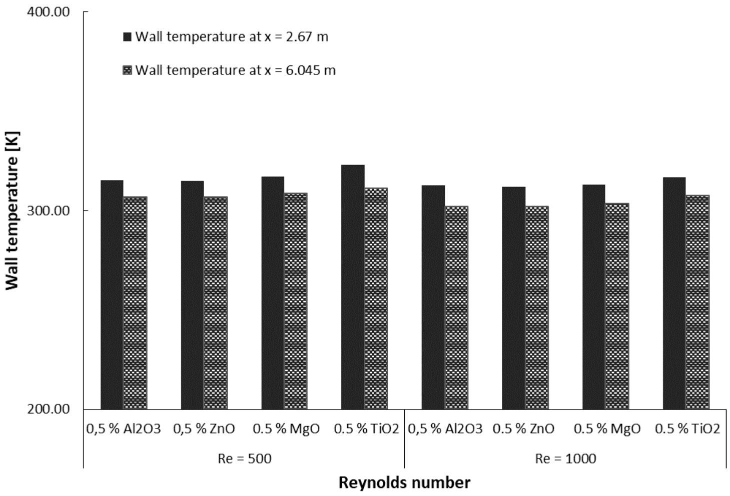

Fig. 5 − Wall temperature evaluation.

3. Conclusions

In this paper, a numerical analysis was performed to estimate the thermal transfer performance of some nanofluids based on PEG 400 and several dispersions with nanoparticles with a maximum mass concentration of 1.5% wt. The results were discussed in terms of the convective heat transfer coefficient and the Nusselt number. As a general observation, it can be assert that the numerical results strongly depend on the concentration of nanoparticles in the base fluid, the type of nanoparticles and the Reynolds number. Focused on the results obtained, the conclusions of this numerical study can be summarized as follows:

– Nanofluids are shown to be a very interesting class of nanofluids for many engineering applications, namely in heat transfer (HTF's) and storage.

– Nusselt number is highly rising with the Reynolds number.

– Medium temperature at the end of the pipe is greater.

– Wall temperature in the middle of the pipe is higher.

– Heat transfer of the studied nanofluids is influenced by Reynolds number and fluid structure (i.e. nanoparticles addition).

Acknowledgements. This paper was financially supported by the Project „Network of excellence in applied research and innovation for doctoral and postdoctoral programs"/InoHubDoc, project co-funded by the European Social Fund financing agreement no. POCU/993/6/13/153437. The authors acknowledge the support of Technical University "Gheorghe Asachi" of Iași within the project "Performance and excellence in postdoctoral research 2022".

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STUDIU NUMERIC PRIVIND FLUIDUL PEG 400 ÎMBUNĂTĂȚIT CU NANOPARTICULE OXIDICE

(Rezumat)

Nanofluidele sunt amestecuri omogene de solide și lichide, cu particule solide mai mici de 100 nm suspendate uniform și stabil într-un fluid. Nanoparticulele care au o conductivitate termică ridicată includ particule metalice (Ag, Cu, Al etc.) și nemetalice (TiO_2, Al_2O_3, ZnO, MgO, nanotuburi de carbon etc.) și pot fi utilizate ca aditiv pentru prepararea nanofluidelor. Există mai multe avantaje privind dispersarea nanoparticulelor în fluidele de lucru în comparație cu particulele de dimensiuni milimetrice, cum ar fi o stabilitate mai bună a nanoparticulelor în fluidele de bază, vâscozitate mai scăzută, conductivitate termică îmbunătățită și coroziune scăzută. Astfel, prepararea nanofluidelor cu stabilitate bună este pasul cel mai crucial în efectuarea de studii experimentale asupra proprietăților termofizice și a transferului de căldură. În această lucrare am realizat un studiu numeric al fluxului laminar al unui fluid printr-o conductă, utilizând software-ul Ansys Fluent. Pentru a obține nanofluide, nanoparticulele de MgO și TiO_2, în diferite concentrații masice au fost dispersate în lichidul de bază PEG 400. Proprietățile nanofluidelor au fost determinate experimental (vâscozitate și căldură specifică) și teoretic (densitate și conductivitate termică). Analiza numerică a fost implementată pentru două numere Reynolds, Re = 500 și Re = 1000. Viteza fluidului care intră în conductă este constantă și a fost calculată pe baza numărului Reynolds pentru fiecare fluid. În ceea ce privește rezultatele, performanța transferului de căldură al nanofluidelor a fost definită de coeficientul de transfer de căldură convectiv. În concluzie, cercetările numerice contribuie semnificativ la analiza critică a noilor fluide studiate și este absolut necesar să se determine mai întâi proprietățile termofizice ale fluidelor și variația acestora cu temperatura, creând astfel premisele unei analize numerice corecte.

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ŞTIINŢA ŞI INGINERIA MATERIALELOR

CULTURAL AND CREATIVE INDUSTRIES IN THE NORTH-EASTERN REGION OF ROMANIA: ANALYSIS OF THE CREATIVE ECONOMY

BY

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Abstract. The fact that the creative industries are an important and growing part of a country's economy is not a surprise anymore. That is also the case of Romania where the National Institute for Cultural Research and Training (INCFC) places a strong emphasis on the relationship between creativity, culture, economy, and society, highlighting the interdependence between these areas. The paper proposes an analysis of the active cultural and creative industries in the North-East Region of Romania, looking at their distribution, establishment date, and turnover over the last five years. The aim of this paper is to identify the impact of the pandemic on the cultural and creative industries in the North-Eastern Region, based on the fluctuations in turnover. This will allow for a comparison of the sectors that were most affected by the pandemic with those that managed to find ways to mitigate the impact. Overall, the paper demonstrates a strong understanding of the importance of the creative industries in Romania's economy and the need for an analysis of their response to the pandemic.

Keywords: creative industries, entrepreneurship, innovation, pandemic, and turnover.

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1. Introduction

Creative industries are an important part of modern economies, increasingly recognized by governments, businesses, and the public at large as sources of beauty expression as well as financial value and jobs (Landoni *et al.*, 2019; Rodríguez-Gulías *et al.*, 2020). Scholars have conducted significant research in the creative industries, distributed across the fields of business and management, economics, geography, law, or studies of individual sectors or activities such as design or media.

Creative industries refer to a range of economic activities that are based on individual creativity, skill, and talent, i.e., factors of production for which high-income countries have a comparative advantage. In contrast to most other industries, their main output is intellectual property rather than material goods or immediately consumed services (Müller *et al.*, 2009). These industries include fields such as art, design, fashion, film, music, literature, theatre, gaming, and advertising, among others.

Creative industries are often seen as a vital part of the global economy, as they contribute to economic growth, job creation, and innovation. They are also important for cultural and social reasons, as they help to shape the way people think about the world and express themselves.

One of the key features of the creative industries is their reliance on intellectual property, which includes copyrights, trademarks, and patents. These legal protections are essential for creators to be able to profit from their work and encourage further innovation in their respective fields. Overall, the creative industries play an important role in the global economy and society, and their contributions are likely to continue to grow in the future.

First identified in December 2019 in the city of Wuhan, Hubei Province, China, COVI-19 (highly contagious respiratory illness caused by the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2)) has spread rapidly worldwide, leading to a global pandemic, by causing among others business closures, job losses and unemployment, supply chain disruptions (at business level), travel restrictions and border closures, lockdowns and social distancing, mental health challenges, educational disruptions, changes in cultural events (at social and cultural level).

This COVID-19 pandemic has had a significant negative impact on countless businesses, leading to serious disruptions for many industries (Leite *et al.*, 2020; Khlystova *et al.*, 2022; Škare *et al.*, 2021), including the creative industries worldwide (Comunian and England, 2020; Harper, 2020; Vitálišová *et al.*, 2021; Popa *et al.*, 2021; Snowball and Gouws, 2022; Gnezdova *et al.*, 2022; Gouvea *et al.*, 2023).

In this context, the need for an analysis with the focus on the COVID-19 impact on cultural and creative industries is an essential step in understanding industry dynamic as the research focusing on this is very limited (Dümcke, 2021; Majdúchová, 2021).

The present study covers the COVID-19 impact on cultural and creative industries in the North-Eastern Region of Romania, analysing the turnover fluctuations.

2. Creative Industries in the North-East Region of Romania

The creative industries in the North-East Region of Romania have known over the years a continuous recognition as true engines of economic growth, especially since 2004, when the city of Iași was chosen to be part, as a representative of Romania, of the "creative cities network" in South East Europe (British Council Library, 2014), along with Plovdiv (Bulgaria), Split (Croatia), Novi Sad and Belgrade (Serbia/Montenegro) Tuzla (Bosnia), Pristina (Kosovo), Skopje (Macedonia), Tirana (Albania). Following this moment, Iasi began to be increasingly recognized as one of the main cultural-creative cities in Romania, and alongside with other five, among the 190 cultural-creative European cities, as highlighted by the Cultural and Creative Cities Monitor 2019 Report (Montalto *et al*., 2019).

The network was built by the British Council in Southern Europe, and the chosen cities were considered representative of the creative industries and creative potential, an essential component of the project being the focus on regional development, something pursued in the continuation and within this postdoctoral research.

According to the National Institute for Cultural Research and Training (INCFC), the cultural and creative sectors in Romania, are researched and analyzed considering the cultural, social, and economic values they generate, placing a strong emphasis on the relationship of interdependence between creativity, culture, economy, and society.

INCFC carries out the research of the cultural and creative sectors starting from their definition established in the ESSnet-Culture model but adapted to the Romanian environment and in accordance with the strategic vision proposed in the White Paper of the Cultural and Creative Sectors in Romania, thus taking into account the technological progress that led and lead to changes in the economy, cultural practices and society (INCFC, 2017).

Consequently, INCFC proposed a model for classifying these sectors into three main categories: cultural, creative, and transversal, with eleven sub-domains: libraries and archives; cultural heritage; craft art; performing arts; architecture; books and press; visual arts; audio-visual and multimedia; advertising; IT, software and electronic games; Research and Development.

3. Methodology

The current research was carried out in order to identify the impact of the pandemic on the cultural and creative industries, based on the relevance of the Nomenclature of Economic Activities (NACE) at the regional level.

Hence in carrying out the proposed analysis:

- ✓ all 54 NACE codes were taken into account, grouped into 10 cultural and creative sectors, called "CCI sectors", from the total of NACE codes defined in official documents at national and European level, as presented in Table 1; the necessary data, such as the number of active creative businesses, their fluctuation over time, as well as the turnover recorded in the period 2017-2021 were taken from official public databases;
- ✓ out of the 9508 active creative businesses identified in the North-Eastern region of Romania, only 3541 companies were considered, the filtering criterion being the choice of those that had their e-mail address available for contact.

Table 1

Creative Industries businesses active in the North-East Region of Romania, according with NACE classification

	Cultural and Creative sectors	Corresponding NACE	Total no of CCI in the N-E Region of Romania
1	*Archives and Libraries*	*8542, 8559, 8560, 9101*	*546*
2	*Book and Press*	*1811-1814, 1820, 4761, 4762, 5811-5814, 5819*	*618*
3	*Visual Arts: Fine Arts, Photography and Design*	*4778, 7410, 7420, 8552*	*1384*
4	*Performing Arts (Music, Dance, Theatre, Combined Arts and Other Live Performances)*	*7430, 9001-9004, 9321, 9329, 9412*	*1070*
5	*Audio-visual and media (film, radio, television, video, phonograms, multimedia works, videograms)*	*2680, 4763, 5911-5914, 5920, 6010, 6020, 6203, 6209, 6391, 7722*	*478*
6	*Software, IT, games*	*5821, 5829, 6201, 6202, 6311, 6312*	*2355*
7	*Architecture*	*7111*	*569*
8	*Advertising*	*7311, 7312*	*758*

Table 1
Continuation

	Cultural and Creative sectors	Corresponding NACE	Total no of CCI in the N-E Region of Romania
9	*Cultural heritage (museums, historical monuments, archaeological sites, intangible heritage)*	*9102-9104*	*5*
10	*Crafts*	*1320, 1411, 1419,1420, 1431, 1439, 1511, 1512, 1520, 1629, 2041, 2042, 2313, 2332, 2341, 2349, 2370, 2550, 2559, 3109, 3212, 3213, 3220, 3240, 3291, 3299*	*1642*
11	*Research and Development*	*7211, 7219, 7220*	*83*
Total of ICC businesses in the North-East Region of Romania			***9508***

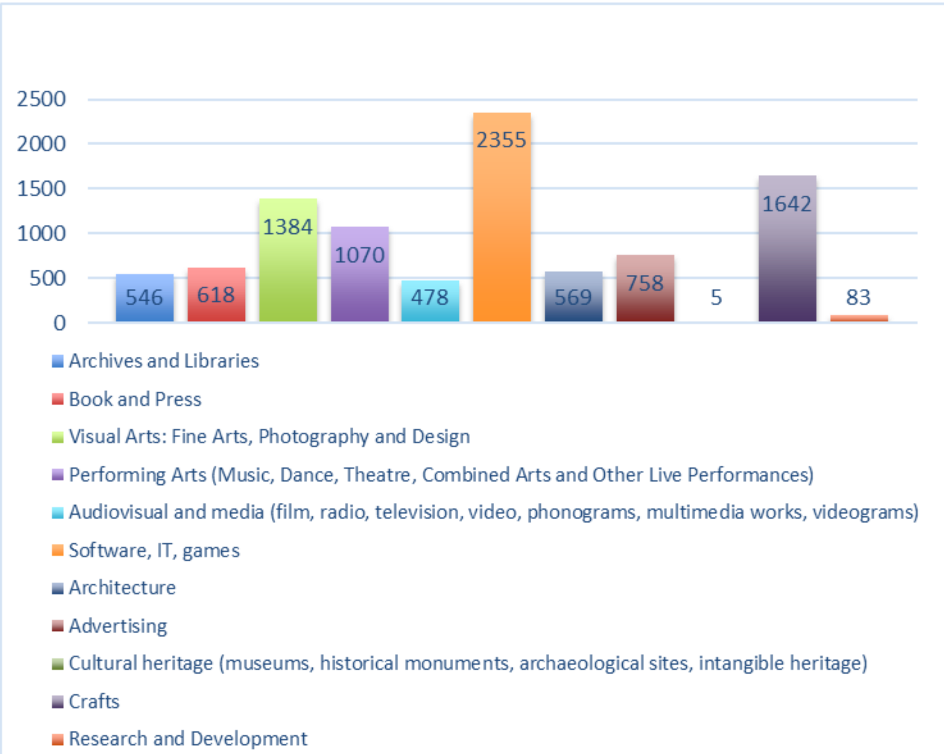

Fig. 1 – CCI businesses in the North-East Region of Romania.

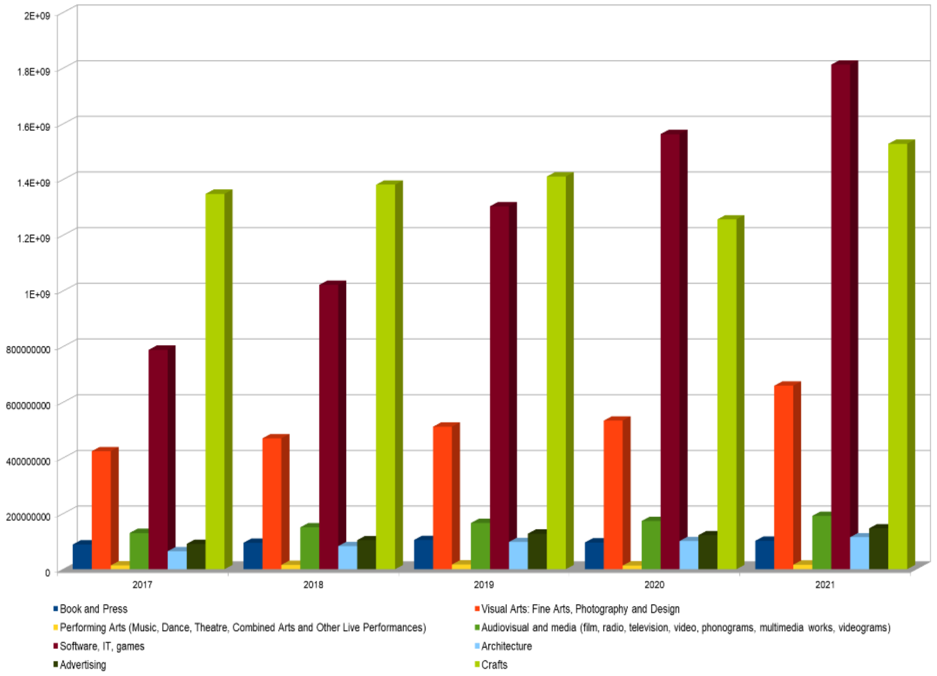

Fig. 2 – The evolution/fluctuation of the number of companies established in different ICC sectors, in the North-Eastern region.

The *Software, IT, games* sector occupies a leading position not only in the analysed region, but at the national level, and not only in terms of volume, but also in terms of turnover, for many years in a row (Figs. 1 and 2). For example, in 2018, this creative sector stood out by far, dominating with 41.5% of the total. The share is the same even as in 2015 (also 41%), but the volume of the sector knowing a spectacular increase of over 50% in the 3 years. At the level of the analysed region, the businesses classified in four (5821, 6201, 6202, and 6311) of the six NACE codes in the *Software, IT, games* sector experienced significant yearly growth in the period 2017-2022 (Figs. 3, 5-7), which proves that for them the COVID-19 pandemic was not an obstacle to their organic growth but an advantage due to the increased need for digitization (Alekseieva *et al*., 2021; Cone *et al*., 2022; Zancajo *et al*., 2022). After experiencing an upward evolution in the period 2017-2020, in 2021, the other two sectors (5829, 6312), felt the negative impact of the COVID-2019 pandemic, the data showing a decrease in both cases in terms of turnover (Figs. 4 and 8).

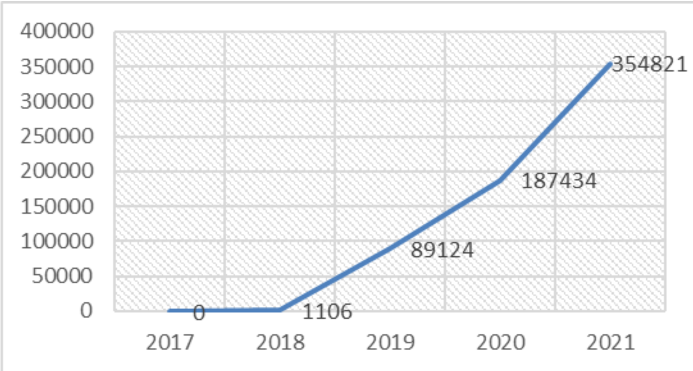

Fig. 3 – The evolution of turnover in the *Computer game publishing activities* sector (5821 NACE code).

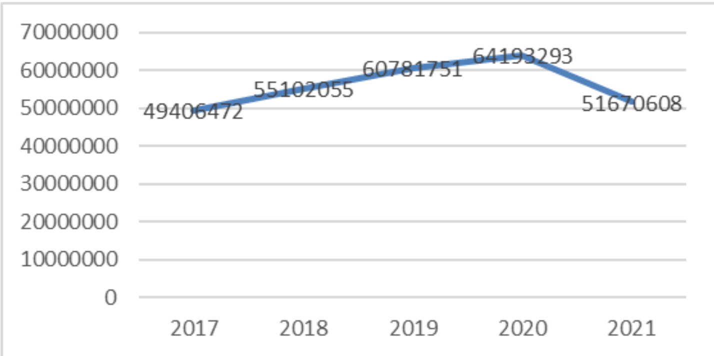

Fig. 4 – The evolution of turnover in the *Other software editing activities* sector (5829 NACE code).

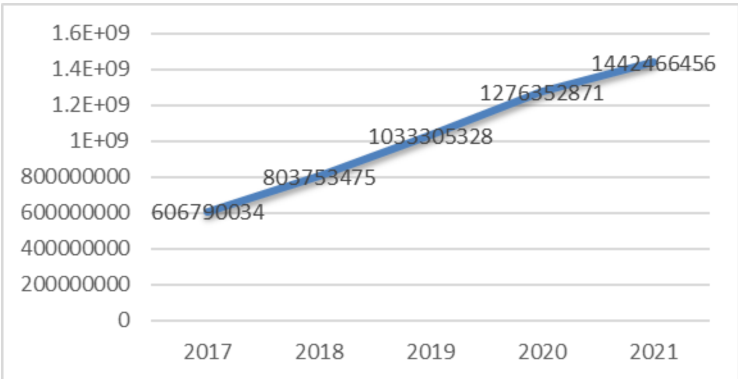

Fig. 5 – The evolution of turnover in the *Custom software development activities* sector (6201 NACE code).

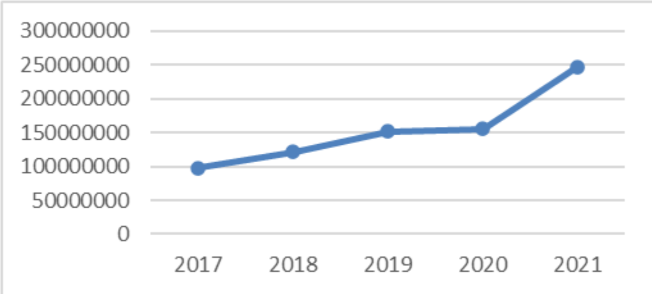

Fig. 6 – The evolution of turnover in the *Information technology consulting activities* sector (6202 NACE code).

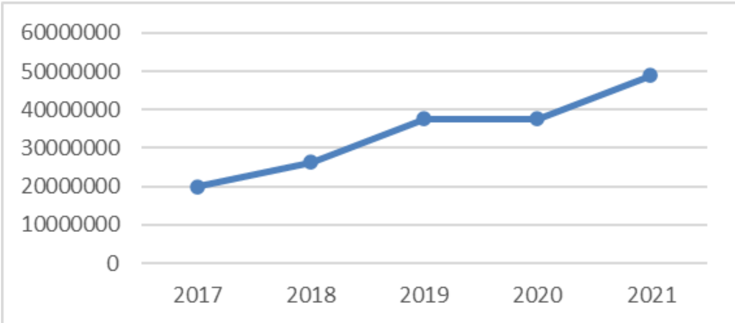

Fig. 7 – The evolution of turnover in the *Data processing web page management and related activities* sector (6311 NACE code).

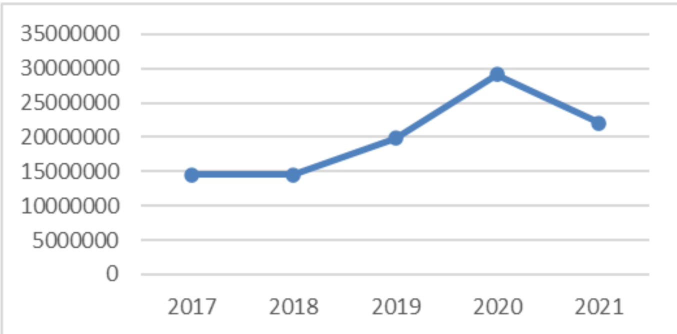

Fig. 8 – The evolution of turnover in the *Activities of web portals* sector (6312 NACE code).

The second-ranked on the podium, the *Crafts* sector in the period 2017-2019, registered an annual increase in terms of turnover of 2.10% in 2018 compared to 2017 and 2.41% in 2019 compared to the previous year (Fig. 9). Compared to the *Software, IT, games* sector, the *Crafts* sector felt the pressure of the COVID-19 pandemic, registering a decrease of 12.23%. The good news, according to the data, is that in the following year, post-COVID-19 pandemic, the sector made a significant comeback, registering a substantially better percentage increase than previous years, of 17.74%. An explanation for the increase can also be related to the digitization process of companies which begun to sell their merchandise online.

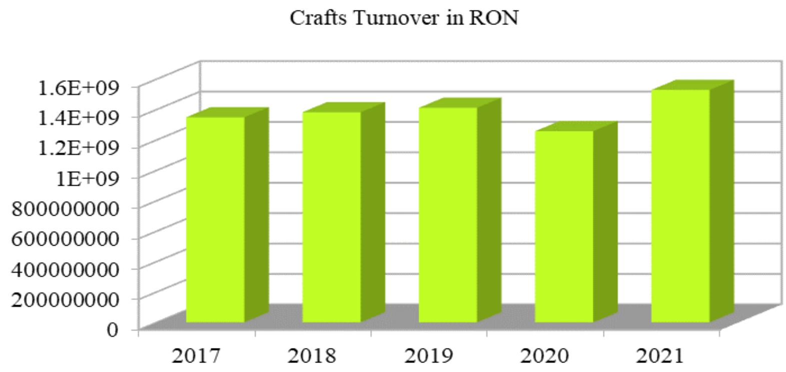

Fig. 9 – The evolution of turnover in the *Crafts* sector.

If overall, according to the data, the *Visual Arts: Fine Arts, Photography and Design* sector does not seem to have been negatively influenced by the COVID-19 pandemic (Fig. 10), the situation on each individual code is completely different, 3 codes registering a decrease, while the businesses classified under the 4778 NACE code (Other retail sale of new goods in specialized stores) managing to register an increase of 5.48%, which led to an increase in the turnover of this sector by 4% in 2020 compared to 2019. In the year 2021, the entire sector managed to recover after the 2020 crucial year, registering substantial increases in turnover, of 19% in total.

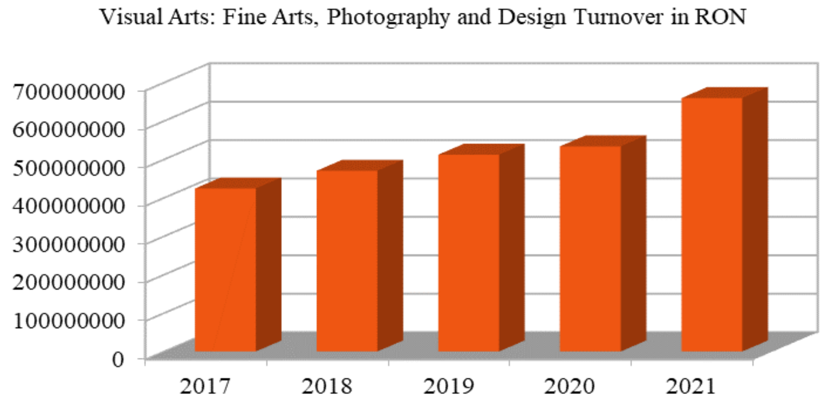

Fig. 10 – The evolution of tunover in the *Visual Arts: Fine Arts, Photography and Design* sector.

Audio-visual and media (film, radio, television, video, phonograms, multimedia works, videograms), and *Architecture* were in roughly the same situation. For the first sector, although 4 of the 7 NACE codes registered decreases in 2020, and 3 increases between 3-12%, overall, the sector managed to cope with the pandemic period, still registering a 4% increase in 2020 compared to 2019 and an increase of 9.55% in 2021.

Performing Arts (Music, Dance, Theatre, Combined Arts and Other Live Performances), *Book press*, and *Advertising* sectors are among the CCI sectors within the NE region of Romania that between the years 2017-2019 experienced an organic increase in turnover, but which were significantly impacted by the COVID-19 pandemic crisis (Table 2).

If *Performing Arts* was the most affected, registering a 28% decrease in the pandemic year, compared to the pre-pandemic one, this sector managed to recover, with statistical data showing a significant increase of 19.7% in the post-pandemic year (2021). After a decrease of 9.73% compared to the year before the pandemic, *Book and Press* sector also managed to surpass the year of the pandemic crisis, recording in 2021 an increase of 6.35%. It cannot be overlooked that although the other NACE codes suffered decreases in turnover in 2020, there was still one code that recorded an increase this year compared to all sectors belonging to the CCI. It is about 1811, *Printing of newspaper*, with an increase of 17.24% in 2020 compared to 2019. A significant recovery was made by the *Architecture* sector, which after the recorded decrease of 4.34% managed in 2021 a spectacular recovery of 16.68% in turnover.

Table 2

The turnover` fluctuation of CCI businesses active in the N-E Region of Romania, according with NACE classification, in RON

No	NACE Code	2017	2018	2019	2020	2021
Performing Arts (Music, Dance, Theatre, Combined Arts and Other Live Performances)						
1	*7430*	10.561.890	11.542.560	11.796.631	11.764.939	13.171.461
2	*9001*	2.894.198	4.036.627	4.933.985	1.296.779	3.094.152
3	*9004*	88.040	72.202	171.147	64.471	80.322
TOTAL		*13.544.128*	*15.651.389*	*16.901.763*	*13.126.189*	*16.345.935*
Book and Press						
1	*1811*	1.304.333	1.698.271	1.227.961	1.483.739	1.850.532
2	*4761*	41.938.387	45.102.813	48.613.569	39.195.946	46.458.474
3	*4762*	45.620.511	48.068.705	55.243.985	55.084.759	53.951.118
TOTAL		*88.863.231*	*94.869.789*	*105.085.515*	*95.764.444*	*102.260.124*
Advertising						
1	*7311*	80.213.757	93.114.820	116.517.424	115.031.391	137.417.019
2	*7312*	10.700.902	11.371.791	11.259.090	7424597	9.547.522
TOTAL		*90.914.659*	*104.486.611*	*127.776.514*	*122.455.988*	*146.964.541*

3. Conclusions

The COVID-19 pandemic has had a significant impact on the creative industries worldwide. Due to the pandemic, many creative industries had to adapt to new ways of working to ensure the safety of their employees and customers, as other industries had also to act. For example, music concerts and festivals were cancelled or postponed, and many artists turned to live-streaming performances instead (Agostino *et al*., 2020; Gu *et al*., 2020). Similarly, movie theatres and production houses faced challenges due to the restrictions on public gatherings and social distancing requirements, leading to delays in the release of new films and TV shows.

More than that, many businesses, such as theatres and art galleries, were forced to close temporarily or, even worse, permanently, due to decreased revenue and increased cost associated with complying with health and safety regulations. In addition, many freelancers and self-employed individuals in the creative industries, such as musicians and artists experienced a significant reduction in work opportunities, leading to financial hardship.

Despite these challenges, the pandemic also created new opportunities for innovation and creativity in the cultural and creative industries. For example, some artists and designers used their skills to create protective equipment and other items that were in high demand during the pandemic. Additionally, some businesses in the creative industries were able to pivot their offerings to better suit the needs of customers during the pandemic, such as offering virtual art exhibitions or selling products online.

IT, software and games sector has registered an annual increase, in terms of turnover, between 2017-2021, showing the fact that what can be a threat for an industry can be an opportunity for another, in this case the COVID-19 pandemic.

The biggest drop during the COVID-19 pandemic was recorded in the *Performing Arts* (Music, Dance, Theatre, Combined Arts and Other Live Performances) sector, with a percentage of 28.76%, followed by Crafts (-12.23%), Book and Press (-9.73%) and Advertising (-4.43%).

Other sectors that were in similar situations to the previously mentioned sector, registering increases during the COVID-19 pandemic compared to the previous year, even if to a lesser extent, are *Visual Arts: Fine Arts, Photography and Design* (+4%), *Audiovisual and media (film, radio, television, video, phonograms, multimedia works, videograms)* (+4%), and Architecture (3.35%).

Overall, the pandemic has had significant impact on the creative industries, presenting both challenges and opportunities for those working in these fields. A very important thing that could also be concluded from the analyzed data is the fact that all sectors belonging to CCI managed to overcome the moment of the pandemic, registering significant increases, the smallest being 6.35% by Book and Press, while the largest being 19.69% by Performing

Arts (Music, Dance, Theatre, Combined Arts and Other Live Performances), the one that therefore suffered the biggest drop during the pandemic period.

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INDUSTRIILE CULTURALE ȘI CREATIVE ÎN REGIUNEA DE NORD-EST A ROMÂNIEI: ANALIZA ECONOMIEI CREATIVE

(Rezumat)

Faptul că industriile creative reprezintă o parte importantă în dezvoltarea economiei unei ţări nu mai este o surpriză. Acesta este și cazul României, unde Institutul Național de Cercetare și Formare Culturală (INCFC) pune un accent puternic pe relația dintre creativitate, cultură, economie și societate, evidențiind interdependența dintre aceste domenii. Lucrarea propune o analiză a industriilor culturale și creative active din Regiunea Nord-Est a României, analizând distribuția, data înființării și cifra de afaceri a acestora în ultimii cinci ani. Scopul acestei lucrări este de a identifica impactul pandemiei asupra industriilor culturale și creative din Regiunea Nord-Est, pe baza fluctuațiilor cifrei de afaceri. Acest lucru va permite o comparație a sectoarelor care au fost cele mai afectate de pandemie cu cele care au reușit să găsească modalități de atenuare a impactului. În ansamblu, lucrarea demonstrează o înțelegere puternică a

importanței industriilor creative în economia României și necesitatea unei analize a răspunsului acestora la pandemie.

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STUDY OF MACHINABILITY OF X4CrNiMo16-5-1 STEEL WHEN PROCESSED BY DRILLING, MILLING AND REAMING FOR SIZES ABOUT Ø 15 mm

BY

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Abstract. The problem of materials machinability in the automotive industry, in lot production using CNC machines is important both from technical and economical point of view, The special quality conditions imposed for the first equipping parts, obtained in lot production and diminishing the fabrication costs make necessary the mechanisation and automation whenever possible. The downtime of the machines because of tool unexpected wear or breaking must be avoided and implicitly it becomes necessary the obtaining of exact values of machinability of the work piece material for a given processing technology. This paper shows the results obtained after studying the machinability by drilling, milling and reaming of a two steps hole placed on a pump body made by X4CrNiMo16-5-1 steel, using carbide tools on a vertical CNC Robodrill Fanuc machine. For the designed and validated cutting regime the stability of sizes and the wear of the finishing tool were investigated. For tool wear measurements a Zoller equipment was used. The tolerances of holes sizes obtained after processing 125 work pieces are in the required range. The sizes variation being explainable the extrapolation needed for obtaining the machinability can be done. After processing a number of work pieces that lead to the complete wear of the tool, the confirmation of the possibility of using extrapolation was also obtained for this material and for the described processing conditions.

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Keywords: tolerances, tool life, wear of cutting tools, cutting regime, processing stability

1. Introduction

The mechanical processing using CNC equipment is very important in the automotive industry because it has the capability of ensuring technical and economical performance in the same time especially for lot quantity production.

Many of the manufacturers of CNC equipment try and succeed in providing more powerful, more productive machines and performance in processing. The trends in the development of such equipment means for example to produce a high productivity vertical milling CNC having 22 kW, 120 Nm, 15000 rot/min for parts weighing up to 1800 kg. The VCN 700 produced by Yamazaki Mazak offers also in the working package solutions for tool and part measurement as well as detection for tool deterioration (https://www.ttonline.ro/revista/masini-unelte/mazak-lanseaza-o-noua-gama-de-centre-verticale-de-prelucrare?_se=Z2hlb3JnaGViYWRhcmF1QHlhaG9vLmNvbQ%3D%3D&utm_campaign=DDT_MU_16noiembrie&utm_medium=email&utm_source=sendinblue). The aim of this last element is to minimize the downtime of the equipment, time necessary for unanticipated tool change, necessary reprogramming of the equipment and readjustment.

Another direction is given by producers like Heidenhein which are committed to ensure sensors for the permanent monitoring of tool during processing to avoid problems (https://www.ttonline.ro/revista/scule/scula-aschietoare-monitorizata-permanent-proces-de-prelucrare-sigur).

When producing, using CNC machines the stability of the process can be obtained if the processing regime, the tools geometry and the machinability of the work piece material are well controlled. Machinability of the work piece can be appreciate or even measured using several methods. This paper shows the results obtained when studying the machinability of X4CrNiMo16-5-1 steel when processed by drilling, milling and reaming.

2. Introduction to machinability of materials and measurement possibilities

Referring to a single surface on a work piece the machining results are: the size and tolerances of the surface, the roughness obtained and the depth of superficially affected layer by the current cutting process.

The machinability of materials is one of the complex characteristics of materials that affects the mentioned results. The complexity consists in a great number of factors that influence the technical and economical results of the cutting processing procedure applied on a given material. These factors are: the processed material factors, cutting data, cutting tool geometry, characteristics of the cutting material, all leading to a set of machining results.

Moreover, the complexity consists in the relations, shown in Fig. 1, between the mentioned factors that affect directly or indirectly the results of the machining process.

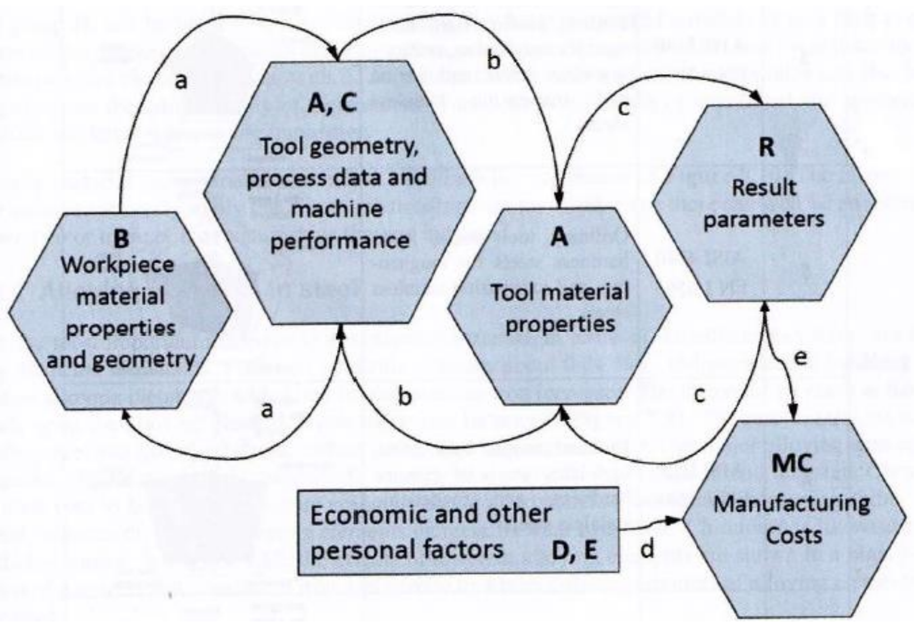


Fig. 1 – Relationships between material factors, cutting data, cutting tool geometry, characteristics of the cutting material and machining results (Sthal, 2012).

On the other hand, regarding from the economical point of view, the manufacturing costs appreciation is obviously influenced by this package of factors and their interaction, Fig. 1.

The machinability can be appreciated by direct and indirect methods and the specialists have as a purpose, the obtaining of an optimum package of adjustments to be made as inputs in a given cutting process system enabling the control of technical and economical parameters as outputs.

The factors determining machinability are shown in a more detailed manner in Fig. 2, and can be divided in two categories as: direct affecting and indirect affecting machinability.

Measuring machinability has a long history and many practiciens and scientists contributed to it. Some of the most important criteria used for measuring machinability are based on the appreciation of: tool life, efficiency of chip removal and work piece quality, Fig. 2, each of them being evaluated using individual parameters.

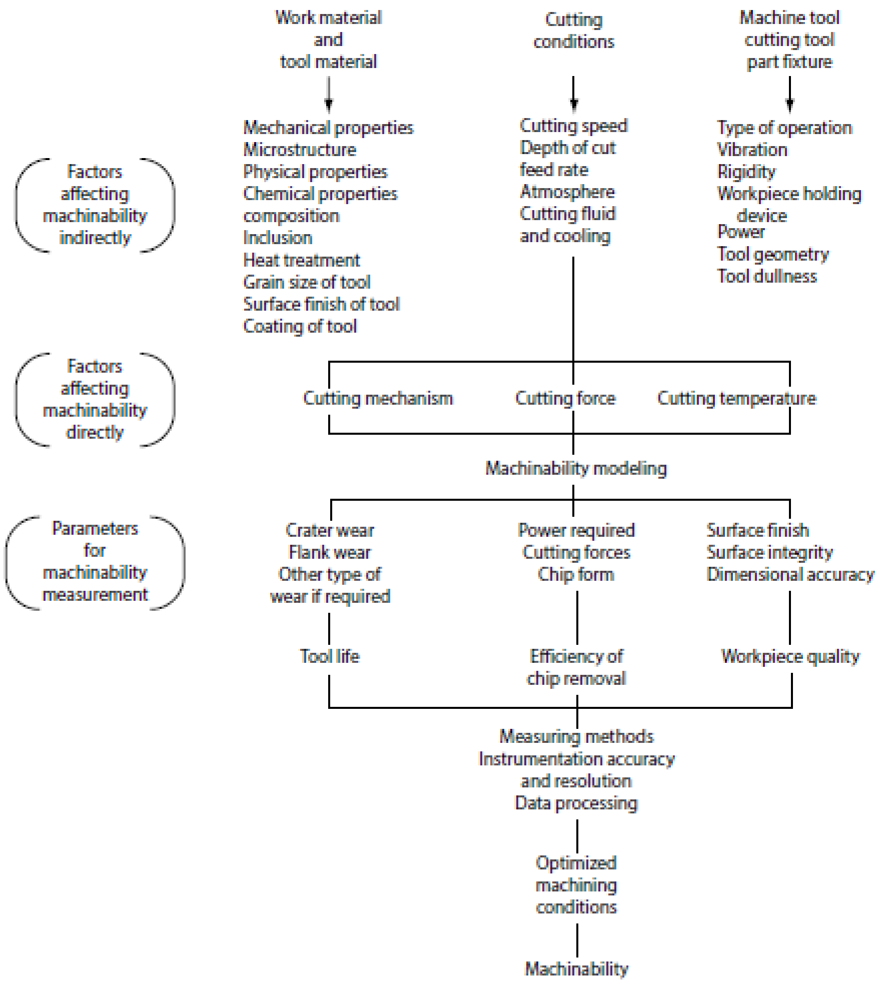


Fig. 2 – Factors determining machinability
(ElGomayel, 1977 apud (Stephenson and Agapiou, 2016)).

The actual methods of determining these parameters are known (Bădărău *et al*., 2002) and efforts to find more comprehensive elements to measure machinability are given also in the literature (Stephenson and Agapiou 2016). Some of these methods based on measurement of a single parameter can be used indirectly for verifying the efficiency of tools design optimation even they have limited resolution (Croitoru and Bocăneț, 2016).

The idea of using polar diagrams, and thus considering in the same time, 5 properties of a material, for the evaluation of potential machinability of work piece materials is a very interesting approach (Sthal and de Vos, 2014) at least destined to compare materials in the phase of materials choice or to shorten machinability experiments when needed.

The importance of accurate determining machinability values can be very important and this is why the literature suggests strategies of machinability testing (Stephenson and Agapiou 2016).

Taking into account the importance of high technico-economic performance brought by CNC machines used in lot quantity production, machinability becomes even more important and appreciating it more exactly is a must. It is easy to understand this, by taking into account the machine downtime and the need of rapid reprogramming of a CNC, just for example, after a tool unpredicted failure (Smid, 2010).

Generally, tool life testing can be used for ranking cutting tool materials and also machinability of work piece materials. Some of these tests are standardized and some of them use for determining tool life a maximum average flank wear as a criterion (Stephenson and Agapiou, 2016; *** Standard Method, 2013).

Other wear parameters, shown in Fig. 3, can be used to evaluate tool life.

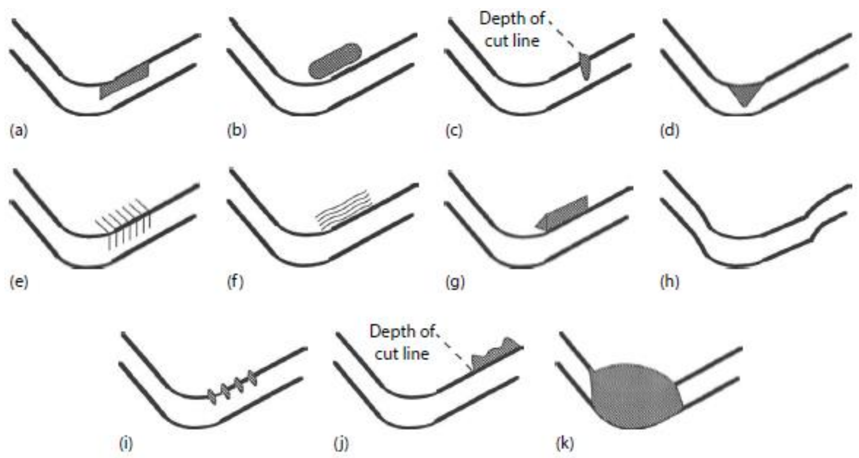


Fig. 3 – Types of wear on cutting tools: (a) flank wear; (b) crater wear; (c) notch wear; (d) nose radius wear; (e) comb (thermal) cracks; (f) parallel (mechanical) cracks; (g) built-up edge; (h) gross plastic deformation; (i) edge chipping or frittering; (j) chip hammering; (k) gross fracture (Stephenson and Agapiou 2016).

Using tool life equations as a way of predict it was for a time an important goal for scientists. One of these equation that link the cutting speed, tool life and some empirical constants is given by Taylor (Taylor, 1907 apud Stephenson and Agapiou 2016).

However, literature agrees that "realistic estimates of tool life in production operations can only be obtained from pilot test results or experience with similar applications" (Stephenson and Agapiou, 2016). This is the approach that we did in this study.

3. Experiment

The goal of this study was to find the parameters for tool life evaluation for a given set of cutting data for processing the cage bore of an injection pump Fig. 4, made by stainless steel EN 10088 3 - X4CrNiMo16-5-1 with the chemical composition given in Table 1.

a b

Fig. 4 – Photographs: a) injection pump; b) processed cage bore.

Table 1

Chemical composition of X4CrNiMo16-5-1

C	Si	Mn	Ni	P	S	Cr	Mo	N
max 0.06	max 0.7	max 1.5	4 - 6	max 0.04	max 0.015	15-17	0.8-1.5	max 0.02

http://www.steelnumber.com/en/steel_composition_eu

The technological process for obtaining the cage bore of the injection pump for lot quantity production supposes three operations.

All these operations are done on a CNC drilling machine Robodrill Fanuc, shown in Fig. 5.

This machine can operate using drills, peripheral milling cutters for bore reaming and also reaming tools. The kinematic possibilities of the machine are rather complex enabling the composition of rotation and translation movements. The rotation speed of the tool performed on Z axis can be controlled simultaneously with the simultaneous translation on X, Y and Z axes for producing the main and feed processing required movements.

Fig. 5 – Photograph of the Robodrill Fanuc (https://www.fanuc.eu/ro/ro/robodrill-ib?gclid=EAIaIQobChMIhOH2isjm_wIVoJRoCR0VqAcNEAAYASAAEgKf0fD_BwE).

The first operation is drilling, using a special type of drill having the channel for cutting fluid inserted inside the tooth, Fig. 6a.

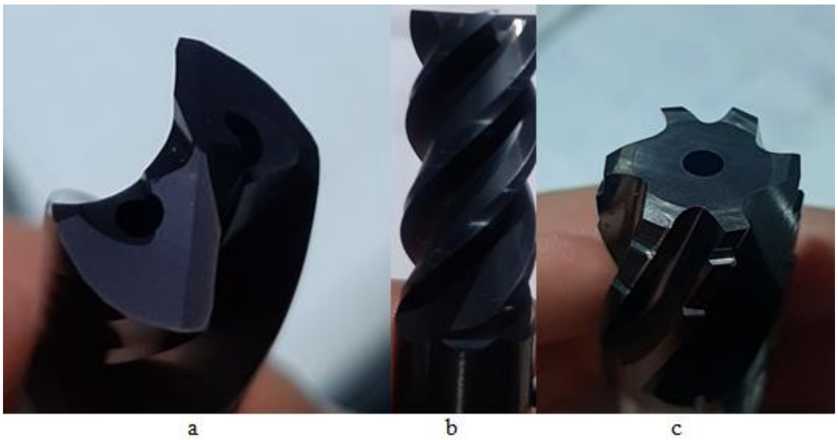


Fig. 6 – Photograph of a solid carbide tools:
a) drill; b) milling cutter; c) special reaming tool.

The parameters of the cutting regime for drilling the Ø 14.15 mm hole with the tolerance + Ø 0.018 mm are: drill diameter = 13.95 mm; drill rotation speed = 1400 rpm; axial feed on Z - 0.13 mm/rot.

The second operation is reaming a segment of the Ø 14 mm hole, using a milling cutter, Fig. 6b for obtaining the Ø 15.4 mm hole segment.

The parameters of the cutting regime are: mill cutter rotation speed - 5300 rpm; axial feed on Z - 0.8 mm/rot; circular feed in XY plane 0.2 mm/rot .

The third operation is line reaming using a special tool consisting in two segments having specific length and diameters Ø 14.15 and Ø 15.4, Fig. 6c.

The parameters of the cutting regime for reaming are: rotation speed 850 rpm and axial feed on Z = 0.25 mm/rot.

Having in view the fact that this processing is made for lot quantity production for obtaining a part used in the automotive industry, special organization measures were taken.

The cutting regimes for all three operations were computed and optimized, then tested and validated on the bases of the measurements made to find out the tools wear and sizes obtained.

In the testing stage, using the computed values of the cutting regime, the designed cutting processes are being achieved and the surface quality parameters: roughness, holes tolerances, shape and sizes and also the shape and color of chips are the parameters to be monitored.

If one of these parameters is not satisfactory a fine tune of the cutting regime has to be performed. For example if the roughness is not small enough and do not meet the requirements, the cutting speed can be enhanced and the feed can be diminished. With the adjusted values a new test has to be performed and the procedure continues until all goes right.

After establishing the values of cutting parameters the tool life test must be performed. In these tests measurements of specific wear are performed on a certain limited number of processed work pieces, namely 125, using the designed cutting regime. By extrapolation the wear values obtained after processing 125 parts the durability of the tool can be evaluated.

For determining the values of the wear produced on the tool active parts we used an equipment produced by Zoller company. The machine control is shown in Fig. 7.

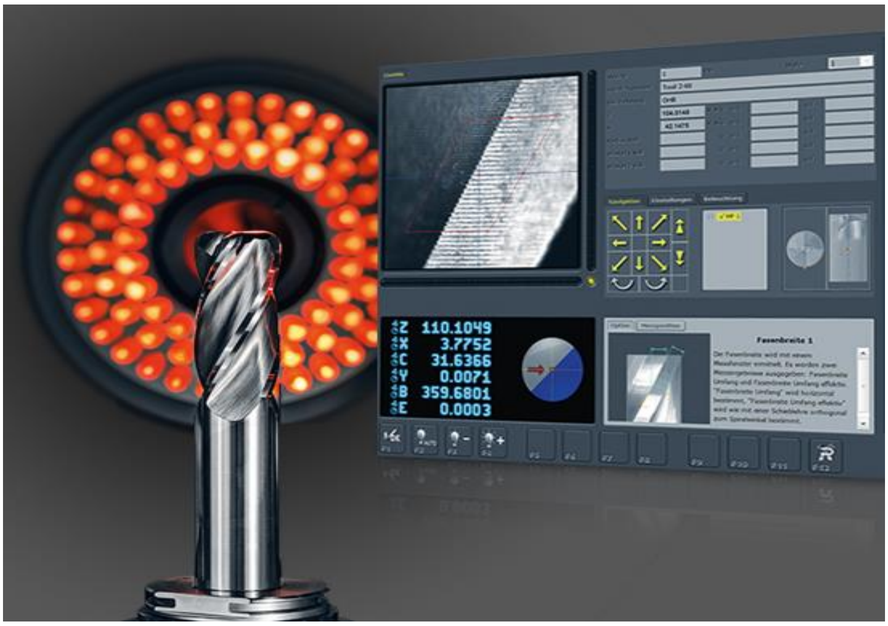


Fig. 7 – Zoller - measuring machine control (https://www.zoller.info/en).

This equipment is able to measure and inspect products especially tools parameters, namely complex inspection of geometries, degree of preparation of cutting edges after resharpening, verification of wear and registering of relevant data for the polishing program. The results can be registered without any difficulty and documented in detail.

4. Results

For establishing the wear values we started from measuring the profiles and sizes of tools, before use. Figure 8 shows the drill put inside the Zoller equipment for determining the cutting edge profile and a macroscopic photo.

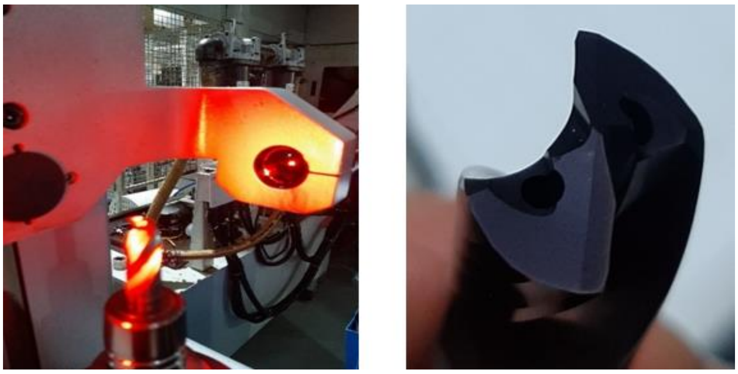
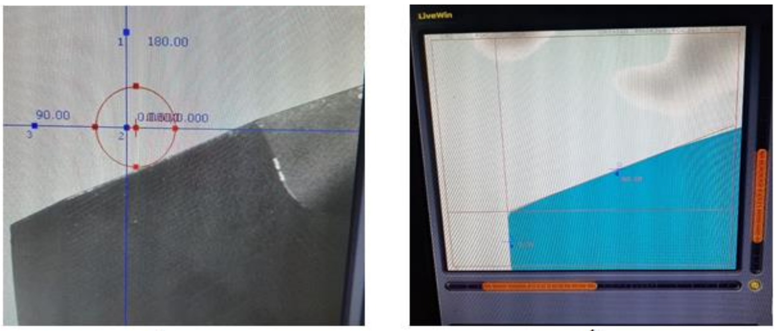


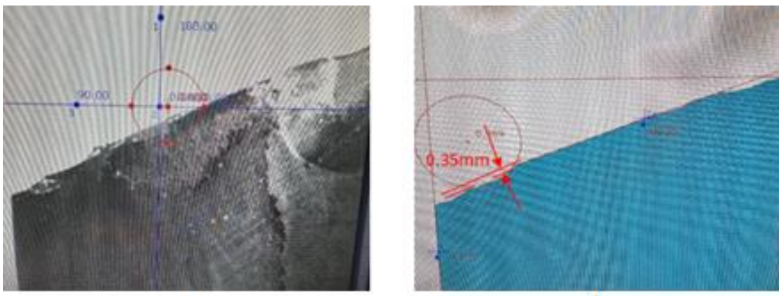
Fig. 8 – Drill.

In Fig. 9 there are shown the cutting edges of the drill for a new one and in Figs. 10 and 11 for a worn one. The equipment enables the precise measurement of the sizes of the lost material by comparing with the initial shape.



a b

Fig. 9 – Images obtained on Zoller equipment for a new drill cutting edge: a) infrared light method; b) shadow method – magnification 10 x.



a b

Fig. 10 – Images obtained on Zoller equipment for the worn drill cutting edge: a) infrared light method; b) shadow method – magnification 10 x.

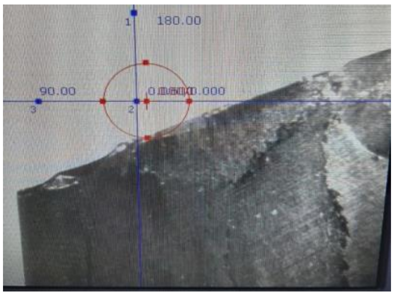
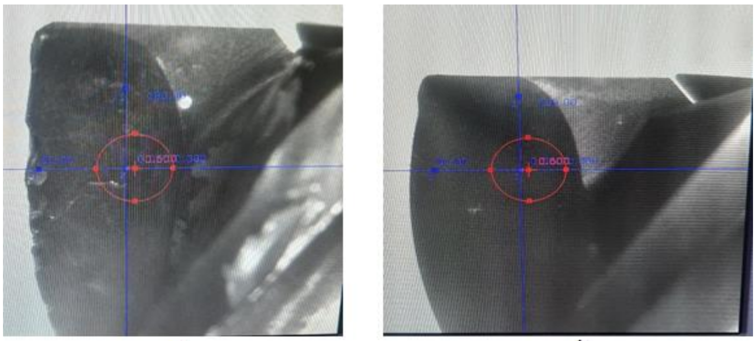


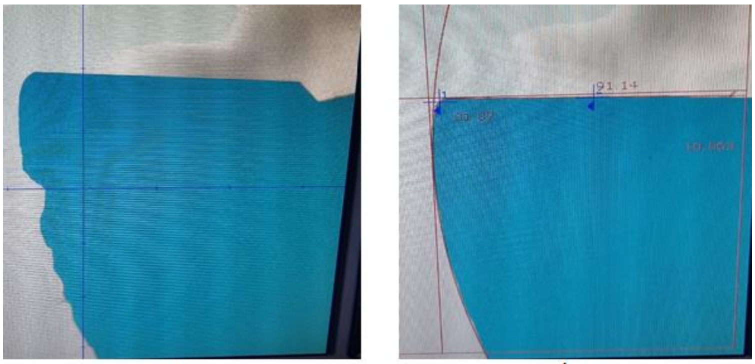
Fig. 11 – Image obtained on Zoller equipment for a drill cutting edge, non uniform wear: infrared light method; – magnification 12 x.

Figures 12 and 13 show images obtained using the Zoller equipment for the new cutting edge and worn cutting edge of the mill cutter, using the infrared light method and also using the shadow method.



a b

Fig. 12 – Images obtained on Zoller equipment for a mill cutter cutting edge - infrared light method: a) non uniform wear - magnification 12 x; b) new cutting edge; – magnification 10 x.



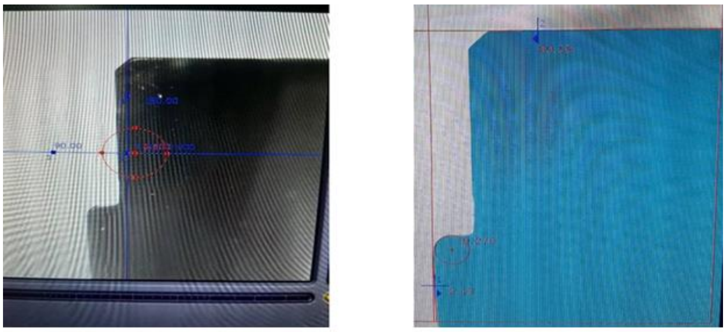
a b

Fig. 13 – Images obtained on Zoller equipment for a mill cutter cutting edge – shadow method: a) non uniform wear - magnification 12 x; b) new cutting edge; – magnification 10 x.

Figure 14 shows the carbide reaming special tool. This tool is designed to process two diameters and lengths simultaneously or, two coaxial holes, in a single pass. Figures 15 and 16 show the carbide reaming special tool profiles obtained on the Zoller equipment using the infrared light method and the shadow method.

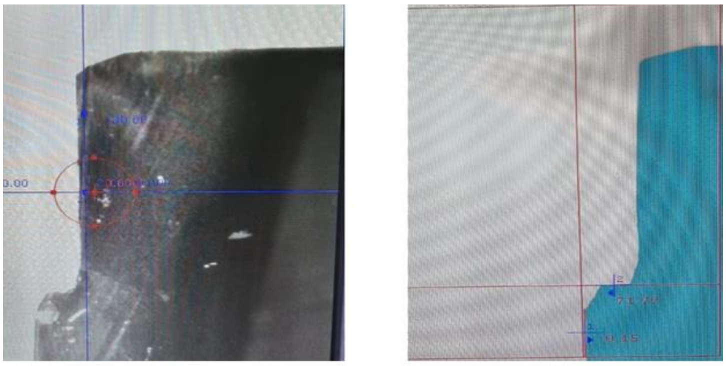
a b c

Fig. 14 – Photographs of reaming special tool: a) on Zoller equipment; b) worn tool; c) new tool.



a c

Fig. 15 – Images of a new reaming special tool on Zoller equipment – details of the cutting edge profiles: a) infrared light method; c) shadow method.



a c

Fig. 16 – Images of a worn reaming special tool on Zoller equipment – details of the cutting edge profiles: a) infrared light method; c) shadow method.

Figures 17 and 18 show the sizes obtained at the reaming of 125 parts for the diameter Ø 14.15 mm hole with the tolerance + Ø 0.018 mm and for the diameter Ø 15.4 mm hole with the tolerance + Ø 0.020 mm using the special tool and the designed cutting regime.

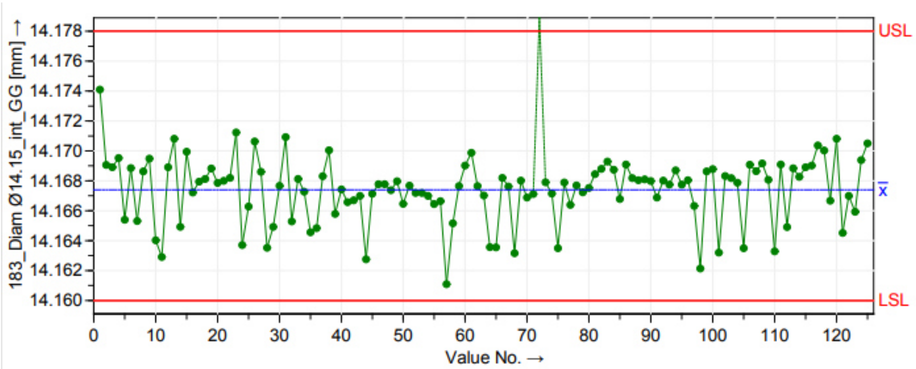


Fig. 17 – Graphic representation of the diameters obtained at the processing of the Ø 14.15 mm hole.

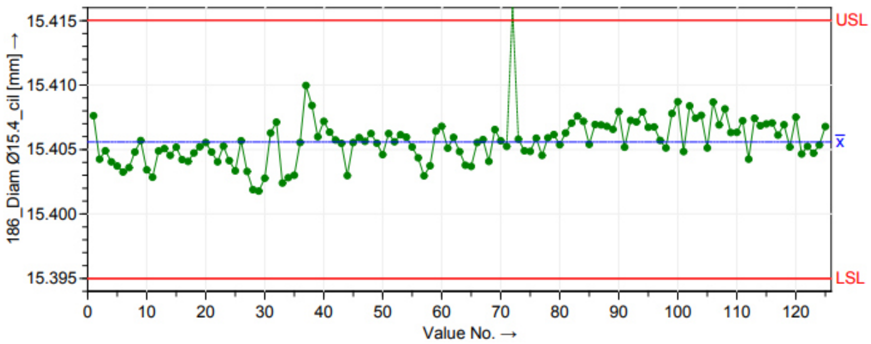


Fig. 18 – Graphic representation of the diameters obtained at the processing of the Ø 15.4 mm hole.

The part number 72 is outside the tolerance for both diameters. The probable cause is the driving of a chip inside the hole during processing.

In Fig. 17, 48 values are below the average size for the Ø 14.15 mm hole, 72 value are above. More over the first forty work pieces show “a big dispersion of sizes” indicating the initial wear of the tool, inside 10 thousandths of a millimeter tolerance. After this point, the processing can be considered stable, most of the values being very close to the average one.

For the Ø 15.4 mm hole, Fig. 18 shows less dispersion of the sizes measured, 54 values being below the average and 52 being above it, also inside 10 thousandths of a millimeter tolerance. However it can be seen that after 80 parts processed the tolerance of the parts is grouped above the average value. The trend of the plotted values shows a slight increasing concentrated in the middle of the tolerance range.

The difference between the two hole processed exists and the cause can be the slight difference in cutting speed but also the increasing temperature of the tool that caused its thermal expansion that is larger for a bigger size. In these conditions of stability an extrapolation can be done and thus the good approximation of machinability.

5. Conclusions

After processing 125 parts the sizes obtained at the finishing operation were inside the tolerance field and the technological process was considered to be stable. The measurements of the tools profile were performed and the results obtained can be considered as a second point of an extrapolation diagram for determining the tool life. After processing a larger number of parts, with the same tool and material and after the moment when the cutting edge was considered worn, measurements of the tool profile were done again figure 16. The point were the wear is important is on the larger diameter of the tool and near the step between diameters. This can be explained taking into account that this specific place is the one having the higher stress and worth cooling conditions.

In conclusion, for the determined cutting regime, the material studied, X4CrNiMo16-5-1 steel, can be considered machinable by drilling, milling and reaming of holes using carbide tools and Robodrill Fanuc CNC equipment.

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STUDIUL PRELUCRABILITĂȚII OȚELULUI X4CrNiMo16-5-1 LA PRELUCRAREA PRIN GĂURIRE, FREZARE ȘI ALEZARE LA DIMENSIUNI DE APROXIMATIV Ø 15 mm

(Rezumat)

Problema prelucrabilității materialelor în industria de autovehicule, în producție de serie utilizând mașini cu comandă numerică este importantă atât din punct de vedere tehnic cât și economic. Condițiile de calitate deosebite impuse pentru piesele de primă echipare ale autovehiculelor, obținute în condiții de productivitate mare și diminuarea prețului de fabricație fac necesară mecanizarea sau automatizarea de fiecare dată când este posibil. Opririle accidentale din cauza uzurii sau ruperii neașteptate a sculelor de prelucrat trebuie evitate și implicit devine necesară cunoașterea cât mai exactă a prelucrabilității materialului semifabricatului supus unui anumit proces de prelucrare. Lucrarea de față prezintă rezultatele obținute în urma studiului prelucrabilității prin găurire, frezare în scopul lărgirii și alezare a unei găuri în două trepte situată pe un corp de pompă din oțel X4CrNiMo16-5-1, utilizând scule din carbură de W pe o mașină verticală de prelucrat alezaje cu comandă numerică Robodrill Fanuc. Pentru regimul de așchiere proiectat și validat prin testare, s-au urmărit stabilitatea dimensională a alezajului și uzura sculei de finisare. Pentru măsurarea uzurii sculelor s-a folosit un echipament Zoller. Toleranțele la dimensiune ale alezajului în trepte obținut în urma prelucrarii a 125 piese se încadrează în cerințe. Variația dimensiunilor fiind explicabilă, poate fi realizată extrapolarea necesară pentru determinarea prelucrabilității prin așchiere. După prelucrarea unui număr de piese care au dus la uzura completă a sculei s-a putut confirma posibilitatea efectuării extrapolării pentru acest material în condițiile de prelucrare descrise.

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ELECRONIC TEXTILES AS POTENTIAL FUNCTIONAL PRODUCTS FOR PEOPLE WITH SPECIAL NEEDS

BY

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Abstract. Electronic textiles, also known as e-textiles, are textile products that enable electronic devices or components to be embedded into them. The range of textile products from this category is from fashion products to military and medical equipment. A path of potential research is the area of e-textiles designed for people with special needs or disabilities products, where highly functional products can improve the quality of life.

A general problem associated with wearable electronics is that of the electrical conductors. Because of the flexibility of textiles products, the conductors of an electrical circuit will be subjected to the same flexing and risk of losing functionality due to wearing over time. Several potential solutions are available, such as: conductive ink that can be screen printed or coated onto a textile or non-textile base; conductive thread that can be sewn onto the fabric and between electronic components; traditional insulated wires that can be incorporated into the base product; conductive wire incorporated into a fabric’s structure (knitted or woven). Depending on the type of textile product and location on the product, several solutions are more recommended than others. Several of the aforementioned solutions used in the same product will provide a working functional textile product. The main problems consist of designing, prototyping and testing the products, due to a varied necessity of specific materials and equipment. Clothing that will incorporate electronic devices will

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also require design adaptations to allow the electronic devices, not only to function properly, but also to minimize deterioration over time. In conclusion, a potential direction for research would be towards the use of electronic textiles, both sensors and apparel, in the case of benefitting individuals with special needs or disabilities.

Keywords: conductive ink, conductive wire, smart textiles, e-textiles, functional apparel items, wearable electronics, special needs.

1. Introduction

Any textile apparel product is required to conform to the need of the user for comfort, which includes many characteristics such as breathability, light weightness, freedom of movement but also easy maintenance of the product. An apparel textile product, including electronic textiles, needs to respect such conditions in order to have high wearability otherwise it's unlikely to become commercially viable or practical.

In the context of people with special needs and electronic textile solutions, the functioning products are most likely to include sensors that give the product its' functionality but might also make the product less comfortable to wear and more difficult maintain. This same issue of comfort and maintenance has been a major obstacle in the commercial success of electronic textiles.

As presented in (Roh, 2018; Dias, 2015; Linz *et al.*, 2006), it has been demonstrated to be perfectly possible to use computer numerically controlled (CNC) sewing machinery for embroidering electronic circuits on a textile substrate using conductive thread, applying flexible electronic modules to said substrates and using various interconnection solutions. This process requires that the conductive thread to be not only highly conductive and resistant to breaking but also easily manipulated by the machinery.

This paper includes efforts to achieve similar results using Juki AMS CNC machines, the AMS-210EN series in particular, but also potential solutions to issues related to manufacturing and maintenance.

2. Juki AMS CNC machines

These machines are commonly used to apply labels, pockets, small-sized embroidering, bartacks and box & cross shaped stitches for non-apparel products. The stitching programs used by the machines can be imputed either via the included touch input panel or created separately on a workstation with proprietary software and later downloaded on the machine. As described on the Juki website (Linz *et al.*, 2005), the machines' work area has a resolution of 0.05 mm, making it possible to achieve very detailed circuits if needed.

Depending on the electrical circuit and textile substrate, any machine can be reconfigured for a particular circuit design in a fairly short amount of time due to pressing plates being able to be swapped in and out of the pressing frame for the substrates and quick selection of uploaded programs.

An important factor of the practicality of embroidering electrical circuits on such machines is circuit size and machine work area size. Depending on the desired circuit it may be necessary to break up the circuit and connect the segments later or use a different type of machine.

Fig. 1 – Juki AMS CNC sewing machine (Linz *et al*., 2005).

Fig. 2 – Close-up of the AMS machine applying a later by using a pressing plate (Linz *et al*., 2005).

2.1. Bekinox steel thread

For the purposes of this paper, the thread chosen for conducting experiments is the Bekinox VN14 2X90 175S by Bekaert. It is made from steel filaments and presented (https://www.sparkfun.com/datasheets/E-Textiles/thread1.pdf) to be highly durable as well as having superior washing characteristics. This makes it an ideal candidate for solving the issue of durability of electronic textiles.

First attempts of using Bekinox thread with Juki AMS machines using the conductive thread as the top (needle) thread as done in other research (Dias, 2015). What was learned was that the machine required fine tuning (thread tension, presser height, sewing speed etc.) and careful selection of needles to prevent the thread from breaking frequently when sewing.

Further attempts moved unto winding the thread onto a bobbin and using a non-conductive polyester thread for the needle thread. This allowed for making only one face of the substrate conductive and also proved to be highly effective as the thread never created problems if the machine was properly configured.

2.2. Designing circuits

Simple circuits were designed for these early experiments which consist of two, four or more conductive lines to be embroidered on the substrates.

The substrates available used included non-stretchable ribbons and elastic bands. Both offered good conductivity for lighting an LED and maintained electrical tension when being bent. For the elastic band samples, the circuit was adapted from a straight line to a zigzag line in order to make it stretchable. For the elastic bands, zigzag lines were added to the ends to mimic electrical pads (Dias, 2015).

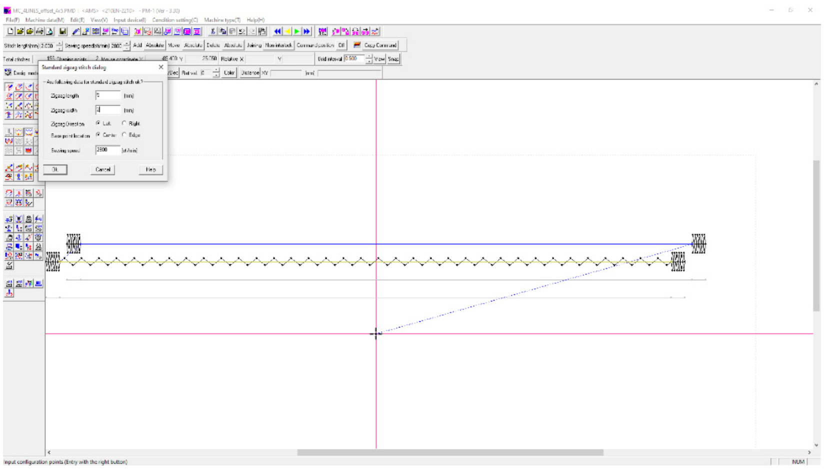

Fig. 3 – Screenshot of Juki PM-1 and a stitching program.

2.3. Velcro interconnectors

Many traditional textile materials, including Velcro, can be used as interconnectors,. Efforts were made to use Velcro as an interconnector with the elastic bands by applying the Velcro strips at both ends on Juki AMS machine.

Conductive thread was later embroidered onto the Velcro-ended bands so that the zigzag pads at the ends were located inside the Velcro strips' boundaries. Later tests showed that electrical conductivity was achieved between Velcro-connected band segments. Further tests can involve improving the quality of the electrical connection between the velcro connectors.

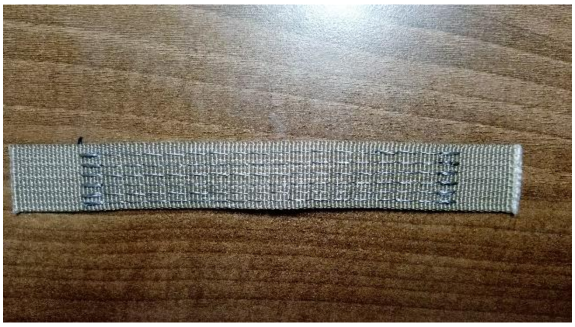

Fig. 4 – Ribbon with Bekinox circuits.

Fig. 5 – Elastic bands with Bekinox circuits and velcro: 2 lines (up) and 6 lines (down).

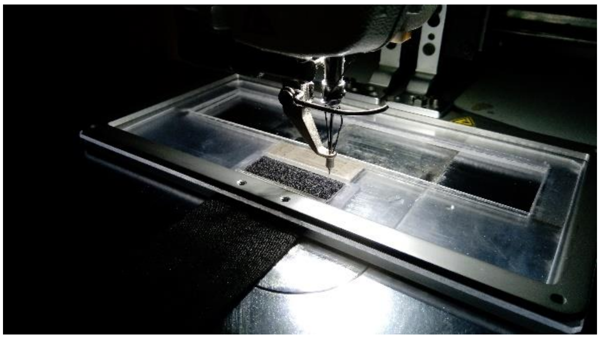

Fig. 6 – AMS machine ready to sew a velcro strip using a custom made holding plate.

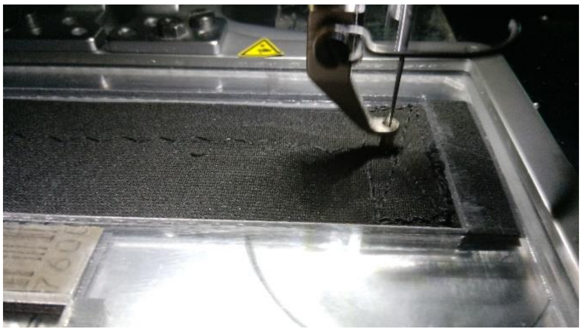

Fig. 7 – AMS machine embroidering on an elastic band.

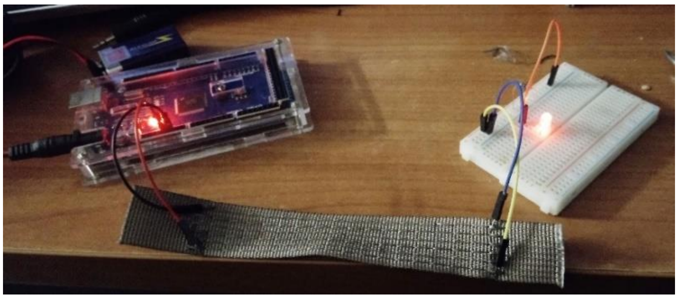

Fig. 8 – Ribbon with Bekinox thread providing power to an LED.

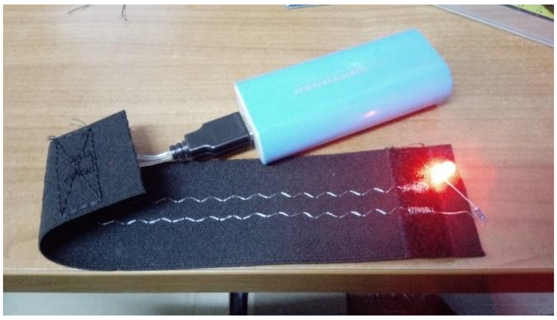

Fig. 9 – Elastic bands with Bekinox thread providing power to an LED.

3. Conclusions

For products designed for people with special needs, these would benefit greatly of high product durability, easy maintenance and cost effectiveness. Bekinox thread may prove an ideal choice for durability. A product with a modular design can fulfil the need for easy maintenance, washing and replacement of damaged components. Design choices can be made so that the blind can disassemble and reassemble the product for cleaning, such as Braille printing or embroidery. By using existing established technology and manufacturing processes, manufacturing costs can be reduced and high quality products seem to be in reach.

Further research will need to include concrete situations of special needs that can be addressed with assistance in the form of electronic textiles products, the most effective interconnectors as well as maintaining cost effectiveness. Also, the benefits of using screen printed or epoxy-based solutions, likely even knitted solutions, likely in conjunction with currently investigated solutions, would likely ensure higher quality solutions.

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TEXTILE ELECTRONICE CA PRODUSE POTENȚIAL FUNCȚIONALE PENTRU PERSOANELE CU NEVOI SPECIALE

(Rezumat)

Textilele electronice, cunoscute și ca e-textiles, sunt produse textile ce permit încorporarea de dispositive sau componente electronice. Gama de produse textile din această categorie variază de la produse de modă la echipament militar și medical.

O direcție de cercetare potențială este zona de e-textiles menite pentru persoanele cu nevoi speciale sau dizabilități unde produsele cu un grad ridicat de funcționare poate îmbunătăți calitatea vieții.

O problemă generală asociată cu electronicele purtabile este nevoia de conductori electrici. Din cauza flexibilității produselor textile, conductorii unui circuit electric vor fi supuși acelorași flexiuni și riscă să își piardă din funcționalitate în timp de la uzare. Sunt disponibile mai multe soluții potențiale precum: cerneluri conductive ce pot fi imprimate serigrafic sau peliculizate pe un substrat textil sau non-textil; fire confuctive ce pot fi cusute pe substratul textil și între componente electronice; cabluri tradiționale izolate ce pot fi încorporate în baza produsului; fire conductive încorporate în structura substratului textil (tricotat sau țesut). În funcție de tipul de produs textil și de locația produsului, unele soluții sunt mai preferabile față de altele. Problemele principale constau în proiectarea, prototiparea și testarea produselor din cauza unei nevoi variate de materiale și echipamente specifice. Îmbrăcămintea ce are să încorporeze dispositive electronice va necesita adaptarea designului pentru a permite nu numai funcționarea corectă, dar și pentru reducerea deteriorării în timp. În concluzie, o direcție de cercetare potențială ar consta în folosirea de textile electronice, atât ca senzori cât și îmbrăcăminte, pentru a beneficia persoanele cu nevoi speciale sau dizabilități.

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EXPERIMENTAL STUDY OF SHAPE MEMORY EFFECT IN A NiTi ALLOY WIRE SUBJECTED TO STRETCHING WITH VARIABLE LOADS

BY

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Abstract. For several decades, a special class of alloys has found its use in our daily lives. From indestructible glasses to the communications industry, coronary stents, robotics, or the textile industry, this material is used in a varied range of applications. In this paper, we will refer to shape memory alloys (SMAs). From the discovery of the shape memory effect by Arne Ollander in 1932 in an Au-Cd alloy, to the development of the Ni-Ti alloy in 1959 at the U.S. Naval Ordnance Laboratory, the commercial and scientific uses of this material are numerous, but the multiple applications of these alloys still represent a challenge for designers and researchers. The exceptional properties of shape memory alloys make them extremely important today, through their outstanding potential to be used for sensors, superelastic elements, actuators, regulators, dampers, and in cutting-edge fields such as biomedical technology, aerospace industry, nanoelectronic systems, microelectromechanical systems, or complex bio and optoelectromechanical systems.

Keywords: shape memory alloy, NiTi, wire, stretching.

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1. Introduction

Shape memory alloys (SMAs) were known in the early 1970s under the name "marmems" (which emphasized the connection between martensite and memory), but for a period of time, access to them was reserved only for military applications.

Currently, a series of non-metallic shape memory materials have also appeared, including ceramic materials, polymers, and composite materials. In these circumstances, the name of shape memory materials has become generalized. These materials are characterized by the ability to recover a shape that they had before a deformation by simply heating them. In addition to this effect, known as the simple shape memory effect (SSME), the two-way shape memory effect (TWSME) can also be observed, obtained after complex thermomechanical treatments called "training". In this case, shape modification occurs both during heating and cooling.

Shape memory alloys are a unique class of materials that can recover their initial shape due to reversible martensitic transformation (Wen, 2014). The shape memory effect (SME) consists of the alloy's ability to be deformed at low temperature and to recover its original, undeformed shape when heated above a certain temperature.

In fact, SMAs can exhibit two different phases with as many crystal structures (martensite and austenite) and six possible transformations (Sun and Huang, 2009; Mihálcz, 2001; Lagoudas, 2010), Fig. 1. The austenitic structure is stable at high temperatures, while the martensitic structure is stable at low temperatures. Upon heating, martensitic SMAs undergo austenitic transformation once the start temperature (As) is reached, which continues until the temperature limit marking the end of the transformation (Af). When a SMA undergoes a martensitic phase transformation, it transforms from the high-symmetry austenitic phase, usually face-centered cubic (fcc), into a low-symmetry martensitic phase, e.g. body centered tetragonal (bct). For most SMAs, this phase transformation is described as being thermoelastic. During the phase transformation, the basic (austenite) and product (martensite) phases coexist. Because the crystal lattice of the martensitic phase has lower symmetry than that of the basic austenitic phase, several martensite variants can form from the same basic crystal (Dasgupta, 2014).

When we talk about "shape memory alloys", we are referring to metallic alloys with two, three, or more components (Lexcellent, 2013), with each component modifying the alloy's properties and characteristics in such a way as to meet the criteria that led to its selection for the intended application (Coccia Lecis, 1997).

It is also important to mention the superelastic behavior of these alloys which can undergo large elastic elongation (4-8%) under certain conditions and temperatures (Ozbulut, 2011).

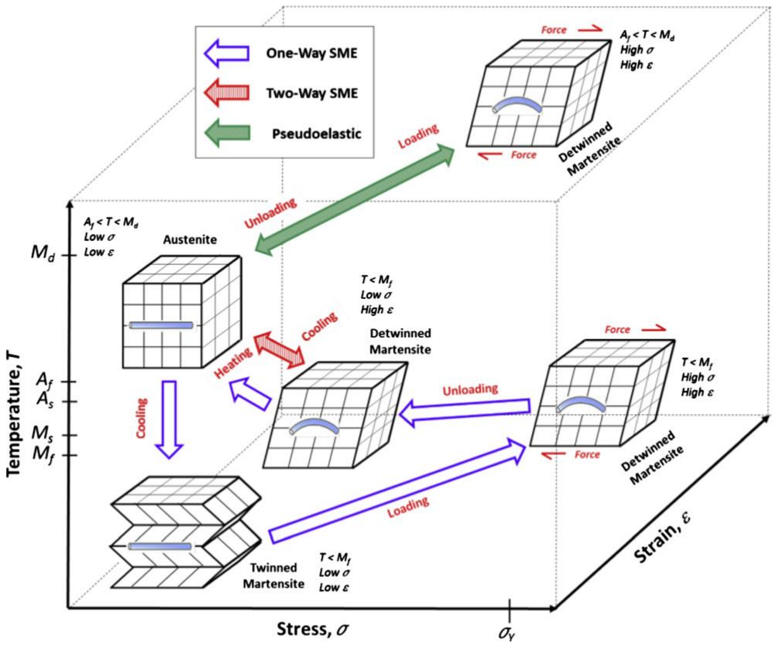


Fig. 1 – SMA phases and crystal structures
(Stöckel, 1995; Duerig, 1990; www. kiniticsautomation.com).

Thermoelasticity involves the continuous compensation of the thermal effect by the elastic effect, such that a certain martensitic phase can be obtained either by cooling (temperature variation) or by mechanical loading (elastic behavior variation) (Bujoreanu, 2002).

There are four important groups of shape memory alloys:

Ni-Ti-X (where X can be one or more elements in small quantities: Fe, Cu, Co, etc.);

Copper-based alloys: Cu-Al-X (where X can be one or more elements: Zn, Ni, Be, etc.);

Iron-based alloys: Fe-Mn-Si-X; Fe-Ni-X (where X can be one or more elements: Cr, Ni, Co, Ti, etc.);

Magnetic alloys: Ni-Mn-Ga; Co-Ni-Ga.

Of all the four groups of shape memory alloys listed above, the alloy with the best memory properties and corrosion resistance is the Ni-Ti alloy (Nitinol), but its use is limited due to its high production cost, resulting from the difficulties in processing and shaping it.

Many of industrial applications use copper-based shape memory alloys, as well as iron-based ones, which are an economic alternative to Ni-Ti type alloys. It should be noted that Fe-based alloys (Fe-Mn-Si) exhibit a non-thermoelastic martensitic transformation and do not exhibit super-elasticity

(Sawaguchi *et al*., 2016). Although the NiTi alloy was discovered by William Buehler in 1959 (Khol, 2010), it became commercially available in 1962, and its first successful application consisted of a coupling made by the Raychem Corporation for the F-14 military aircraft pipes of Grumann Aerospace Corporation in 1969, followed by a successful use in orthodontics proposed by George B. Andreasen in 1971 (Khol, 2010).

Recent research has shown that shape memory alloy actuators represent a viable alternative to conventional pneumatic, hydraulic or electric motors (Hartl and Lagoudas, 2007; Reynaerts and Brussel, 1997), due to their technological simplicity and ability to directly react to stimuli (Gheorghiţă *et al*., 2013). For example, the NiTi shape memory alloy has the capacity to develop 10J/cm3, which is 25 times more than an electric motor, and can lift weights 100 times its own weight (Winzek *et al*., 2004).

Furthermore, NiTi alloys are biocompatible (Mantovani, 2000), (Ryhänen *et al*., 1998), exhibit high wear resistance (Hodgson *et al*., 1990; Buehler and Wang, 1968), and their tribological behavior is comparable to that of other Ni alloys.

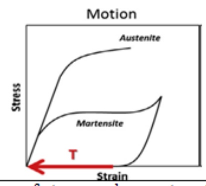
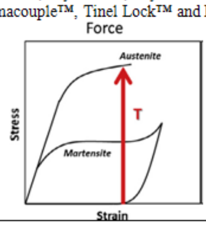
2. Applications of shape memory alloys

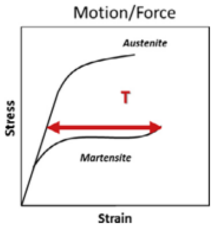
Due to their unique behavior, numerous ideas have emerged for the use of shape memory alloys in various fields: aerospace, space, automotive industry, household appliances, medical (orthopedic implants, stents, prostheses), robotics (Table 1).

Table 1

Shape memory application categories

(Hodgson et al., 1990; Stöckel, 1995; Duerig, 1990)

Category and description	Examples
Free recovery The sole function of the memory element is to cause motion or strain on the applications. Working principle: The memory element is stretched and then released (no load applied). It remains in stretched condition until heated above the transition temperature and shrink back to its original form, and subsequent cooling below the transition temperature does not cause any macroscopic shape change (e.g.OWSMA)	NiTi eyeglass frames (TiFlex™, TITANFlex) and Simon IVC 
Constrained recovery The memory element is prevented from changing shape and thereby generates a stress or force on the applications. Working principle: The memory element is prevented from returning to its original form after being stretched and considerable force generated if heated above the transition temperature.	Hydraulic couplings, fasteners and connectors: CryoFit™, Cryocon™, UniLok™, CryOlive™, CryoFlare™, CryoTact™,Permacouple™, Tinel Lock™ and BetaFlex™ 

Category and description	Examples
Actuator or work production (force actuator, proportional control and two-way-effect with external reset force)	
There is motion against a stress and thus work is being done by the memory element on the applications. Most of applications enter in this category. Can be either OWSMA or TWSMA. Three types of actuators: Force actuator: The memory element exerts force over a considerable range of motion, and often for many cycles. Proportional control: The memory element used only part of its selected portion of shape recovery to accurately position the mechanism, because the transformation occurs over a range of temperatures rather than at a single temperature. Two-way-effect with external reset force: The memory element generates motion to overcome the opposing force, and thus do work. The memory element contracts upon heating to lift a load, and the load will stretch the heating element and reset the mechanism upon cooling (e.g. TWSMA)	Electrical actuators (VEASE™, SMArt Clamp™), thermal actuators (Memrysafe™, circuit breaker, window or louvre opener, valves), and heat engines. 

2.1. Actuators

Actuators are elements used in automated systems to execute commands. Classic solutions for actuators usually involve bulky, heavy, and expensive elements such as electric motors, pumps, pipes, screws, rotors, etc. Actuators with active elements made of SMA represent a separate category in the field of mechanical actuators.

Unlike other systems, they do not use motors, pumps, or magnetic fields to generate force, functioning based on the shape memory effect that generates mechanical work. Additionally, they are not generators of electric or acoustic noise or disruptive magnetic fields. Figure 2 illustrates a comparison between SMAs and other traditional actuators.

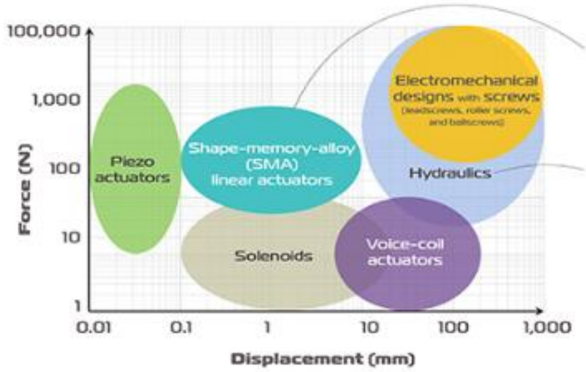


Fig. 2 – Comparison between SMAs and other traditional actuators (www.kiniticsautomation.com).

Small size, ease of use, and high durability are factors that have led to the increasingly frequent use of SMAs in various applications. SMA actuators have been proven to be a suitable technological alternative to conventional actuators such as electric motors, pneumatics, and hydraulics (Hartl and

Lagoudas, 2007; Reynaerts and Brussel, 1997), due to their unique characteristics and ability to directly react to environmental stimuli (Zhang, 1996), thus leading to the development of more advanced and cheaper actuators with a significant reduction in mechanical complexity and size (Butera *et al*., 2007; Leary *et al*., 2010). For example, NiTi SMA has one of the highest energy capacities of 10 J cm^{-3} (see Table 1), which is 25 times greater than the energy capacity of electric motors (Khol, 2010) and is capable of lifting more than 100 times its own weight (Winzek *et al*., 2004).

Table 2, (Lederlé, 2002; Hunter *et al*., 1991; Tadesse, 2013), presents a comparison of some constructive solutions for actuators from which it can be seen that the NiTi alloy is suitable for realizing actuators that provide significant displacement and forces, without critical requirements for short response time or high efficiency. This makes NiTi an attractive candidate for a variety of industrial applications, "intelligent" structures, and "intelligent" systems (Angioni *et al*., 2011; Smith *et al*., 2011). SMAs can offer innovative solutions to solve a wide range of technical problems, sometimes representing the only viable technical option for complex applications. For example, the realization of the lens cleaning system of a surgical endoscope (Hu *et al*., 2021), is shown in Fig. 3.

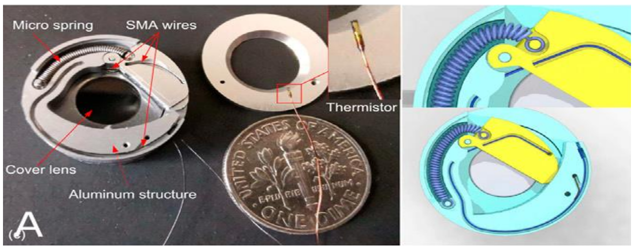


Fig. 3 – A mesoscale SMA actuator for cleaning the contaminated lenses of surgical cameras during minimally invasive robotic surgery (Hu *et al*., 2021).

Table 2

Comparison of the performance of actuators made from different materials (Lederlé, 2002; Hunter et al., 1991; Tadesse, 2013)

Actuator type	Stress	Strain	Efficiency	Bandwidth	Work per volume	Power per volume
	MPa	%	%	Hz	J/cm^3	W/cm^3
NiTi SMA	200	10	3	3	10	30
Piezoceramic	35	0.2	50	5000	0.035	175
Single crystal piezoelectric	300	1.7	90	5800	2.55	15000
Human muscle	0.007-0.8	1-100	35	2-173	0.035	0.35
Hydraulic	20	50	80	4	5	20
Pneumatic	0.7	50	90	20	0.175	3.5

Table 3 (Hartl and Lagoudas, 2007) summarizes some of the properties of SMAs and their practical effects. SMAs are also capable of acting in a fully three-dimensional manner, allowing the manufacture of actuation components that can expand, bend, and rotate, and can be used in various configurations and forms, such as helical springs, torsion springs, wires, strips, and tubes (Stöckel, 1990; Waram, 1993).

Table 3
Summary of various SMA properties and their effects (Hartl and Lagoudas, 2007)

SMA traits	Practical consequences
Shape memory effect	Material can be used as an actuator, providing force during shape recovery
Pseudoelasticity	Material can be stressed to provide large, recoverable deformations at relatively constant stress levels
Hysteresis	Allows for dissipation of energy during pseudo-elastic response
High actuation stress (400–700 MPa)	Small component cross-sections can provide substantial forces
High actuation strain (ca. 8%)	Small component lengths can provide large displacements
High energy density (ca. 1200 J/kg)	Small amount of material required to provide substantial actuation work
Three-dimensional actuation	Polycrystalline SMA components fabricated in a variety of shapes, providing a variety of useful geometric configurations
Actuation frequency	Difficulty in achieving high component cooling rates limits use in high frequency applications
Energy efficiency (10–15%)	Amount of thermal energy required for actuation is much larger than mechanical work output
Transformation – induced plasticity	Plastic accumulation during cyclic response eventually degrades material and leads to failure

3. Experimental Procedure

For the study of the behavior of active elements in AMF for different types of previously described applications, a stand (Fig. 4) was designed and executed, which offers the possibility of measuring displacement under different loads, at temperatures that can be adjusted and measured in real-time.

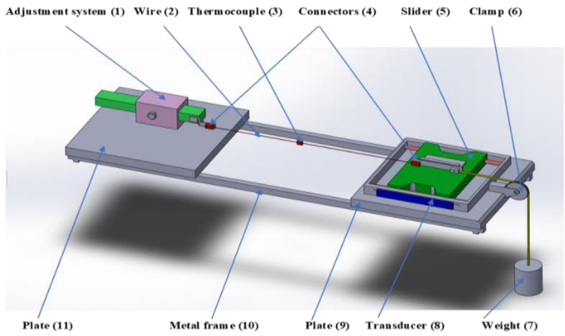


Fig. 4 – Experimental Stand Model.

A NiTi wire with a diameter of 0.35 mm and a useful length of 560 mm, produced by Kellogs Laboratory (USA), was subjected to testing. To ensure electrical and mechanical contact, the wire ends were twisted and inserted into a tubular sheath. At room temperature, the wire is in a martensitic state, meaning it is soft and stretches under applied load at the end, and once heated, it transitions back into an austenitic state and tends to return to its original length (prior to load application). A voltage source with an adjustable intensity of 12V was used for heating, and information regarding temperature and displacement was collected by sensors, translated into a digital signal through an interface, and stored in a computer. The stand consists of two plates (9;11) fixed to a metal frame (10). On one plate, the adjustment system (1) of the wire length (2) subjected to testing is located, and on the other plate, there is a slider (5) with a displacement-measuring transducer (8). The wire is heated by the Joule effect, and cooling is done freely, in the air. The wire's attachment elements (4) are provided at the testing ends for connecting the power supply with electricity. Temperature measurement is done with a thermocouple (3) attached to the tested wire through a clamp. Weights (7) placed on a tray are used for loading, which tensions the wire through a tensioner (6). The slider ensures pure axial loading.

The experimental device is shown in Fig. 5.

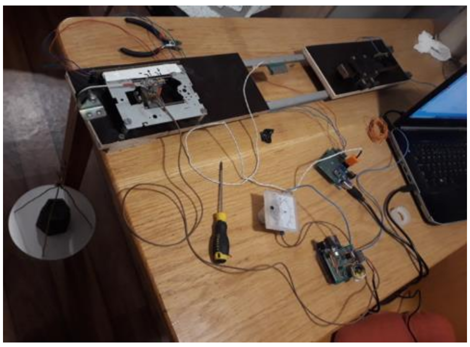


Fig. 5 – Experimental Stand (Laboratory).

The wire was successively loaded with loads of 2N, 5N, 10N, 15N, 20N, 22N, 27N, and 29N, and data regarding temperature and displacement were collected for each load. The obtained data was processed, and the results are presented in graphs. The measured values of temperature and displacement are read by an interface and sent to a computer for processing and analysis.

4. Experimental Results

The experimental results are presented as comparative graphs (Displacement-Temperature) presented in Fig. 6.

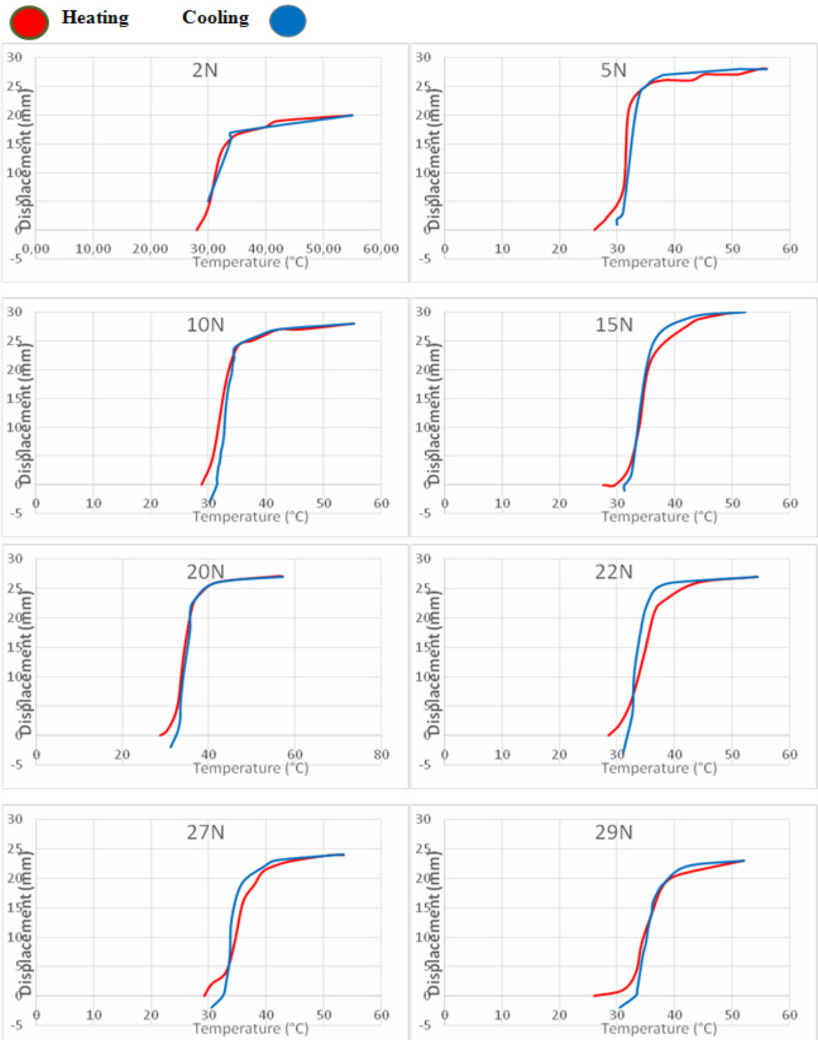


Fig. 6 – Experimental graphic results.

It is noticeable that, under the effect of all the six applied loads, the NiTi wires developed work-generating SME with a thermal hysteresis below 2°C. In all of the experiments the displacement ceased at 50°C. The active strokes were initially developed between 30 and 35°C but with increasing the applied load they shifted between 35 and 40°C. So, it appears that the critical transformation temperature A_s increased with the applied force. At the end of cooling, the wires recovered their initial length at temperatures as much as 7°C higher than the initial temperature.

5. Conclusions

The following conclusions can be drawn:

– the experimental NiTi wires experienced work generating SME by lifting applied loads between 2 and 29 N, over distances ranging between 20 and 30 mm;

– the thermal hysteresis, between distance variation with temperature during heating and cooling was below 2°C;

– the critical transformation temperature As had a tendency to increase, from 30 and 40°C while the applied force increased from 2 to 29 N.

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STUDIUL EXPERIMENTAL
AL EFECTULUI DE MEMORIA FORMEI LA O SÂRMĂ DE ALIAJ NiTi
SUPUSĂ LA ALUNGIRE CU SARCINI VARIBILE

(Rezumat)

Timp de mai multe decenii o clasă specială de aliaje și-a găsit utilizarea în viața cotidiană. De la sticle indestructibile, la industria de comunicații, stenturi coronariene, robotică în industria textilă, acest material este utilizat într-o largă varietate de aplicații. În această lucrare ne vom referi la aliajele cu memoria formei (AMF). De la descoperirea efectului de memoria formei de către Arne Ollander, în 1932 la un aliaj Au-Cd, până la dezvoltarea aliajului Ni-Ti la U.S. Naval Ordnance Laboratory, utilizările comerciale și științifice ale acestui aliaj sunt numeroase însă aplicațiile multiple ale acestor aliaje încă reprezintă o provocare pentru proiectanți și cercetători. Proprietățile excepționale ale aliajelor cu memoria formei le fac extrem de importante astăzi, prin potențialul lor remarcabil de a fi utilizate pentru senzori, elemente superelastice, actuatori, regulatoare, amortizoare precum și domenii de vârf cum ar fi tehnologia biomedicală, industria aerospațială, sistemele nanoelectronice, sistemele microelectromecanice sau sistemele bio și optoelectronice complexe.

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CHARACTERISTICS OF STAINLESS STEEL USED FOR PERSONAL PROTECTIVE EQUIPMENT IN THE FOOD INDUSTRY

BY

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Abstract. The food industry is an area where the risks of accidents at work can manifest themselves in various forms, and personal protective equipment is an important segment in their prevention because they can be a barrier between risks and workers.

Based on previous studies, the limitations of stainless steels in the design of personal protective equipment are identified so that they maintain their function as a physical barrier between danger and performer, to protect the body according to the directions in which the dangerous factor can act and to meets the requirements of ergonomics and maintenance of health. The characteristics of stainless steels in terms of hardness, corrosion resistance, elasticity, thermal conductivity, resistance to acids and alkaline solutions are advantageous properties that can be used to find optimal solutions in the production of personal protective equipment. Currently, more than 200 types of stainless steels are known, which are used in all fields of activity: food, medical, chemical, construction, automotive, naval, aerospace, etc. As stainless steel is a low-carbon steel that contains at least 11% chromium, this addition of chromium gives the steel its unique properties of stainless steel and corrosion resistance. The presence of chromium allows the formation of an extremely thin hard, invisible

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layer of chromium oxide on the steel surface, resistant to the action of corrosive media, capable of self-repair in case of mechanical or chemical alteration (http://www.osha.gov).

The paper is also a review of studies on the properties of stainless steels in correlation with the maintenance of protective functions against risk factors acting on the human body. Based on previous studies, the limitations of stainless steels in the design of personal protective equipment are identified so that they maintain their function as a physical barrier between danger and performer, to protect the body according to the directions in which the dangerous factor can act and to meets the requirements of ergonomics and maintenance of health. At the end of the paper, study ideas are proposed on improving the structure and obtaining more efficient characteristics of these types of steels.

Keywords: stainless steel, characteristics, personal protective equipment, resistant. corrosive media.

1. Introduction

In the food industry, according to statistics, among the main causes of work accidents in the food industry we also identify the faulty use or without personal protective equipment of the objects and cutting tools used (which have as consequences: cuts, stings, hits, etc.).

Every year, the EU provides statistics on accidents at work in Europe. In this paper, we analyzed the results from 2020 and found that the food industry has a high rate of work accidents. Figure 1 shows a statistic in relation to the areas of activity and parts of the human body that were affected. Thus, we find that in the food industry, the extremities are affected in a percentage of about 3.8%.

The food industry is an area where the risks of accidents and illness at work can manifest themselves in various forms, and personal protective equipment (PPE) is an important segment in their prevention because they can be a barrier between risks and workers.

	Upper extremities	Lower extremities	Back	Head	Whole body & multiple sites	Torso & organs	Neck	Other parts of body	Not specified
Total (all activities)	1,0	1,7	1,7	21,1	29,8	12,6	1,3	2,1	28,6
Agriculture, forestry and fishing (A)	0,5	3,3	2,7	27,9	34,0	19,5	3,0	0,3	8,8
Mining and quarrying (B)	0,0	2,1	2,1	20,8	35,4	22,9	2,1	0,0	14,6
Manufacturing (C)	1,2	1,6	1,6	25,2	30,9	13,1	1,4	1,4	23,5
Construction (F)	1,4	1,7	1,3	29,6	30,9	11,4	1,0	2,0	20,7
Wholesale and retail trade (G)	1,8	2,1	2,1	17,8	29,2	12,8	1,4	1,8	31,0
Transportation and storage (H)	1,0	0,8	3,3	14,3	34,7	13,1	0,8	2,7	29,1
Accommodation and food service activities (I)	0,0	0,0	3,1	16,9	18,5	9,2	1,5	6,2	43,1
Administrative and support service activities (N)	0,5	2,4	0,5	16,9	35,7	8,7	0,5	4,3	30,4
Public administration and defence (O)	0,0	2,6	0,9	7,7	26,5	7,7	1,7	1,7	50,4
Human health and social work activities (Q)	0,0	1,2	0,6	7,0	25,0	2,9	0,0	1,7	61,0

Source: Eurostat (online data code: hsw_n2_06)

Fig. 1 – Fatal accidents at work by part of body injured and economic activity, EU, 2020 (% of fatal accidents for each activity) (https://ec.europa.eu/eurostat/statistics).

If we study research from other continents of the world, we find that there are similar problems throughout the food industry.

A descriptive cross-sectional study was conducted among 157 butchers in Uyo, Nigeria, using a questionnaire to identify occupational risks and health problems published in 2019, shows that knife injury among butchers is a major risk factor because this is a key working tool in their occupation. Thus, not wearing personal protective equipment was identified as a problem.

The results from this study are similar to findings from other studies that reported that butchers are the most prone to physical hazards due to knife cuts, namely: “Occupational health risks among abattoir workers in Abeokuta 2013”; “Occupational risks and self-reported health problems of butchers in Ibadan 2013”; “Occupational risks among abattoir workers associated with non-compliance with meat processing and waste disposal laws in Malaysia 2016” (Abdullahi *et al*., 2016).

All so, this paper is a review of studies on the properties of stainless steels in correlation with the maintenance of protective functions against risk factors acting on the human body. We will also try to present the improvement of the structure of a stainless steel semi-finished product in order to obtain performance characteristics of a finished product, respectively of an Personal Protective Equipment (PPE) (https://www.azom.com).

Based on previous studies, the limitations of stainless steels are identified in the design of individual protective equipment, so that they mention the function of a physical barrier between the danger and the performer, to protect the body according to the directions in which the dangerous factor can act and to satisfy the requirements. of ergonomics and health maintenance.

An analysis of EU statistics, by age group, shows that the most affected workers in the food industry are those between the ages of 25 and 55 (% of non-fatal accidents for each activity), Fig. 2.

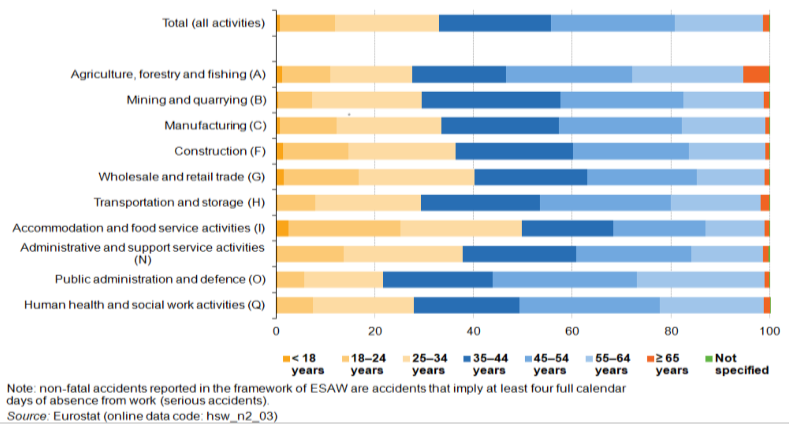

Fig. 2 – Non-fatal accidents at work by age and economic activity, EU, 2020 (% of non-fatal accidents for each activity) (https://ec.europa.eu/eurostat/statistics).

2. Personal protective equipment used in the meat industry

Individual protective equipment for workers in the meat industry is special equipment that ensures their protection against major risks of work injury. In this paper we will highlight three categories of such equipment that have in common the material from which they are designed, namely steel.

All so, The TPLUS tunic is a category III PPE, made of 100% stainless steel (Fig. 3). The sleeves are equipped with a self-closing system with stainless steel spring. For the bust: 0.5 mm thread diameter, 3 mm inner ring diameter, 4 mm outer ring diameter, and for the sleeve: 0.4 mm thread diameter, 3.2 mm inner ring diameter and outer ring diameter of 4 mm.

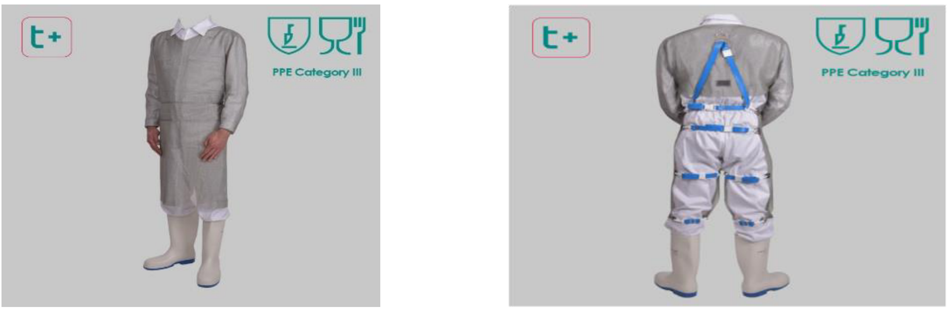

Fig. 3 – The TPLUS tunic is a category III PPE.

The TPLUS range is recommended for the use of a hand cutter or slice tools, especially for withdrawing or cutting of meat and fish (Fig. 4). The TPLUS tunic is essential for use in bloodbath and fish shops.

WILCO glove is a order II personal protective equipment (PPE), made of 100% stainless steel links with a wire diameter of 0.5 mm, inner ring with diameter of 3 mm, outer ring diameter of 4 mm, wrist closure and mesh-protected stainless steel spring forearm, long cuff and blade stop cuff with stainless steel stiffeners.

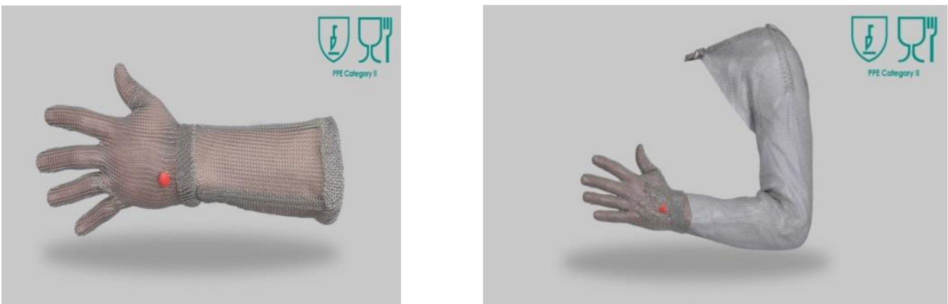

Fig. 4 – TPLUS range.

Areas in which they can be used: slaughterhouses, in the meat industry, during boning and cutting operations; catering units for processing meat, fish and shellfish; plastics industry, leather, textiles and paper, laying the floor and similar works.

Characteristics protective gloves resistant to punctures and cuts (butcher's gloves): made of stainless steel, mesh diameter of 4 mm, weight 380 gr., cuff length 20 - 80 mm, sizes from XS to XXL (https://www.azom.com).

Fig. 5 – Stainless steel rings.

Structurally, the individually welded stainless steel ring gloves, offer the best cut protection and offer maximum strength, flexibility and durability (Fig. 5). The steel used is a highly corrosion resistant 316L stainless steel.

3. Applications of 304, 316 stainless steel in Personal protective equipment used in the meat industry

More than a quarter of all nickel produced worldwide is destined for stainless steel products related to the food and beverage sector, where it is a vital ingredient in the food supply chain, from "farm to fork" (Johnson and Etokidem, 2019).

Nickel - containing stainless steel is suitable for a wide range of operations in the food industry. There is an austenitic stainless steel for almost any food operation, from milk and beer, where type 304 is standard; fish and meat products that may bear high quality, such as type 316L; to super-austenitic steels developed to withstand extremely aggressive conditions, such as sauce production. The most used stainless steels are (according to the AISI Mark), Table 1.

Robust corrosion resistance and ease of cleaning make stainless steel both. When in contact with various corrosive environments, stainless steel 304 and 316 have excellent corrosion resistance. Its cracking, through stress corrosion, can occur at temperatures above 60°C, durable and hygienic, two very valuable properties in food preparation (https://www.azom.com).

Table 1
Types of stainless steel, examples

304	Cr (18%); Ni (8%); C (0.05%);
304 L (low C content)	Cr (18%); Ni (10%); C (<0.03%);
316	Cr (16%); Ni (11.3 - 13%); Mo (2 - 3%);
316 L (low C content)	Cr (16.5 – 18.5%); Ni (10.5 – 13.5 %); Mo (2 – 2.25%); C (< 0.03%);
430	Cr (16 - 18%); C (0.08%).

The steel chain protection glove has a number of advantages: high resistance to cutting, easy to wash, withstands a water temperature of 122°F (50°C). Thus, all microorganisms are destroyed.

Also, stainless steels containing nickel do not alter the taste or color of food and do not contaminate food.

Disadvantages of using chain protection are: uncomfortable, heavy, difficult to use, can interfere with workers' ability to perform tasks effectively, and even create additional safety risks.

4. Conclusion

Taking previous studies as a starting point, we have identified the limits of stainless steels in general and especially in the design of PPE so that they maintain their function as a physical obstacle between danger/risk and the worker, to protect the body depending on the directions on which can act the dangerous factor and meet the ergonomic and health maintenance requirements.

Finally, in the paper we propose ideas for studies on improving the structure and obtaining better performance characteristics of these stainless steels, which will aim to improve the structure of the semi-finished product of an individual protective equipment in order to obtain performance characteristics of the finished product, under given conditions exploitation.

The advantages of using individual protection equipment made of stainless steel links, lead us to consider that a research is necessary on the improvement of the structure of the stainless steel used in their manufacture.

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*** Occupational Safety and Health Administration, http://www.osha.gov, South Australia WorkCover Corporation, Safer Industries Project, GPO Box 2668, Adelaide, SA 5001.

https://www.azom.com/Stainless Steel as a Structural Material (azom.com)

https://ec.europa.eu/eurostat/statistics explained/index.php?titleAgricultural_production livestock_and_meat&oldid=549389

CARACTERISTICILE OȚELULUI INOXIDABIL UTILIZAT PENTRU ECHIPAMENTELE INDIVIDUALE DE PROTECȚIE ÎN INDUSTRIA ALIMENTARĂ

(Rezumat)

Industria alimentară este un domeniu în care riscurile de accidente la locul de muncă se pot manifesta sub diverse forme, iar echipamentele individuale de protecție reprezintă un segment important în prevenirea acestora deoarece pot constitui o barieră între riscuri și lucrători.

Pe baza unor studii anterioare, se identifică limitările oțelurilor inoxidabile în proiectarea echipamentelor individuale de protecție, astfel încât acestea să își mențină funcția de barieră fizică între pericol și executant, pentru a proteja organismul conform direcțiilor în care poate acționa factorul periculos și pentru a satisface cerințele de ergonomie și de menținere a sănătății. Caracteristicile oțelurilor inoxidabile în ceea ce privește duritatea, rezistența la coroziune, elasticitatea, conductibilitatea termică, rezistența la acizi și soluții alcaline sunt proprietăți avantajoase, care pot fi folosite pentru a găsi soluții optime în producerea echipamentelor individuale de protecție. În prezent, sunt cunoscute peste 200 de tipuri de oțeluri inoxidabile, care sunt utilizate în toate domeniile de activitate: alimentar, medical, chimic, construcții, auto, naval, aerospațial etc. Întrucât oțelul inoxidabil este un oțel cu emisii scăzute de carbon care conține cel puțin 11% crom, acest adaos de crom conferă oțelului proprietățile sale unice de oțel inoxidabil și rezistență la coroziune. Prezența cromului permite formarea unui strat extrem de subțire, dur, invizibil de oxid de crom pe suprafața oțelului, rezistent la acțiunea mediilor corozive, capabil de auto reparare în caz de alterare mecanică sau chimică.

Lucrarea este, de asemenea, o trecere în revistă a studiilor privind proprietățile oțelurilor inoxidabile în corelație cu menținerea funcțiilor de protecție împotriva factorilor de risc care acționează asupra organismului uman. Pe baza unor studii anterioare, se identifică limitările oțelurilor inoxidabile în proiectarea echipamentelor individuale de protecție, astfel încât acestea să își mențină funcția de barieră fizică între pericol și executant, pentru a proteja organismul conform direcțiilor în care poate acționa factorul periculos și pentru a satisface cerințele de ergonomie și de menținere a sănătății. La finalul lucrării sunt propuse idei de studiu privind îmbunătățirea structurii și obținerea unor caracteristici mai eficiente ale acestor tipuri de oțeluri.

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INVESTIGATION ON BRAKE PAD WEAR EMISSIONS

BY

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Abstract. The pollution of the environment and the health concerns related to particulate matter (PM) released by the usage of vehicles have shown increasing attention in past years. The sources are exhaust, and non-exhaust emissions. The first category is heavily researched and regulated within the EU, being the main subject of the European Emission Standard, currently at the Euro 6 level.

The emissions caused by vehicles, from sources other than exhaust systems, that can be either particles from brake systems, clutches, tires, suspension, the road itself, or material deposited on the road surface that is getting airborne due to traffic induced turbulence, account for almost half of the total emissions in the urban environment, for which the vehicles are responsible. From this category, the brake pad emissions gather 55% of the total PM released in the atmosphere.

The purpose of the report will be to assess the different types of the brake pads, that are currently on the market.

There are four main types of brake pads that are used on vehicles: semi-metallic, non-asbestos organic (NAO), low-metallic NAO, and ceramic. Scanning electron microscopy and light microscopy will be used for structural characterization and insigths on chemical composition will be taken with a Energy dispersive spectrometer (EDS). After the wear cycle, the dust resulted in the testing can be analyzed both from a physical perspective (mass, shape,

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particle size, etc.), as well as from the perspective of the chemical composition. The most important chemical components found in brake wear emissions are Fe, Cu, Pb, Zn.

The effect on the disk brake wear can also be quantified from a physical perspective, analyzing the brake disk wear on an electronic microscope in the search of threads and micro cracks on the disk surface.

Limiting and regulating the brake pad emissions will have an important benefit in protecting the health of the population and lowering the impact on the environment.

Keywords: Brake pad, emission, pollution, health, NAO.

1. Introduction

For years, the friction and wear of car braking materials has been widely researched and analyzed. But in the last two decades, the rapid development in the automotive industry has been accompanied by the increase in speed, load and engine power, including for commercial vehicles, which has led to the need for high braking performance (MacDonald, 2016). Modern materials for the production of brake pads are abrasives, friction modifiers, binders, fibers and fillers (Chan and Stachowiak, 2004; Dante, 2016; Iijima *et al*., 2007; Garg *et al*., 2000). The tribological behavior of these materials is directly influenced by the amount of additives, the shape, dispersion and size of their particles. High levels of particulate matter (PM) in the air have proven to be dangerous for the environment and human health, especially in urban areas (UNEC, 2018). Depending on the size, shape and elemental composition of these airborne particles, they can cause respiratory health problems, contribute to smog and even negatively affect water resources. For this reason, many studies have been done on the human activities that contribute to the levels of these small particles in the ambient air. Without a doubt, one of the main contributors to the increase in the levels of these particles is the transport industry, and especially road transport, which contributes 30% of the total particle emissions. And in recent decades, exhaust emissions have been the focus of efforts to reduce particulate matter, but as these emissions are declining due to these efforts and improvements in diesel engines, the focus is expected to shift to particulate matter that does not they result from exhaust gases, which are estimated to drastically exceed exhaust PM in the coming years (WHO, 2019; Shepard and Jerram, 2015). Today, internal combustion engine (ICE) vehicle braking is done using friction between two materials, which causes the car to decelerate or stop, and with this reaction between the two friction materials, the materials produce heat and material residues, some of which are in the air in the form of suspended particles (Dante, 2016). However, electric vehicles (EVs) and hybrids use both friction for braking and regenerative braking, which is another factor to consider when looking at the future of braking emissions, as

EV sales are expected to increase by 24% annually by 2030. Braking emissions are dangerous considering the metals used in friction materials, such as iron, copper, titanium and zinc, and therefore it is important to understand how to reduce these emissions by changing the properties of the friction material and switching to the use of electric vehicles (Park *et al*., 2020; Amato, 2018; Bunsen *et al*., 2018).

2. Braking

Braking systems include friction braking, and now, with the increase in electrification within the vehicle manufacturing industry, regenerative braking is also considered (MacDonald, 2016).

A vehicle's braking system is responsible for allowing the vehicle to slow down or come to a complete stop. The fundamental concept of braking is directly related to the law of conservation of energy: energy cannot be created or destroyed. It takes energy to accelerate a vehicle and therefore energy must be removed or transferred to decelerate a vehicle (Sanders *et al*., 2002; Sanders *et al*., 2003, Hagino *et al*., 2016).

In the case of friction braking, this energy is dissipated as heat, and in the case of regenerative braking, this energy is stored and reused when the vehicle is accelerated.

The equation for the kinetic energy involved in decelerating a vehicle, E_{decel} from speed v_2 to speed v_1 is the following:

$$E_{decel} = \frac{1}{2}m(v_2^2 - v_1^2)$$

Where m is the mass of the vehicle in kilograms. E_{decel}'s calculated value is essentially the amount of energy that must be thermally absorbed in a friction brake (or stored in the regenerative braking system).

The friction braking system is one of the most important components of a vehicle in terms of safety. For this reason, friction braking systems are subjected to extreme tests. These tests typically include 10 consecutive complete stops from 130 km/h to 0 km/h at a deceleration level of 0.8G (7.85 m/s^2). Some of the crucial parameters for braking performance that the tests focus on in this regard are described below:

– *Magnitude of deceleration*: the capacity of a friction braking system is directly related to the braking force or the necessary deceleration.

– *Disc temperature*: the brake disc temperature affects the performance and effectiveness of the braking system. As previously stated, the friction between the plate and the disc is used to transform the vehicle's kinetic energy into thermal energy. Therefore, the disc and pads absorb heat during braking.

– *The coefficient of friction*: The coefficient of friction is used to quantify the amount of friction between two surfaces. It is a value without a designated unit and has a minimum value of 0 referring to the lack of friction between surfaces. A typical coefficient of friction is 0.4. The coefficient of friction between two materials is very non-linear in relation to temperature, but the value decreases when the temperature is significantly higher than the normal operating temperatures (AQT, 2018; EPA, 2018).

Emissions resulting from the use of braking systems are the particles in the air that are removed from the friction surfaces of the braking system as a result of the braking action. These brake wear particles can be very difficult to quantify in the field because so many other sources of particles are present in vehicle transport, including exhaust emissions, road wear/dust, tire wear, and re-suspended particles from on the road. However, brake emissions are increasingly becoming a subject of concern due to their heavy metal content. The particles resulting from fuel combustion have been very well studied and characterized, and improvements and technological progress have led to a significant reduction of them. But the abrasion processes that result in the direct emission of particles (such as: tire, brake pad, clutch and road surface wear) are either insufficiently studied, or can be improved to reduce these emissions (EPA, 2018; Shepard and Jerram, 2015).

Particles are generally classified according to their aerodynamic diameter. The most common classification is PM10 and PM2.5, however PM1 is also becoming a prominent category. PM10 represents the measurement of all particles with an aerodynamic diameter of less than 10 μm, PM2.5 less than 2.5 μm and PM1 less than 1 μm.

Particle measurements are traditionally evaluated by their mass $\frac{\mu g}{m^3}$, or number $\frac{number\ of\ particles}{m^3}$

Exposure to air pollution, especially in the form of particles, has been associated with acute and chronic effects on human health. According to the US Environmental Protection Agency (EPA, 2018), scientific studies have linked exposure to particulate matter with non-fatal heart attacks, premature death in people with lung or heart disease, irregular heartbeats, worsening asthma, decreased lung function, and increased respiratory problems. In addition, the International Agency for Research on Cancer has certified that ambient air pollution and especially because of these particles, is carcinogenic to humans.

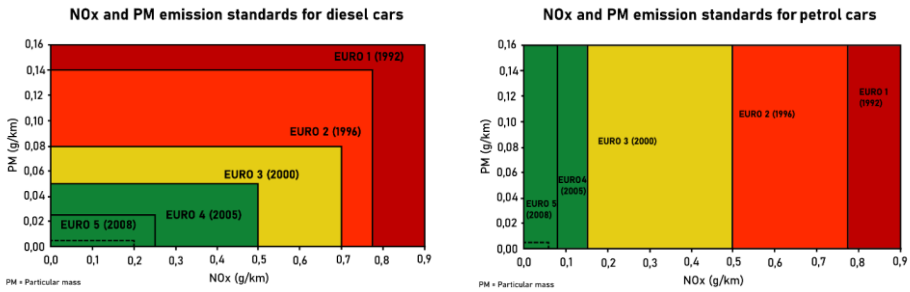
Among the different sources of particles, the emissions resulting from the use of braking systems is particularly particular because of their composition and because they are mostly smaller, which are more likely to enter the respiratory tract and the circulatory system. That said, there are not enough studies on the health effects directly caused by non-exhaust particles (Carbiketech.com, 2019).

Some estimates of non-exhaust particulate emission contributions are around 50%. It is very difficult to quantify the amount of exhaust emissions and non-exhaust particles because it is difficult to distinguish between them. Tests for exhaust emissions are highly developed, while studies for non-exhaust emissions, and especially braking emissions, are relatively premature and undeveloped.

However, some harmful particles, mainly with metallic composition, have been identified as traces of non-exhaust particles and associated with adverse health effects: Fe, Al, Cu, Zn, Ca, Ni, V, Ti, Cr, Mg, S, Si, K and Mn. The most prominent evidence linking brake wear to negative health effects is the oxidative stress that occurs in cells, as this is obviously caused by metal particles, which are known to be the composition of many emissions resulting from brake system wear.

Oxidative stress is a term used to describe the imbalance between antioxidant and prooxidant agents in the body. Brake wear particles contain organic compounds and metals, which serve as pro-oxidants, having only one unpaired electron, making them therefore very reactive and capable of triggering a chain reaction in the body, causing cellular damage. Studies have been conducted to show the long-term effects, or chronic effects, as well as the short-term effects, following exposure to particulate matter. In the short term it can be described as daily or hourly exposure to PM emissions causing an acute response, while in the long term it can be described as annual exposure causing chronic health deterioration (EPA, 2018; EU Publications Osce, 2017).

Currently, there is no regulation imposed on the emissions resulting from the use of braking systems. In any case, as emissions of exhaust particles have been decreasing in the last decade, attention is shifting more towards the regulation of non-exhaust PM emissions, as they are becoming comparatively more prominent. Moreover, metals are some of the most problematic particles and they are heavily regulated in the industry in general. Therefore, it can be predicted that non-exhaust emissions become the largest contributor to metal particles in the urban environment.



There were, however, some projects financed by the European Union to analyze the harmful effects of braking emissions. One of the projects is called REBRAKE, coordinated by Freni Brembo Spa, Kungliga Tekniska Hogskolan and Universita Delgi Studi Di Trento which took place between 2013-2017. The main objective of this project was to reduce PM10 emissions from braking by 50% in order to prepare for the EU2020 target of a 47% reduction in particulate matter. This was achieved by gaining a better understanding of the materials and the interactions between the friction of the materials in the braking systems, resulting in a new design and composition of the brake pads and disc. The composition proposal also considered the tendency to eliminate copper from the materials used in the brake pads.

Another EU-funded project on braking system sustainability is LOWBRASYS, also coordinated by Freni Brembo Spa, which took place more recently from 2015-2019. The goal was to develop a "braking with low impact on the environment environment" by reducing PM braking emissions by 50%. To achieve this goal, the project worked with the materials of the braking system and the control systems of this system.

The Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) is a regulation adopted at the EU level with the aim of "better and earlier identification of the intrinsic properties of chemical substances", to protect the environment and human health. In essence, the materials must be registered for a specific application, otherwise they cannot be used. This is trying to avoid the potential risk of widespread adoption of the use of a new material without knowing the full extent of the health and environmental hazards associated with it. There are also similar REACH Initiatives in many countries outside Europe, such as China and the USA.

3. Wear

PM resulting from non-exhaust emissions is due to the general wear and tear of brakes, tires and the vehicle. Several studies have shown that car brake wear is the biggest contributor to PM compared to other sources of non-exhaust emissions. Wear is defined as the continuous loss of material from the surface of a solid body due to mechanical action, i.e. the contact and relative movement of a solid, liquid or gas. A wear coefficient is a physical coefficient used to measure, and characterize, and is denoted by K

$$K = \frac{Wear\ Volume * Hardness}{Load * Sliding\ distance}$$

During a braking event, the friction material is exposed to high thermomechanical loads leading to 2 distinct types of wear. These are:

– Wear dominated by mechanical wear of materials.

– Wear dominated by chemical wear of materials.

A more detailed classification is presented below in Table 1.

Table 1
Clasification of wear paterns

Wear Type	Wear Type	Cause	Visual identification
Mechanical Wear	Abrasive Wear	Abrasion between two contact surfaces and removal of the material surface	Hard glassy phase, irregular mineral chips, larger mineral fragments
	Adhesive Wear	The contact interface between two surfaces in contact has sufficient adhesive strength to resist relative sliding	The shearing of ductile materials and the transfer of the material on the contact surface
	Traction wear	Similar to abrasive wear	Grooves on the surface, large areas of resin
	Wear by particle extraction	Imperfect compaction between pad constituents	Fragile components of irregular shape, mineral fragments
	Fatigue wear	Wear generated after repeated cycles of contact	Peeling of mineral layers followed by cracks
Chemical Wear	Corrosion	Reaction products formed by the interaction of the surface with the corrosive environment	Additional increase of the oxidative layer on the surface
	Diffusion	Due to the heat produced during the continuous frictional contact between 2 surfaces	Increasing the strength of the softer metal, but a degradation of the harder metal.

The friction and wear behavior of car brakes is determined by the characteristics of the active surface between the pad and disc and the third layer of the body formed between these surfaces. The brake wear mechanism takes place in 3 steps:

1) Formation of the friction layer

When the brake pad and disc rub against each other during a braking event, there is initially abrasive wear that creates frictional debris between the surfaces. Later, these debris adhere to the friction surface of the brake pad, which results in the formation of a friction layer.

The formation of the friction layer is directly proportional to the speed, temperature and braking energy. So, as the frequency of braking increases, there is abrasive/traction wear that creates long grooves on the brake pad which, in turn, will be filled with wear debris over the braking cycle forming a thick layer of abrasive material.

2) Development of the contact plateau

Microscopically, there is a complex contact situation. The unevenly distributed wear and the compaction of wear debris result in a surface characterized by planes that rise above the rest of the surface. There is a formation of primary and secondary plateaus. The primary plateau consist of the wear-resistant components of the pad and act as accumulation sites for the secondary plateau (Fig. 1).

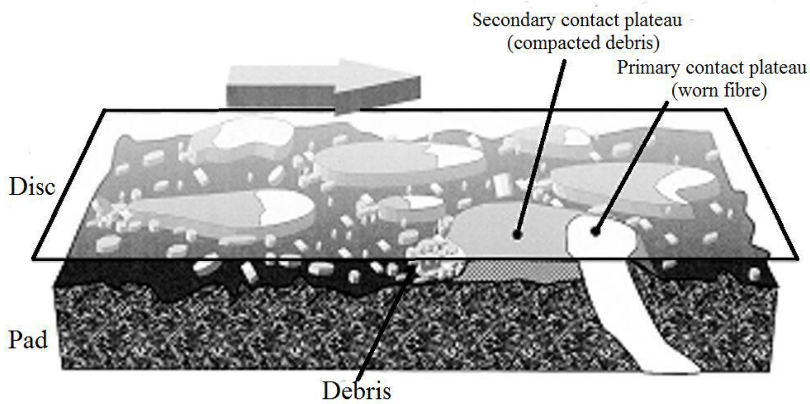


Fig. 1 − Disk – pad plateau components.

A labyrinth of grooves forms between the plate and the disc, due to the frequent contact between the moving disc and the debris, in the form of tiny particles. Intermittently, these remnants accumulate on the primary plateaus. Normal braking pressure, shear forces and frictional heat result in the compaction of debris, forming secondary plateaus. These can be seen on the brake pads as shiny spots on a dark background.

So, to form a secondary plateau, the wear residues are very necessary, together with the increase in the disc-plate space. This can only happen when there are more braking events and this is the reason why secondary plateaus form at a slower rate compared to primary plateaus. That is why it is believed that the performance of the brake pads increases after the polishing cycle.

3) Wear

Wear occurs when the load applied to the material exceeds the material's resistance. So, in the case of a brake pad, wear occurs when the contact surfaces fail. In situ studies have shown that secondary plans require primary plans for structural stability. The hardness and strength of the contact plane that contains the primary and secondary plane shows that the global resistance of the contact plane is dependent on the plateaus plane which is made up of fibers. Therefore, the depth of the primary planes is much greater than the secondary planes. A graphical visualization of the different types of wear can be seen in Fig. 2.

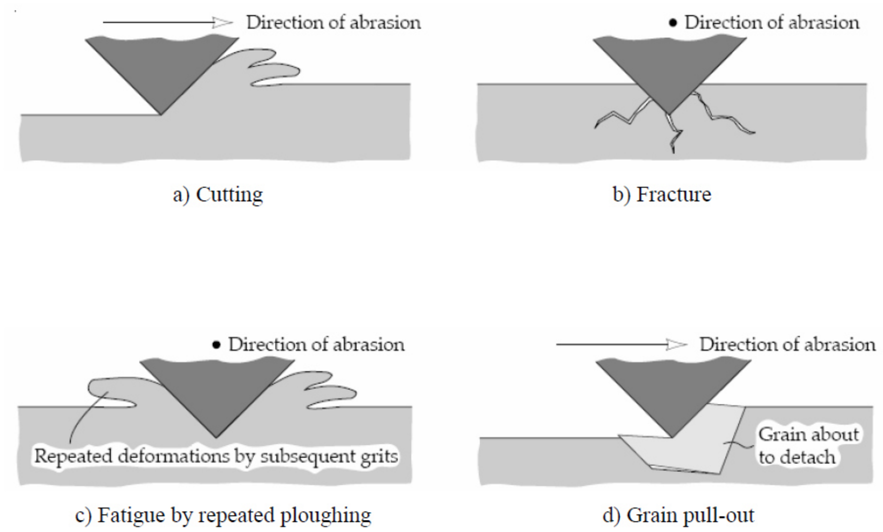


Fig. 2 – Types of wear: a) cutting; b) fracture; c) fatigue; d) grain pull-out.

The micro-scratch shows that the secondary plane has a higher compressive strength compared to the tensile strength. The hardness of the secondary plane is much lower than that of the primary plane.

The nanoindentation of the secondary plane shows that the hardness values vary between 0.2 and 4Gpa, depending on the depth of the indentation. This means that the higher hardness value is contributed by the friction layer which has a depth of approximately 50 µm. The secondary plane degrades within milliseconds after the primary plane and the friction layer fail due to shear forces acting during a sliding contact.

4. Conclusion

The main points that can be drawn from the present literature review are summarized below:

– Sources from exhaust gases and those resulting from abrasive wear contribute almost equally to the total traffic-related PM10 emissions. Brake wear has been recognized as one of the most important sources of pollution, apart from emissions from exhaust gases, with its relative contribution to emissions between 16 and 55% and to total PM10 emissions, resulting from road traffic.

– It is estimated that approximately 50% of total brake wear is emitted as PM10 in the air. The rest can be deposited on the road or nearby or can be pulled by the vehicle. The fate of larger particles has not yet been well investigated.

– Several factors affect both the physico-chemical characteristics and the generation rates of brake wear particles, which makes it very difficult to understand the generation mechanisms and study the properties of brake wear particles. In addition, there is a wide variety of sampling methodologies and measurement techniques that very often lead to incomparable results.

– The most important chemical constituents of brake wear are Fe, Cu, Pb, Zn. Carbon is also present in significantly high concentrations. On the other hand, there is very limited information regarding the specific organic constituents of PM10 brake wear.

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INVESTIGAȚII PRIVIND EMISIILE REZULTATE DIN UZURA PLĂCUȚELOR DE FRÂNARE

(Rezumat)

În ultimii ani s-a acordat o atenție sporită cercetărilor asupra poluarii mediului înconjurător şi asupra problemelor de sănătate corelate cu concentrația particulelor în suspensie (PM) eliberate de vehicule. Cauzele poluării provin atât din emisiile de gaze de eșapament cât și din alte surse. Prima categorie este intens cercetată și reglementată în UE, fiind subiectul principal al Standardului European de Emisii, în prezent stabilit la nivelul Euro 6.

Emisiile cauzate de vehicule din alte surse decât sistemele de evacuare pot fi fie particule de la sistemele de frânare, ambreiaje, anvelope, suspensie, drumul în sine, fie materiale depuse pe suprafața drumului. Acestea reprezintă aproape jumătate din totalul emisiilor din mediul urban, pentru care vehiculele sunt responsabile. Din această categorie, emisiile plăcuțelor de frână adună un total de 55% din totalul PM eliberate în atmosferă.

Limitarea și reglementarea emisiilor plăcuțelor de frână va avea un efect benefic important în protejarea sănătății populației și reducerea impactului poluării asupra mediului.

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ŞTIINŢA ŞI INGINERIA MATERIALELOR

PHOSPHATE COATINGS SUITABLE FOR STEEL REBARS USED FOR REINFORCED CONCRETE

BY

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Abstract. The paper aims to conduct a complex and multidisciplinary study in the field of materials science and engineering. It focuses on the thin superficial layers of OB 37 steel reinforcements used in reinforced concrete structures. In order to obtain a phosphate layer that will improve the corrosion resistance of OB 37 steel, as well as a layer that can be used as a substrate for future coatings, three solutions were prepared/applied, different from the point of view of the principal elements (MgCO3, Mn-Ni-Fe-Zn and Zn). The quantities of active substances used were calculated for one liter of phosphate solution, supplemented with distilled water. The phosphate layers were deposited by immersion of the samples in a phosphate solution at a temperature of 95°C for 60 minutes. Before this, the sample surface was prepared by immersion into a degreasing solution, respective a pickling solution.

Keywords: phosphate coatings, concrete, zinc phosphate, manganese phosphate, magnesium phosphate.

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1. Introduction

The paper aims to carry out a complex and multidisciplinary study in the field of materials science and engineering of the thin superficial layers on the OB 37 steel reinforcements used in the reinforcement of reinforced concrete structures.

The aim of the research will be to develop phosphated layers on OB 37 steel supports, in order to obtain surfaces with anti-corrosion resistance and better adhesion between the reinforcements and concrete compared to the use of untreated reinforcements.

2. General description of the microcrystalline phosphating process of OB 37 steels intended for reinforced concrete

The microcrystalline phosphating process of OB 37 steels intended for reinforced concrete was designed in order to obtain thin layers of high porosity capable of allowing the insertion/embedding of solid lubricating structures, with the multiple action of improving the processing characteristics and implicitly protection (Taranu *et al*., 1997).

In order to obtain thin layers by sequential coprecipitation of sparingly soluble salts of the pyro-phosphate and/or nitrate ion, with the role of anti-corrosive protection, but also aesthetic, the processes of passivation of metallic iron surfaces are used, which are based on acid-base processes, assisted by redox processes (Brouwer and Kuhm, 2005).

These processes are carried out by treatment with solutions based on orthophosphoric and/or nitric acid, which require previous cleaning operations by degreasing and pickling, when uniform, compact and adherent films are obtained on the substrate, hardly soluble nitrates and/or of orthophosphates of transition metals, in stable oxidation states, in the presence of polyacrylamide, epoxy esters, silicates, citric acid and sulfamic acid and others (Kazuya *et al*., 2000; Noriaki and Tomohiro, 2007; Michael and Gerald, 2001; Harry and Cape Thomas, 1991; Heinz *et al*., 2006 ; Masahiko and Shinichi, 2006; Kiyokazu and Atsushi, 2005; Kiyokazu and Koichi, 2005; Song-Gu, 1988).

These processes have the disadvantage of obtaining a passivating layer that is very thin, up to transparent, compact, often uneven, affected by oxidic stains, formed in situ or induced after installation, in the presence of humid climatic environments and which for lubrication requires the application of overlapping layers, poorly adherent or with low bearing capacity (Ho and Soo, 2005; Tamotsu *et al*., 1999; Sigeki, 1989).

The process of microcrystalline phosphating of OB 37 steels intended for reinforced concrete is a relatively new method of coating by converting the surfaces of steel and cast iron parts, it compensates the initial investment with high quality production and low material consumption (Jae-Ryung, 1992; Varentsova and Chumaevskij, 1998).

After degreasing and pickling, a sequential chemical treatment is applied in two stages:

• first, iron pyrophosphate is precipitated in the presence of nitrogen ion and hydroxylamine sulfate (SHA) in an acidic medium after the reaction,

$$3\underline{Fe}^{o} + 2H_3PO_4 \xrightarrow{HNO_3/SHA} \underline{Fe_3(PO_4)_2} + 3H_2\uparrow \quad (1)$$

• after which the interstitium is made by coprecipitation of zinc pyrophosphate, by immersing the samples in the orthophosphoric acid solution containing dispersed fine metallic zinc powder, at a temperature of 90°C, for 30 minutes, after the reaction,

$$y\underline{Fe_3(PO_4)_2} + 3x\underline{Zn} + 2xH_3PO_4 \rightarrow (xFe/yZn)_3(PO_4)_{2(x+y)} + 3xH_2\uparrow \quad (2)$$

Thus, the process is based on the process of phosphating in an acidic environment through an additive/subtractive mechanism, in the presence of Cu, Zn and Mn cations, stable in the oxidation state (II), which after precipitation become inert in relation to Fe(0) from the substrate (Gosset and Malras, 1989; Askienazy *et al*., 1990; Kolberg *et al*., 2004).

The procedure has a number of advantages:

– reduced solution consumption;

– it allows the creation of a thin porous structure through synergy that allows the insertion of colloidal lubricating systems;

– it can be applied to any iron-based metal substrate, such as cast iron and steel, in the form of finished, cast, volumetric plastic deformed or cold surface parts;

– the films formed have great reliability and stability over time (Burduhos-Nergis *et al*., 2020).

Whatever the type of piece, first the metal surfaces are prepared, by applying the classic methods of degreasing and pickling. If the surfaces contain coarse deposits, tunder and burrs, they will be removed by sandblasting, brushing or other mechanical processes (Brouwer and Kuhm, 2005; Chasan and Ribeaud, 2010).

For degreasing, aqueous solution systems are used, which contain the components and concentrations from Table 1.

Table 1
The composition of the alkaline chemical degreasing solution and the working parameters

No. crt.	Chemical components	Concentration, [g/l]
1	Hidroxid de sodiu, NaOH	40
2	Sodium carbonate, Na_2CO_3	30
3	Trisodium phosphate, $Na_3PO_4 \cdot 10H_2O$	30
4	Sodium silicate, $Na_2SiO_3 \cdot 9H_2O$	5
5	Detergent (surfactant)	3...10
Working parameters		**The value**
1	Temperature, [°C]	70
2	pH	11...12
3	Degreasing time, [min]	10

For the pickling of oxide and saline films we used the aqueous solution according Table 2.

Table 2
The composition of the acidic chemical pickling solution and the working parameters

No. crt.	Chemical components	Concentraţia, [g/l]
1	Hydrochloric acid, HCl (ρ=1,19g/cm^3)	150
2	Hexamethylenetetramine, $C_6H_{12}N_4$	0.45
3	Sodium sulfate decahydrate, $Na_2SO_4 \cdot 10H_2O$	0.15
Working parameters		**The value**
1	Temperature, [°C]	20...25
2	Pickling time, [min]	10

3. Development of the technological flow for microcrystalline phosphating of OB 37 steels intended for reinforced concrete

The technological process for the crystalline phosphating of steels intended for reinforced concrete involves going through several stages and phases, with the following development:

– obtaining steel semi-finished products;
– alkaline chemical degreasing (temperature: 70°C, time: 10 min);
– wash with cold water (20-25°C, 10 sec);
– acid chemical pickling (20-25°C, 10 min);
– phosphating (90°C, 30 min);
– passivation (20-40°C, 0.5-0.7 min);
– taking phosphated blank samples for the analysis of the phosphated layer;
– finished pieces.

4. Phosphate layer deposition technology

Phosphating is one of the most important conversion deposition processes, being widely used in many industries for corrosion protection, wear resistance and as a paint support.

In order to ensure uniform coverage of the material surface, the phosphating process includes several stages. Depending on the properties of the surface on which the phosphate layer is to be deposited, as well as depending on the substances that are used to make the solutions, some steps can be added or removed.

Stages of the phosphating process:

– preparation of samples;
– alkaline chemical degreasing;
– washing with cold running water;
– washing with hot water;
– acidic chemical pickling;
– washing with cold running water;
– phosphating;
– washing for neutralization;
– double washing with running water;
– drying.

In order for the phosphate coating to improve the corrosion resistance of OB 37, the surface on which the phosphate coating is to be applied must be prepared. Therefore, before the sample is immersed in the phosphating solution, it must go through two other previous surface preparation steps. After each stage, they must be rinsed in water to remove the chemical compounds from their surface, which appeared as a result of degreasing and pickling. The last stage of the phosphating process, drying, can be carried out at room temperature or at high temperatures 100 ÷ 150°C using ovens (Burduhos-Nergis, 2020).

The heating of the degreasing and phosphating solutions is done in DIGIBATH-2 Raypa thermostatic digital baths, thus maintaining the working temperature. The agitation of the degreasing and pickling baths is done by means of two agitators driven by electric motors type SIEMES 1AF 2210 0A, 220V, and the agitation of the phosphating solution is done with the aid of the R2120 Heidolph agitator at a speed of 500 rpm. The drying of samples after crystalline chemical phosphating is carried out in an oven model APT.lineTM ED (E2) with a temperature range of 100-150°C.

5. Phosphating solutions

Phosphating solutions can be classified according to the nature of the metal ions that constitute the major component of the phosphating solution as follows: zinc, manganese or iron phosphate baths. The compositions of these solutions are chosen depending on the material to be phosphated, as well as the properties to be obtained after deposition.

In order to obtain a phosphate layer that will improve the corrosion resistance of OB 37 steel, as well as a layer that can be used as a substrate for future coatings, the solutions presented in Tables 3, 4 and 5 were used. The quantities of substances actives used were calculated for 2 liters of phosphating solution, being supplemented with double-distilled water.

In Romania, the STAS 7969-85 standard presents the main categories of phosphating solutions, as well as the quantities and ratios that must be taken into account for their production.

Table 3
Chemical composition of the phosphating solution I

Name of the active substance	**Quantity**
Orthophosphoric acid (H_3PO_4)	22.00 ml
Nitric acid (HNO_3)	11.00 ml
Sodium nitrite ($NaNO_2$)	0.6 g
Zinc (Zn)	9.00 g
Sodium tripolyphosphate ($Na_5P_3O_{10}$)	0.1 g
Sodium hydroxide (NaOH)	0.9 g

Table 4
Chemical composition of the phosphating solution II

Name of the active substance	**Quantity**
Orthophosphoric acid (H_3PO_4)	20.00 ml
Nitric acid (HNO_3)	10.00 ml
Sodium nitrite ($NaNO_2$)	0.5 g
Magnesium carbonate ($MgCO_3$)	10.00 g
Sodium tripolyphosphate ($Na_5P_3O_{10}$)	0.1 g
Sodium hydroxide (NaOH)	6.00 g

Table 5
Chemical composition of the phosphating solution III

Name of the active substance	**Quantity**
Orthophosphoric acid (H_3PO_4)	20.00 ml
Nitric acid (HNO_3)	15.00 ml
Sodium nitrite ($NaNO_2$)	0.3 g
Zinc (Zn)	0.9 g
Sodium tripolyphosphate ($Na_5P_3O_{10}$)	0.05 g
Sodium hydroxide (NaOH)	0.8 g
Nichel (Ni)	0.5 g
Iron (Fe)	0.04 g
Manganese (Mn)	21.00 g

Phosphate layers were deposited on the surface of the material by spraying or immersion, the most suitable method being chosen depending on the size and shape of the surface to be phosphated, as well as its subsequent use.

Although the immersion process takes longer, the need for uniform coverage of the material surface and containing size, shape and manufacturing process, for this application, it was considered more suitable for the deposition of the phosphate layer. The samples were immersed in the phosphating solutions at a temperature of 95°C for 60 minutes.

6. Conclusions

The phosphating solutions used to obtain thin surface layers on steel reinforcements used in concrete structures were chosen based on previous experimental research. Solutions based on zinc, manganese and nickel were chosen. The composition of each phosphating solution is presented in Tables 3, 4 and 5 and the chemistry was stable following numerous experimental laboratory researches.

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STRATURI FOSFATATE ADECVATE PENTRU ARMĂTURI DE OȚEL FOLOSITE PENTRU BETON ARMAT

(Rezumat)

Lucrarea îşi propune realizarea unui studiu complex şi multidisciplinar în domeniul științei și ingineriei materialelor a straturilor superficiale subţiri pe armăturile din oțel OB 37 utilizate la armarea structurilor din beton armat. Cercetarea va avea drept scop elaborarea unor straturi fosfatate pe suporturi din oțel OB 37, în vederea obţinerii unor suprafeţe cu rezistenţă anticorozivă şi cu o aderență mai bună între armături si beton comparativ cu utilizarea armăturilor netratate. Pentru a obține un strat de fosfat care să îmbunătățească rezistența la coroziune a oțelului OB 37, precum și un strat care poate fi folosit ca substrat pentru viitoarele acoperiri, s-au pregătit/aplicat trei soluții

diferite din punct de vedere al elementelor principale ($MgCO_3$, Mn-Ni-Fe-Zn și Zn). S-au calculat cantitățile de substanţe active utilizate pentru un litru de soluție de fosfat, completată cu apă distilată. Straturile de fosfat au fost depuse prin imersarea probelor într-o soluție de fosfat la o temperatură de 95°C timp de 60 de minute. Înainte de aceasta, suprafața probei a fost pregătită prin imersare într-o soluție de degresare, respectiv o soluție de decapare.

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THE ANALYSIS OF THE ASSORTMENT OF PRODUCTS FOR PEOPLE WITH LOWER LIMB AMPUTATIONS

BY

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Abstract. The amputation of the limbs represents a serious intervention of a person’s physical integrity. It modifies the initial form of the body and significantly affects locomotor abilities of a person. Persons who had their limb recently amputated face a set of complex tasks and problems which need to be overcame. The study presents the results of a thorough research of the range of products of clothes meant for the persons who have lost their inferior limbs due to amputation, as well as their functionality. The timeliness of the theme is determined by the increase in the number of people with lower limb amputations and the increased interest of specialists in creating clothing for people with disabilities. The goal of this study is to establish the needs of persons with lower limb amputations, to identify the products and accessories of a complete set intended for a person with locomotor disability and to propose the directions of multilateral development of the functional clothing product assortment.

Keywords: Amputation, clothes for people with disabilities, adaptive clothing, functional clothing.

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1. Introduction

According to the estimation of the World Health Organization (WHO), 650 million individuals suffer from a disability worldwide. About 80% out of 650 million individuals reside in developing countries. Among 650 million, approximately 3 million suffer from the upper limb amputation and 2.4 million of which live in the developing countries (Hussain *et al.*, 2019).

Clothing represents an essential element in human's life. The majority of them, purchase clothes easily. They keep in mind the size, the style, the price. But, when it comes to the disabled persons with both inferior limbs amputated, choosing clothing products becomes difficult, especially when there is the need to satisfy their personal requirements and impairment characteristics (Na, 2007).

For a disabled to participate to community life, and to have the boost to develop its needs to live in a community, it is necessary for him to start feeling confident, to adapt and enjoy the way he looks. The outfit may have an eloquent role, when it comes to proper security and self-confidence. Even small changes, may influence the way we are perceived by the others. This thing influences our confidence and self-respect. When you look fine and you are aware of that, you feel well and comfortable, which gives you the power to impose yourself with persuasion and authority. Studies show that more and more people strongly affirm that clothing marks an impact over person's personality.

In the cases involving the disabled, clothing may not be just a simple boost for increasing self-confidence, but even a possibility to decrease the massive effort they impose to have a normal life.

2. Level of amputation

People who had their inferior limbs amputated face a set of problems when trying to return to normal life. The amputated limbs present a major restriction, when it comes to their activity and participation in social life. The reduced mobility and the limited ability of self-service affects their interaction with the society. The usage of the functional clothes, as well as the whole set of accessories, increases the chance of social integration of people with amputations.

When selecting products for the disabled with both inferior limbs amputated, it is mainly kept in mind the type of the prosthesis. The prostheses are the artificial devices that improve the quality of life of a disabled person by replacing the missing or lost limb due to congenital disease or trauma or injury. She may replace the lost or missing limb in terms of appearance, functionality, or both. The prostheses may be classified by the level of amputation and by their functionality.

The lower limb prosthesis design and functionality varies with the level of amputation (Hussain *et al*., 2018; *A Beginner's Guide*, 2019). There are five major levels of amputation at lower limb (Fig. 1).

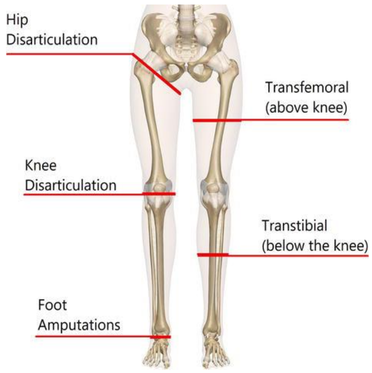

Fig. 1 – Level of amputation for lower limb.

1. Foot amputation. The foot amputation may occur below the ankle at any part of the foot. In this type of amputation, the amputee only needs a robust esthetic prosthesis to help in walking.

2. Transtibial (below knee). In transtibial amputation, the amputee loses limb between the ankle and knee. Most of the time, the residual muscle and bones may be used to drive the prosthesis being used to increase the quality of amputee.

3. Knee disarticulation. In knee disarticulation, the amputation occurs at the knee joint. In this type of amputation, the amputee loses muscles and bones below knee; however, the muscles responsible for the movements of the leg are intact.

4. Transfemoral (above knee). Transfemoral amputation occurs between knee and hip. In this type of amputation, the amputee loses most of the leg muscles and bone. The prosthesis designed for this amputation must include the movements of the knee and ankle.

5. Hip disarticulation. In hip disarticulation, the complete leg has been amputated. The amputee may not be able to perform hip movements and may need a fully functional biomimetic leg prosthesis to recover from his/her disability.

3. The analysis of actual products assortment

For people with disabilities, everyday clothing can be a struggle. Some wheelchair users have dressing challenges, such as uncooperative limbs, stiffness, or circulation problems. Additionally, staying in a seated position can create issues like pressure problems and sensitivity to seams. For people with sensory processing issues or autism, seams, certain fabrics, and tags can make typical clothing a nightmare as they may find this clothing irritating and uncomfortable. Buttons, zippers, laces, and snaps can make dressing difficult or even impossible for people with limited mobility. For those who struggle with standard clothing, there are brands and stores that carry adaptive clothing and shoes.

At the present time, persons with both inferior limbs amputated, possess a small range of products, such as: trousers, shorts, jumpsuits, socks. In Table 1, it is shown the characteristics of the trousers (https://hcbsprovider.com/adaptive-clothing-for-special-needs/; https://usa.tommy.com/en; https://www.silverts.com/; https://ilcaustralia.org.au/).

Table 1
The characteristics of the trousers for disabled persons with both inferior limbs amputated

Design	Features
	**Side opening pants** - Both sides opening with easy adjustable velcro fastening - convenient for dressing up and undressing - are designed for the elderly, and persons with other disabilities
	**Pants with open side stiches** -both parts open based on a velcro system or zippers, from waist to ankle -offers access and open space to waist, hips, and the superior/inferior part of the leg -are designed for the elderly, with locomotor disabilities
	**Pants with open interior stiches:** -the stiches from the sole and the foot open by zippers -offer access and open space to feet -are designed for the elderly, with locomotor disabilities
	**Pants with magnetic opening/ zippers/velcro** -both sides open by magnets/zippers/velcro from waist to ankle -offer access to the inferior part of the limb -are design for the elderly, with locomotor disabilities

	**Pants with anterior opening** -the opening is adjustable with magnets or velcro -it is comfortably and easy to put on -are design for the elderly, with locomotor disabilities
	**Pants with posterior opening** -the opening is adjustable with magnets or velcro -offer access to the posterior part of the body, for treatment and therapy -are design for the elderly, with locomotor disabilities

Upon this research, it is remarkable the interest of the designers over products assigned for persons with disabilities, especially for persons with both inferior limbs amputated.

Those adaptive products represent some innovative elements, as: hidden openings for abdominal access, side closure, zippers and other fasteners that are easier to manage, seamless socks and clothing, etc. All those elements offer access to the disabled body parts, offer comfort when using and correspond to the necessities of the locomotor disabled persons.

4. The characteristics of the materials

From previous studies, we observe that adaptive clothing differs from usual clothing by their characteristics of the disabled persons. Also, adaptive clothing is made out of special materials and fabrics, that would eventually offer comfort to the disabled person.

For the manufacture of products for people with disabilities, materials that meet the requirements submitted by the wearer can be used. First of all, fabrics are made of natural fibers. Nowadays, new generation fabrics are used, due to their characteristics. Following this, we will now present the characteristics of several materials, that are used for clothing assigned for disabled persons (Table 2) (Семьина, 2017; Салимова, 2015).

Table 2

The characteristics of the materials used for designing clothing assigned for persons with both inferior limbs amputated

Characteristics and properties	
Cotton - high level of higroscopicity. - thermoplastic. - high level of antibacterial resistance. - dermatologically tested. - hypo-allergenic - durable enough not to tear up or to be destructed allows ventilation and keeps the body ventilated	**Linen** - protective layer against pathogen microflora - reduces the tension of static electricity - hypo-allergenic - prevents the spread of any type of fungus - UV protection
Wool - highest level of higroscopicity - high level of elasticity - high level of antibacterial resistance - hypo-allergenic - UV protection - durable enough not to tear up or to be destructed	**Bamboo** - high level of exploitation - high esthetic quality - durable enough not to tear up or to be destructed - UV protection - thermoprotective - highest level of higroscopicity - antibacterial
Ramie - durable enough not to tear up or to be destructed - maintains its initial form - high esthetic quality	**Corn** - hypo-allergenic - durable enough not to tear up or to be destructed - maintains color pigment - highest level of higroscopicity and quick drying.

5. Conclusions

The characteristics of human body represent essential element when seeking a quality product. Among healthy persons and the disabled ones, there do exist major eloquent differences, especially their way of living.

Also, for the disabled, the product appears as a way of embellishment, because the disability is hidden up and he disabled feel look better.

The functional design offers comfort and independence when dressing up for day-to-day activities.

Subsequently, the prototype of those products assigned for the disabled, shall be designed carefully and contain functional and decorative elements, that will ensure the enhancement of lifestyle and personal expectations.

Locomotor disabled persons need diverse type of clothes. Upon this research, main points are highlighted:

- the products fulfill two main functions: esthetic and functional,
- fabrics used for those products are average-priced, so, that in the end, the clothing is affordable for everyone,
- even though the body of the disabled may not be symmetric, the clothes will assure the effect of symmetry camouflage,
- innovative elements, such as magnets, velco, zippers and others, allow a more convenient managing of the clothes,
- the design of the elements allows the disabled to be more independent and live a normal life.

In conclusion, clothing for the locomotor disabled shall offer physical and psychological comfort, shall correspond to esthetic and functional requirements, shall be easy to maintain, and shall have reasonable price.

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ANALIZA SORTIMENTULUI DE PRODUSE DESTINATE PERSOANELOR CU AMPUTAȚII ALE MEMBRELOR INFERIOARE

(Rezumat)

Amputarea membrelor prezintă o intervenție serioasă în integritatea fizică a unei persoane. Ea modifică forma inițială a corpului și acționează semnificativ asupra abilităților locomotorii a omului. Pierderea unui membru are un impact puternic asupra pacienților. Persoanele cu o amputație recentă se confruntă cu un set complex de sarcini și probleme, care trebuie rezolvate. Lucrarea prezintă rezultatele cercetării produselor de îmbrăcăminte destinate persoanelor cu amputații de membre inferioare. Aceste cercetări se bazează pe procesul de analiză complexă a literaturii din domeniul medical și tehnic și a produselor funcționale existente, elaborate la nivel local și mondial. Scopul acestui studiu este de a stabili necesitățile persoanelor cu amputații de membre inferioare, de a identifica produsele și accesoriile unui set complet destinat unei persoane cu dizabilități locomotorii și de a propune direcțiile de dezvoltare multilaterală a sortimentului de produse de îmbrăcăminte funcționale.

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TEXTILE PRODUCTS FOR PEOPLE WITH DISABILITIES BY BREAST CANCER

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Abstract. The field of functional clothing is a relatively new segment, at the same time, complex and diverse. The paper presents the results of the study on the functionality of textile products intended for people with disabilities caused by breast cancer, as well as the structure of the current assortment of clothing products intended for post-mastectomy women. The timeliness of the theme is determined by the need for textile products adapted to the new structural, functional and psychological peculiarities arising because of radical treatment in breast cancer. The functionality of the clothing product is determined by its structure, namely, the textile structure, the constructive solution, the processing technology. The study includes a synthesis of the literature in the field in order to determine the aspects of clothing products for people with disabilities caused by breast cancer. The purpose of the study process is to set out new directions for enhancing the assortment of clothing for post-mastectomy women. Study hypotheses: the post-mastectomy women perception; the social context; the concealment.

Keywords: Post-mastectomy clothing, functional clothing, functionality, post-mastectomy women, comfort.

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1. Introduction

Functional clothing is the evolutionary segment in the field of textiles representing the area in which clothing crosses the conventional boundaries and integrates with the domains of medicine, biotechnology, nanotechnology, physics and mathematics, in order to meet the complex user's requirements. Functional clothing represents ergonomically designed assemblies to have minimal inhibitory effect on movement and provide maximum comfort and performance to the user. In the case of functional clothing, aesthetic aspects are often ignored in favour of performance (Gupta, 2011).

Breast cancer is a global problem with a negative impact on the socio-economic sphere of the country (Masleacov *et al.*, 2014). Mastectomy – is a surgery that invalidates the woman's body and soul. The vast majority of all women who are diagnosed with breast cancer require surgical treatment (Chiaburu *et al.*, 2014). Of these, 10% are young women for whom breast removal is a very serious psychological and emotional trauma (Baraliuc *et al.*, 2018). Breast loss is not only a physical disability, but also a psychosocial one, and in most cases it is for a woman a severe mental trauma, which has a decisive impact on her behaviour as well at home and in society (Anghelescu, 2003).

The clothing for women after mastectomy has the role of harmonizing the body and also of ensuring optimal comfort indices and it requires the assignment of specific functions that contribute to the increase of the patients' satisfaction and quality of life. Post-mastectomy women's clothing can be classified in the functional clothing for people with special needs. At present, worldwide, post-mastectomy women have functional clothing such as bras, swim wears, nightgowns, blouses, camisoles, dresses, lymph support arm sleeves, shirts. Post-mastectomy women face social, emotional as well as medical problems that require clothing and accessories optimization that can provide comfort, ergonomic fit and improved aesthetic appearance. Clothing for this lot of wearers still requires individualized research to optimally meet the physical and psychological comfort requirements of each person (Gersak, 2013).

2. Brief History

The literature and the multitude of invention patents demonstrate the multiple worldwide concerns regarding the research, making of functional medical garments, and clothing products for people with special needs. Worldwide there are manufacturers of a diverse range of such products in the U.S., France, England, Germany, India, China, Russia, etc.

Concerns regarding clothing products intended for post-mastectomy women have been attested since 1963, when it was recognized the interest of post-mastectomy women in their appearance, especially in terms of matching clothing with external breast prostheses (Feather *et al.*, 1989).

Ruth Handler created the first pocket bra for external breast prostheses. The bra created, however, did not provide the necessary protection and support for the external breast prosthesis. In June 1985, a group of researchers organized a workshop that ended with the creation of a bra with wide straps and closure with a larger number of hooks. According to the researchers, it would provide the necessary support for the external breast prosthesis, but also an increased comfort to the wearer. In the mid-1980s, the researcher Jobst created compression sleeves. Another group of researchers states the need to wear the breast prosthesis also at night (Chowdhary, 2017).

Clothing can generate social approval and psychological satisfaction. Clothing products and accessories play an important role for post-mastectomy women by their ergonomic compliance, ensuring the state of comfort and ensuring aesthetic appearance. Carol Bread, in his work, mentions the importance of the selection and/or of making clothing products, taking into consideration the style, the elements of design including line and colour which are at the core of the creation of the ensemble of clothing, the ability of the garment product to hide the disability and to provide, physical and psychological comfort to the wearer. To avoid pressure on the body and especially in the area of the incision, clothing intended for post-mastectomy women is recommended to be made of soft, elastic material; ergonomic closures; to provide adequate support for external breast prostheses (Bread, 2011).

Designers Shivan and Narresh (Delhi) made an innovative piece of clothing called "mastectomy blouse". This blouse is intended for post-mastectomy women and was developed in industrial version with the purpose of being distributed to cancer survivors. Nidhi Munim (Mumbay) launched a post-mastectomy swimsuit line with silicone implants (Ayachit and Thankur, 2017).

3. Current assortment

Women who have undergone a mastectomy feel that motherhood, femininity, body image and their appearance are threatened by this loss. In these conditions, the areas of work, rest, sports can be changed. A major importance acquires the requirements to the correct choice of clothing. Clothing performs not only an aesthetic role, but also psychic, utilitarian and even capabilities to speed up the healing process.

In the result of the study conducted in respect of clothing for persons with various disabilities it is noted the creation by designers of innovative clothing products: bras with front closure and Velcro fasteners, closures with staples or zippers of large size, blouses and shirts with back closure systems or expandable neckline, pants with side-positioned Velcro closure, dress with cut back, raglan and kimono tailoring, clothing features fitted with functional folds, shirts with functional cut outs that allow access to treatment areas without the need to put off the product (Ayachit and Thankur, 2017).

Table 1

The current assortment of post-mastectomy women clothing

Product name, manufacturing company	Description of clothing	Destination of the product
Brassiere ANITA Care Esther 5309X; Care Abra 5381X; Care Alicia 5756X; Care Tonya 5706X; Amoena Non Wired Bra – Rose Taupe 44543; Valeria LFO 789K001; Anaono Lelie Soft; Nicola Jane Lucy BRA 7001; Jasmine 423P ; Valerie 7002; Silima Diana 57/255; Womanzone Adore Bra; Leisure Bra	Fitted with pockets for external prosthesis on both sides. Fabric with a high percentage of cotton or microfiber, knit or fabric. Some products are made of materials containing nylon, polyamide.	Post-mastectomy for women wearing external breast prosthesis
Swim wears ANITA Care Lace De Luxe L9; Cocos One Piese Swimsuit 71122; Woman zone Brailian Bikini	Fitted with pockets for prosthesis on both sides. Textile material in the composition of which are found fiber Xtra life LYCRA resistant to chlorine, body creams, sun rays.	
Blouses Valeria LFK0897 П78; undershirt Wear Ease INC	Fitted with pockets for external breast prostheses, on both sides. Preformed Cup. Material: LYCRA fiber and viscose; nylon, spandex.	
Dress Dhazai Molibias	Dress with built-in bra and pockets on both sides for external breast prosthetics. Basic fabric-polyamide, elastane; Lining-microfiber, elastane.	
Bras for sport ANITA Care Isra 5315X; Xcontrol 5736X; bras AMOENA Amy Seamless Bra-Rose 44310	Sports bras with pockets for prosthetics on both sides. Cotton fabric and elastane, microfiber. Cups with seams or preformed. For the Model Xcontrol 5736X are characteristic double-layered pockets made of picket cloth on the outside and of flouted material on the inside.	Sports and leisure activities, during the night

Bras Anaono	Bras with pockets for prosthetics, front closure. Wide rear landmark, adjustable straps. Moderate compression. Made of soft material.	Post-mastectomy, post-surgical recovery period
Shirts MIENA Anaono	Functional shirts fitted with a belt on which the pockets for the drainage bags are fixed.	
Undershirt Wear Ease INC	Special tank top with built-in bra and removable pockets designed to support postoperative fluid drains.	
Bras Elizabeth Masthead	Fitted with pockets for prosthesis on both sides and support designed to support postoperative fluid drains. Medium degree of compression.	
Bras ANITA Camia 5310-1	Soft textile material, cups made of double microfiber layer, suspenders with low elasticity, and wide, lined, wide and soft straps for closure is designed to eliminate compression points that could create discomfort in the situation of high skin sensitivity. Between the two layers of preformed material of cups without seams is an additional layer, which provides proper support to the breasts. The bustier has no pockets for the prosthesis.	Period of treatment, radiotherapy
Sleeve ANITA Care Lymph O Fit 1114	Sleeve for stimulating the lymphatic circulation of the arm. It is made of a special textile fabric with 3D nodes that massage the skin and small lymphatic vessels. Improves the evacuation of water from tissues and speeds up the healing of wounds. The fabric provides an optimal climate for the skin. Compression Class I.	Mild lymphatic edema in the arm and forearm

4. Ensuring functionality and classification of clothing products intended for post-mastectomy women

The clothing product functionality is determined by its structure, namely, the textile structure, the constructive solution, the processing technology. Figure 1 shows how to ensure functionality and classification of clothing products for post-mastectomy women at the current stage, globally.

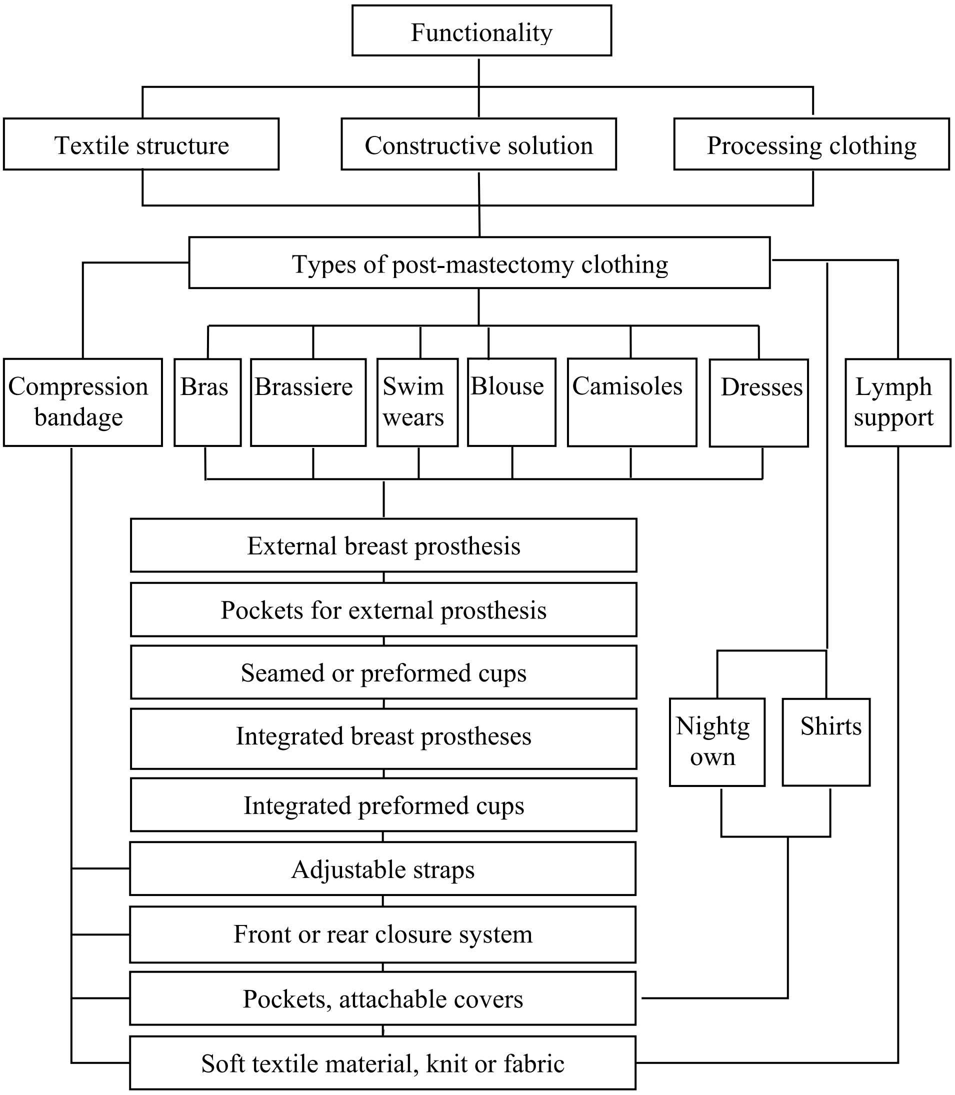

Fig. 1 – Ensuring functionality and classification of clothing products intended for post-mastectomy women.

5. Conclusions

Disability among patients with oncological pathologies of the mammary gland is determined by a number of medical, social, economic, physical and psychological contextual factors. Breast cancer is a global problem with a negative impact on the socio-economic sphere of the country. Clothing intended for this sector of wearers still requires individualized research in order to optimally meet the requirements of physical and psychological comfort of each person. It is necessary to propose comfortable alternatives for heavy breast prostheses by creating clothing products with preformed cups.

Solving the problem of creating optimal comfort conditions in the process of wearing can be ensured by taking into account the ergonomic aspects of the working system "man-product of clothing". Predetermined comfort requirements are necessary to be taken into account when creating clothing products of various categories: underwear products, swimwear, usual clothing.

The requirements imposed on women's clothing post-mastectomy products can be ensured by the optimal functional structure of the clothing ensemble: the use of multifunctional textiles, finding optimal constructive and technological solutions that will enhance the functionality of clothing products. Clothing products intended for post-mastectomy women require the assignment of specific functions that contribute to increasing the satisfaction of patients and their quality of life. In the result of the study there were outlined the directions of development for the assortment of apparel for women with post-mastectomy dictated by the functionality of the product: the needs of the specific group of carriers, the frequency of disease cases, the use of raw materials, the design peculiarities, use of the innovative processing technologies.

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PRODUSE TEXTILE DESTINATE PERSOANELOR CU DIZABILITĂȚI CAUZATE DE CANCERUL MAMAR

(Rezumat)

Lucrarea prezintă rezultatele studiului privind funcționalitatea produselor textile destinate persoanelor cu dizabilități cauzate de cancerul mamar, precum și structura sortimentului actual al produselor de îmbrăcăminte destinate femeilor post-mastectomie. Actualitatea temei este determinată de necesitatea produselor textile adaptate noilor particularități structurale, funcționale și psihologice apărute ca urmare a tratamentului radical în cancerul mamar. Funcționalitatea produsului de îmbrăcăminte este determinată de structura acestuia și anume de structura textilă, soluția constructivă, tehnologia de prelucrare. Studiul include sinteza literaturii din domeniu în vederea determinării aspectelor privind produsele de îmbrăcăminte destinate persoanelor cu dizabilități cauzate de cancerul mamar. Ca direcție ulterioară de cercetare se recomandă evaluarea funcționalității produselor textile destinate persoanelor cu dizabilități cauzate de cancerul mamar. Scopul procesului de studiu constă în stabilirea a noi direcții de dezvoltare a sortimentului produselor de îmbrăcăminte destinate femeilor post-mastectomie. Ipoteze de studiu: percepția femeilor post-mastectomie; contextul social; tăinuirea.

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A CONCISE ANALYSIS OF THE REGULATIONS ON THE ORGANISATION OF INTERVENTION AND RESCUE ACTIVITIES AT INDUSTRIAL ESTABLISHMENTS WITH POTENTIAL DANGER OF TOXIC, EXPLOSIVE, FLAMMABLE GAS EMISSIONS

BY

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Abstract. Persons working in economic operators who work with substances, products or goods capable of creating explosive, toxic atmospheres or having detonating or deflagrating characteristics are exposed to a wide range of hazards. In most cases, these hazards revolve around a hazardous atmosphere for personnel performing work tasks in such environments. Thus, the most common atmospheres for which workers need to be prepared are toxic, oxygen-deficient, explosive or flammable. In the event of an accident, intervention and rescue must be properly prepared and carried out and for this, the regulations must be strictly followed. A summary of these regulations is presented in this paper.

Keywords: rescue station, insulating apparatus, intervention.

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1. Introduction

Workers and staff that participate in the activities of economic agents operating with substances, products, goods capable to generate explosive or/and toxic atmospheres or show detonant or deflagrant characteristics are exposed to a wide range of dangers. In most cases these dangers gravitate around a dangerous atmosphere for the personnel working in such environments (Directive 89/391/EEC; Directive 1999/92/EC). So, most frequent atmospheres for which the workers must be prepared are the toxic ones, those without oxygen, the explosives and flammable atmospheres too (Non-binding Guide of Good Practice, 1999/92/EC). Each one of these atmospheres has unique characteristics and shows dangers that must be identified, evaluated and managed correctly, otherwise existing an extremely high probability of generation of work accidents with dramatic consequences (Directive 2014/34/EU; ATEX-Guidelines, 2014).

2. Main characteristics that stands on the basis of normatives regarding the organization of activities for intervention and rescue in industrial units with potential danger for toxic gases and explosion hazards and short comments

The normative deed concerning the organization of activities for intervention and rescue at industrial units with potential danger for toxic gases and/or explosion hazard was promoted by the Minister order 1637/2007 of finances and economy and Minister order 391/2007 of labor, family and equality of chances, published in the Official Monitor 408/2007 (D.G.P.S.I.-004, 2007).

The main articles that stand at the bases of the proposed normative are the following:

– The present normative has as a purpose the establishing of general forecasts for organizing the activities of intervention and rescue at industrial units with dangers of: toxic gas emissions, explosion and flammable atmospheres occurrence.

– The present normative applies to all economic operators, of which activity is susceptible of developing events, work accidents or dangerous incidents, following accidental emissions of toxic/ explosive/ flammable gases.

The main practical situations can occur:

a) when during the production process there is the danger of occurrence of gas, vapors and powders having toxic, asphyxiating, flammable or explosive characteristics, the economic operator must organize at the level of the unit a station for intervention and rescue in toxic/ explosive/ flammable environments, named in the following rescue stations (NP 099-04, 2005).

2.1. Logistic involved – spaces and personnel

It is allowed the functioning only for the rescue stations authorized and surveyed by the National Institute of Research and Development for Mining Security and Antiexplosive Protection – INSEMEX Petroșani, named in the following INSEMEX (Normativ din februarie, 2005).

For obtaining the notice foreseen at para. (b), the economic operators must submit at INSEMEX a request and a documentation comprising mainly:

– details concerning the space destined for the rescue station;
– the personnel structure of the station;
– the list of necessary endowment;
– the procedures of fast alarming and intervention.

2.1.1. Personnel organization and necessary equipment

The rescue stations will be served by operative rescuers, control and coordination personnel and mechanics for the rescue station. The total number of the station staff must be at least 2% from the entire personnel.

The personnel that activates in the rescue stations must by trained and authorized by INSEMEX.

In the sense of the present Normative, the terms and the expressions bellow have the following signification:

a) explosive atmosphere – according to art. 2, para. (1), lit. B from Government Decision nr. 752/2004 concerning the establishment of conditions for introduction on the market of equipment and systems for protection destined for using in potential explosives atmospheres;

b) potential explosive atmosphere - according to art. 2, para. (1), lit. C from Government Decision nr. 752/2004;

c) toxic atmosphere – the mixture with air in atmospheric conditions of toxic substances in gaseous state, vapors, mist or powders that are dangerous for the health of workers;

d) affected area – the expansion area of toxic, explosive, flammable atmosphere;

e) – rescue station – the formation that include the entire rescue staff of an unit, having at hand the specific space, apparatus, equipment and materials necessary for the intervention in toxic, explosive, flammable environments;

f) operative rescuers – persons recruited voluntarily from the personnel of the economic operator, trained and authorized according to the present normative;

g) rescue team – rescue formation in toxic/explosive/flammable environment composed by minimum 3 operative rescuers, having the qualification necessary for the intervention;

h) rescue group – rescue formation in toxic/explosive/flammable environment made at lest from 2 rescue teams;

i) mechanic for the rescue station – person recruited from the personnel of the economic operator trained and authorized according the present normative;

j) insulating apparatus – individual respiratory protection equipment working with compressed oxygen or compressed air enabling rescuers, control and coordination personnel of the rescue station to act and work safely in the spaces in what the atmosphere become irrespirable;

k) universal apparatus for control – apparatus with the help of which one can determine, before use, the essential operation parameters of the insulation apparatus;

l) resuscitation devices – (lung machines and inhalers) - devices intended for respiratory resuscitation of victims surprised by emissions of toxic/asphyxiating gas emissions;

m) instruction – the process of acquiring of theoretical and practical knowledge in view of certification for a certain field of activity.

The definitions of the terms and expressions from para. (1) are being supplemented with the definitions provided in art. 5 from the Occupational safety and health act nr. 319/2006 (Legea nr. 319/ 2006; NP 018-97).

2.1.2. Spaces, minimum endowment and specific rules

In what concerns the logistic needed for organizing and conducting intervention and rescue some of the most important regulations are given below.

The spaces allocated for the rescue stations must ensure:

a) the appropriate conditions for the theoretical training of the personnel;

b) keeping the insulating equipment, control devices, resuscitation devices in good conditions;

c) keeping the rescue materials and changing parts;

d) storage of pressurized tanks used for the apparatus for respiratory protection, observing the rules and technical prescriptions imposed by ISCIR.

The insulating apparatus and the resuscitation devices will be kept in cabinets foreseen with windows or in special pieces of furniture at a temperature between +15°C and +22°C.

The space allocated for the rescue station must be situated in an accessible place, both for rescuers and for vehicles and must have telephonic connection with the economic operator.

It is forbidden in the rescue station:

a) the access of persons without work duties;

b) carrying out activities not related to the rescue station;

In what concerns the minimum endowment of a rescue station the following are stated in specific regulations:

a) one insulation apparatus for each rescuer in proper working order and one spare insulating apparatus for each 5 insulating apparatus;

b) one universal apparatus for control for each 10 insulation apparatus but not less than two;

c) one resuscitating device for 10 insulating apparatus but not less then two;

d) for each insulating apparatus two fully filled oxygen (air) pressurized tanks, as a reserve;

e) one medical kit bag for each team.

f) one safety belt with rope, equipped with hooks and carabines for each 5 insulating apparatus;

g) one stretcher for each 5 insulating apparatus;

h) one portable gas detection device (specific for the field of activity) at each 5 insulating apparatus.

For rescue stations other than those for underground mining industry where other services can participate at the intervention and rescue actions (ISU, SPSU etc.) the scale of equipment provision is established according to the number of rescuers on the largest shift, to which they add 50% reserve. This provision also applies to economic agents that authorized a number of rescuers greater than the minimum required on the most numerous shift (I 7–2011).

2.1.3 Rescue station staffing and activities

The conditions for staffing the rescue station are as follows:

a) persons declared medically and psychologically fit to perform intervention and rescue activities in toxic/explosive/flammable environments.

b) persons in age between 20 - 65 years;

For the category - operative personnel - over 50 years of age, the specific medical exam will be performed every six months.

Persons in age up to 65 years will be assigned as control and coordination personnel. For this category - over 55 years of age, the specific medical exam will be performed every six months.

In what concerns the control and coordination of the rescue activity during interventions is has to be carried out by personnel with technical training.

The operative personnel for rescue activities consists of:

a) the operative rescuer is the person who meets the conditions above;

b) the team leader is the person who leads the activity of an operational rescue team;

c) the group leader is the person who leads one of the rescue teams as team leader and coordinates the activity of the other teams, being responsible for the correct performance of the tasks received from the head of the rescue station;

d) the head of the rescue station is the person who manages its activity.

e) the deputy head of the station is the person who takes over the duties of the head of the station in his absence.

The appointment of the team leader is made by the head of the rescue station. He is responsible for the correct fulfillment of the tasks received from the group leader or from the head of the rescue station.

The appointment of the head of the group is made by the head of the rescue station.

Both the head of the rescue station and his deputies are appointed by written provisions of the manager of the economic operator.

The deputy in chief of the rescue station can also be appointed from among the chiefs of the rescue group.

Operative rescuers and control and coordination personnel must periodically carry out practical training to maintain physical condition.

Economic operators have the obligation of periodic training of rescue station personnel, in the purpose of maintaining the knowledge/skills to perform the specific tasks within the intervention and rescue operations.

Generally, the checking of the health status of station personnel for interventions and rescue in toxic/explosive/flammable environments is done annually, with the exception of those mentioned above about the age of 50 or 55, for which the specific medical exam will be performed every six months.

It is forbidden to participate in the rescue actions of personnel whose rescue authorization has expired, of personnel on recovery day, rest or medical leave, as well as of those whose medical file has expired (SR EN 1127-1, 2011; Lerena and Suter, 2010; Piotrowski and Domanski, 2012).

The rescuer who has been absent 3 times consecutively from the periodic instruction hours provided for in art. 12 para. (1) will not be admitted to rescue interventions until he regains his practical knowledge and physical condition, which will be recorded by the head of the rescue station.

More over, in all concrete rescue situations some measures must be taken as follows:

(1) The head of the rescue station or his deputy together with a doctor will allow entry rescuers in the affected area in compliance with the provisions of this regulation only after they have checked whether they are fit from a physical and mental point of view, as well as whether they are not under the influence of alcoholic beverages, medicines or drugs.

(2) If the presence of a doctor cannot be ensured, the rescuers are permitted to enter the affected area by the head of the rescue station or his deputy assisted by the team leader.

(3) Before starting a rescue action or an exercise, the rescuers are obliged to check their insulating apparatus assisted by the team leader, and then

signing in the register for checking the insulating apparatus with which they enter the action.

In the affected area, rescue and intervention works are carried out based on the intervention program drawn up by the head of the rescue station or his deputy, according to the action plan drawn up by the leader responsible for the liquidation of the event, work accident or dangerous incident (Stahl, 2020).

The intervention program of the rescue teams in the affected area will include:

a) delimitation of the affected area and endangered areas;

b) rescuers' access and escape routes;

c) security points;

d) the method of evacuating personnel from the affected area and from the endangered areas;

e) the works to be carried out in the affected area to limit the effects of the event, work accident or dangerous incident and their liquidation;

f) safety measures to be taken while working in the affected area;

g) the list of persons who can give orders in the affected area during interventions.

At the end of the intervention shift, the team leader prepares a detailed report containing:

a) the number of rescuers who worked in the field;

b) the works performed;

c) the difficulties encountered and gas concentrations in the affected area;

d) the behavior of rescuers;

e) whether or not work was done with the insulating device in operation;

f) observations, defects, proposals

The intervention program and the report on how the intervention was carried out will be recorded in a register.

Rescuers are considered to be in action from the moment of presentation at the rescue station.

For longer missions, rescuers will be scheduled to work in such a way as to ensure the necessary time for rest.

In the case of the first intervention team, until the necessary number of rescuers for the intervention is ensured, the working time of 8 hours can be exceeded, with the consent of the rescuer and the opinion of the doctor or the head of the rescue station, in the situation where the doctor is not present.

Another regulations specific for rescuers concerning the alarm drills and interventions are following:

(1) During alarm drills and interventions, rescuers are obliged to make themselves available at the rescue station until the alarm or intervention ceases.

(2) Alerting the rescuers in order to check the operational status is done once every quarter, by the head of the unit under which the rescue station

operates, with the notification of the Ministry of Labor, Family and Equal Opportunities - Labor Inspection, respectively the territorial labor inspector.

(3) If a rescuer suffers an accident related to the use of the insulating device, his device is sealed, the cylinder is closed, the oxygen (air) pressure is read and transported to the rescue station, for further technical expertise.

Only persons nominated in the intervention program have access to the affected area. In order to keep the equipment in the rescue stations in proper working order, routine checks and repairs will be carried out at the rescue stations and periodic checks and repairs at service units indicated by the equipment manufacturer.

The maintenance, verification and repair of the rescue equipment, the transfer of pressurized gases used in the insulating equipment at the rescue stations at the units will be done only by trained and authorized rescue station mechanics, according to the provisions of art. 5 (Pepperl+Fuchs, 2012).

3. Conclusions

There are several regulation to be observed when designing and preparing the activities of intervention and rescue at economic agents who work in special conditions, namely with toxic, explosive or flammable gas emissions. Preparing for the worst can save many lives and goods and for this, strict measures must be taken in what concerns the personnel, the logistic endowment and also the procedures to be designed and followed.

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O ANALIZĂ CONCISĂ A REGULILOR DE ORGANIZARE A ACTIVITĂȚILOR DE INTERVENȚIE ȘI SALVARE LA UNITĂȚILE INDUSTRIALE CU PERICOL POTENȚIAL DE EMISII DE GAZ TOXIC, EXPLOZIV, INFLAMABIL

(Rezumat)

Persoanele care muncesc în cadrul operatorilor economici care lucrează cu substanțe, produse sau bunuri capabile să creeze atmosfere explozive, toxice sau care au caracteristici detonante sau deflagrante sunt expuse la o gamă largă de pericole. În cele mai multe cazuri, aceste pericole gravitează în jurul unei atmosfere periculoase pentru personalul care efectuează sarcini de lucru în astfel de medii. Astfel, cele mai frecvente atmosfere pentru care trebuie să fie pregătiți lucrătorii sunt toxice, deficitare de oxigen, explozive sau inflamabile. În cazul unui accident, intervenția și salvarea trebuie pregătite și efectuate corespunzător și pentru aceasta trebuie respectate cu strictețe reglementările. Un rezumat al acestor reglementări este prezentat în această lucrare.