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Experimental Research into the Mechanical Behaviour of Dammar and Sandarac - Based Bio Resins

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ABSTRACT

In this paper, we examine two types of Dammar-based bio resins. In the first type, Dammar alone is used as natural resin, while in the second type a mixture of 70% Dammar and 30% Sandarac is used. Three sample sets were made of each of these resins with a bio resin volume proportion of 55, 65 and 75% respectively, the rest being epoxy resin (used, together with the associated reinforcing material, to generate a quick polymerization process). A SEM analysis is carried out and the surface roughness of each of the studied materials. A series of mechanical properties, determined by tensile testing, are presented. We have determined the characteristic curves, tensile strength and modulus of elasticity and the influence of the epoxy resin volume proportion on the mechanical behaviour of bio resins.

Keywords: bio resin, mechanical properties, roughness

1. Introduction

In the last decades great attention has been paid to composite materials, the components of which, whether matrix or reinforcing material, come from nature. The main advantages of using green composites are given by the fact that both the fibers and the bio resins are abundantly produced by nature, consequently they have a low cost of manufacture compared to synthetic composites. Moreover, they are totally biodegradable and have relatively good mechanical properties. Most composite materials that have been studied so far have focused on natural fibers as reinforcing materials, only in combinations with thermoplastic matrix (polypropylene, polyethylene and vinyl polychloride) or with a thermo-rigid (phenolic, epoxy and polyester resins) (see example [1]). Synthetic resins have the disadvantage of a processing limit due to the high viscosity at meltdown, phenomenon appearing when cast by injection, and the final product is hard to recycle.

This disadvantage may be eliminated by using biological thermo-rigid matrices based on vegetable-oil resins since the latter are bio-degradable and, therefore, the polymerization process is not necessary [2-4]. Bio resins are resins derived from a biological source and, consequently, can be biodegradable and compostable, thus, hypothetically, they can decomposed after use. Natural resins can be fossil (amber), vegetable (Sandarac, Copal, Dammar), or animal Shellac). Natural resins are insoluble in water, however, they are slightly soluble in oil, slightly soluble in oil, alcohol and, partly, in petrol. They form solutions with certain organic solvents, solutions that can be used as covering lacquers. Turpentine, colophony, mastic is products resulted from the distillation of conifer resins. A study concerning the chemical composition of the properties of these resins is carried out in [5], and the applications are shown in [6]. The studies conducted on these resins have focused mainly on their chemical composition and their chemical properties and less on their mechanical properties. Thus, work [7] was intended to broaden the knowledge about microbiological biodegradation of the lacquers based on Dammar in works of art subject to unsuitable protection conditions, particularly to long exposures to relative humidity. In [8] a new binder is introduced, modified from silicon and Dammar, which can reduce the use of the synthetic binder and which has improved, especially ecological, properties. The optimal composition of this binder, which ensures the best properties for impact, hardness, traction and adherence stresses, was determined. The way in which Dammar addition contributed to improve the rigidity, the modulus of elasticity and the hardness of modified silicon was studied in the work [9].

In [10] the Dammar gum is examined as supplementary material used for improving thermal conductivity and performance in preparing the material for changing the composite phase, while the possibility of using bee wax, tallow and Dammar as PCM (phase change materials) in concrete buildings is investigated in [11]. The effect of polymethyl-methacrylate (PMMA) on Dammar's physical properties for the application of covering lacquers was analysed in [12].

A model with free particles used for numerical simulation of charpy impact test of plastic materials is studied in [13].

Sandarac is presented in [14], as well as its uses and chemical composition in comparison with other very similar resins. An identification of Sandarac's main chemical components is performed in [15] and in [16] there is a qualitative and quantitative study on some Sandarac resin types with different origins.

The Young modulus for composite material constituent was obtained based on numerical analysis [17].

Still, there are not enough studies on the mechanical behaviour of natural resins. The mechanical characteristics (the tensile strength, percentage elongation and Young's modulus), the characteristics of water vapour transmission and the characteristics of moisture absorption of Dammar films containing softening agent were studied in the work [18]. The reaction to the compression stress of palm tree trunk treated with different amounts of Dammar resin was analysed in [19]. There are also few studies concerning composites with both their matrix and reinforcing material made of natural material. The mechanical behaviour of some composite materials with a bio resin matrix based on Dammar and with reinforcement made with cotton, flax, silk and hemp fabric is studied in [20] and [21].

Experimental part

To make the studied materials we used natural resins, namely Dammar and Sandarac. The first type of material was made by dissolving Dammar by turpentine. For the second type we dissolved a mixture of

70% Dammar and 30% Sandarac by turpentine too. We cast three plates of each these resins where the volume proportion of natural resin was 55, 65, 75% respectively. The difference up to 100% was made of Resoltech 1050-type epoxy resin together with its associated reinforcing material because natural resins dissolved in turpentine have a very long hardening time and the synthetic component generates points of quick activation of the polymerization process. We also made a specified epoxy resin plate, necessary for assessing the way in which natural resins influence mechanical behaviour. We made three sets of samples of the cast plates, which were submitted to experimental determinations. We will use the following symbols:

- DA 55- resin with a 55% volume Dammar proportion;
- DA 65- resin with a 65% Dammar volume proportion;
- DA 75- resin with a 75% Dammar volume proportion;
- DS 55- resin with a 55% volume proportion of a mixture, composed of 70% Dammar and 30% Sandarac;
- DS 65- resin with a 65% volume proportion made of a mixture of 70% Dammar and 30% Sandarac;
- DS 75- resin with a 75% proportion made of a mixture of 70% Dammar and 30% Sandarac.

Samples of each of the materials mentioned above here submitted to a SEM analysis that was performed by an electron microscope - Hitachi model S3400N/type II, having the following specification:

- SE image resolution: minimum 3 nm at 3kV (100.000X, WD= 5mm, high vacuum mode);
- BSE image resolution: minimum 4.0 nm at 30kV (60.000X, WD = 5mm, low vacuum mode);
- Magnification Range: 5x to 300.000x;
- Accelerating Voltage: 0.3 kV to 30 kV.

As for the presented materials we measured the roughness of the representative samples. In order to do this we used a portable profilometer (Taylor Hobson Surtronic 3+) in which the analysed length varied between 0.25 mm and 25.4 mm, with a sensor speed of 1 mm/s (fig.1).

The examined samples underwent a tensile test, which was carried out according to the ASTM D3019 and ISO 527-4:1997 provisions. The elements obtained from this trial were: the characteristic curve, tensile strength R_m [Mpa], percentage elongation after fracture A [%] and elasticity modulus E [Mpa]. We used the LRX Plus testing machine from LLOYD Instruments with the following specifications:

- Force range: 2.5 kN;
- Travel: 1 to 735 mm;
- Crosshead speed: 0.1 to 500 mm / min;
- Analysis software: NEXYGEN.

Results and discussions

Figure 2 shows images obtained on the basis of the SEM analysis of the epoxy resin (fig. 2.1), the bio resin made of Dammar only (fig. 2.2) and the bio resin with 70% Dammar and 30% Sandarac (fig. 2.3).



Fig. 1. Portable profilometer (Taylor Hobson Surtronic 3+)

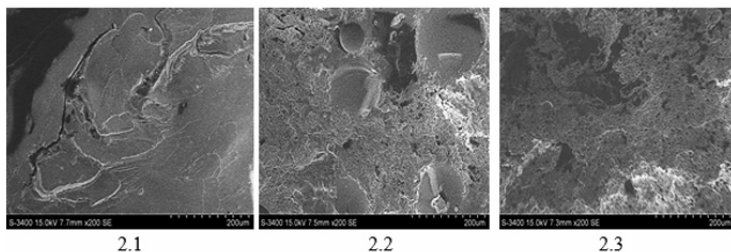


Fig.2. Images obtained by SEM analysis of the three resin types

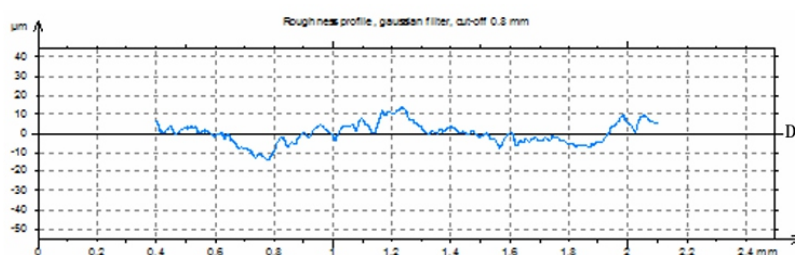


Fig. 3. Roughness diagram of a Dammar natural resin with a volume proportion of 55%

We can see that in the case of the bio resins there is a significant amount of air pockets. This can be explained by the fact that the polymerization takes place more slowly, the hardening of the resin takes a longer time and it is no longer possible to eliminate the air pockets.

In figure 3 we show the roughness diagram obtained for a Dammar natural resin with a volume proportion of 55%. Table 1 presents the results of the arithmetic mean deviation of the evaluated profile R_a , in μm (the arithmetic mean of the profile absolute values of the profile ordinates), of the studied materials.

Table 1

THE ARITHMETIC MEAN DEVIATION OF THE EVALUATED PROFILE R_a , in μm

Resin type	The arithmetic mean deviation of the evaluated profile R_a [μm]
DA 55	3.38
DA 65	2.84
DA 75	2.48
DS 55	1.94
DS 65	2.12
DS 75	1.42
epoxy	1.76

We observe an increase in porosity, compared with the epoxy resin, for all the samples containing natural resin. An explanation may be the polymerization time necessary for resin hardening. Thus, in

the case of the epoxy resin the hardener produces a quick reaction, the air pockets being eliminated shortly, before the complete hardening of the resin, which happened in less than 24 h. In the case of the mixtures of synthetic and natural resins the reaction time is longer, the hardening taking place in 72 - 96 h. Since the reaction is longer, the viscosity has gradually increased until complete hardening. We can see an increase in the surface roughness of the natural resin plates in comparison with the plate obtained from epoxy resin.

Henceforward, by representative sample of a set we understand the sample with the medium values of the studied mechanical properties.

The characteristic curves of each representative sample of the three sets made of Dammar-based resin are shown in figures 4 - 6.

Figures 7 - 9 show the characteristic curves of one representative sample of each of the three sets, made on the basis of the mixture of 70% Dammar and 30% Sandarac.

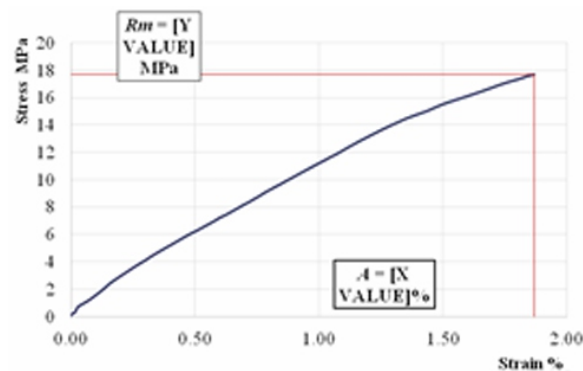


Fig. 4. Characteristic curve of DA 55 resin sample

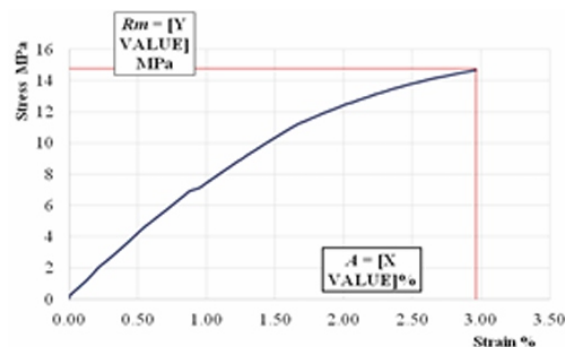


Fig. 5. Characteristic curve of DA 65 resin sample

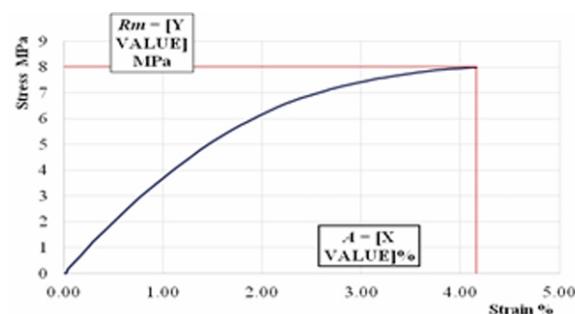


Fig. 6. Characteristic curve of DA 75 resin sample

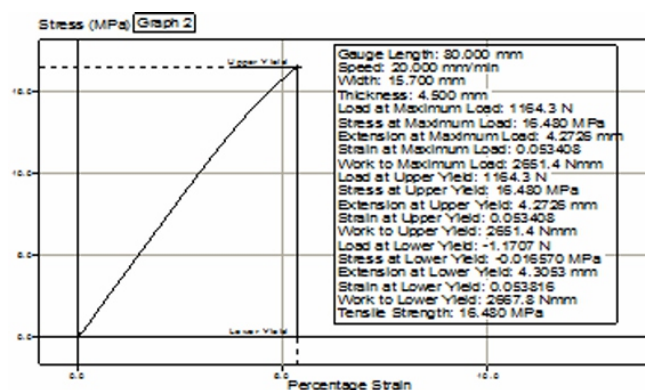


Fig. 7. Characteristic curve of a DS 55 resin sample

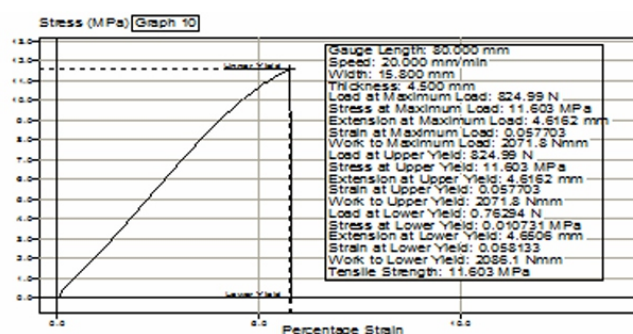


Fig. 8. Characteristic curve of a DS 65 resin sample

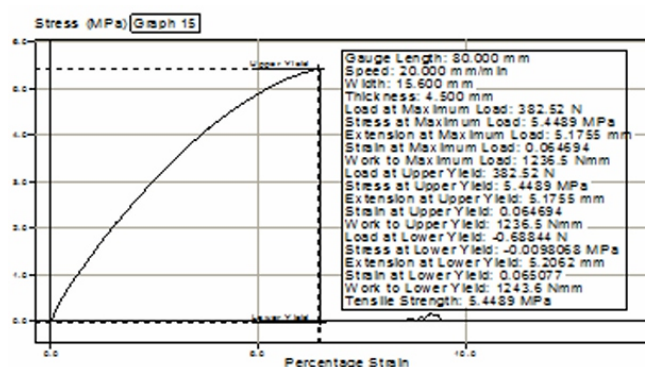


Fig. 9. Characteristic curve of a DS 75 resin sample

Resin	Tensile strength R_m [MPa]	Elongation at break A [%]	Modulus of elasticity E [MPa]
DA 55	17.2-18.3	1.87-2.18	1550-1660
DA 65	13.9-14.8	2.68-3.04	1140-1230
DA 75	7.60-8.20	4.16-4.92	590-720
DS 55	15.90-17.18	4.73-5.34	800-830
DS 65	11.60-12.31	5.45-5.77	560-610
DS 75	5.44-5.90	6.46-7.30	290-310
Epoxy	47.8-51.8	1.52-1.81	3230-3470

Table 2

EXPERIMENTAL RESULTS OF THE TENSILE TESTS

Table 2 shows the results obtained after tensile tests. The highest values of the mechanical properties are obtained for the mixture with 55 % Dammar (DA 55). In comparison with the epoxy resin, the tensile strength is 36% and the modulus of elasticity is 71%. In the case of the mixture with 65% Dammar (DA 65) the tensile strength is 29% and the modulus of elasticity is 71%. In the case of the mixture with 75 %

Dammar the tensile strength is 16% and the modulus of elasticity is 29%. An even more important decrease in properties appears in the case of the resin based on the mixture of Dammar and Sandarac. Comparing with the Dammar-based resin with the same proportion of epoxy resin, the tensile strength went down by 7 % in the DS 55 resin, by 17 % in the DS 65 resin and by around 28 % in the DS 75. Moreover, the moduli of elasticity of the resins based on the mixture of Dammar and Sandarac are half in comparison with the resins based on Dammar only. The increase in the air volume in bio resin, at the same time with the increase in the volume proportion of Dammar or Dammar and Sandarac, may explain this decrease.

Conclusions

The use of natural resins for the manufacture of composite materials can be influenced by the resin properties and the capacity to create a synergetic effect together with the reinforcing materials. The analysis of the results we obtained show an important variation of the properties depending on the proportion between the natural and the synthetic resin. Comparing the experimental results shows a significant modification of the mechanical properties when changing the proportion between epoxy resin and natural resins. We notice a decrease in the values of the tensile strength and the modulus of elasticity as the natural resin proportion is increased in the mixture. Although the mixtures with a higher amount of epoxy resin have superior mechanical properties, we cannot say that there is proportionality between tensile strength, or modulus of elasticity and the volume proportion of epoxy resin. There are the modifications in the forms of the characteristic curves. If in the DA 55 and DS 55 resins, where the natural resin proportion is 55 %, the characteristic curve is almost linear, in the DA 75 and DS 75 resins, where the natural resin proportion is 75 %, there is an obvious nonlinearity of the characteristic curve which points out, in these cases, a plastic behaviour.

There are also modifications of the elongation at break, the latter increasing as the natural resin in the mixture is increased. The elongation at break is higher in the resins based on the mixture of Dammar and Sandarac than in the resins based on Dammar only. As a result, the Sandarac presence leads to an increase in the ductility of the obtained materials. This can be used to control the mechanical properties of the composite materials with a matrix of bio resins based on Dammar and Sandarac.

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Aspects Regarding the Braking Capacity of Composite Brake Shoes for Railway Vehicles

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ABSTRACT

The main target of the study is to highlight, by means of numerical simulations, the advantages and possible drawbacks of using composite materials instead of the classical cast iron to equip the brake system of railway freight vehicles. The qualitative and quantitative evaluations refer mainly to the braking capacity by considering as main parameter the stopping distance, in various operational conditions. Results indicate that composite materials are more efficient in the braking process, but in the case of low speeds, the recommendation is to perform earlier and/or stronger braking actions than usual, in classical cast iron equipment on rolling stock.

Keywords: railway vehicle, composite brake blocks, cast iron brake shoes, braking capacity

1. Introduction

Railway is generally recognised as a very advantageous mean of transportation: environmentally friendly and sustainable, large and rapid carrying capacity over long distances, almost unaffected by weather conditions, reduced chances of accidents and breakdowns are certainly strong arguments. The specific very low rolling resistance associated to the actual tendency of increasing running speeds and tonnages of trains make more attractive the railway transport, but require special safety rules and put supplementary pressure on the braking system [1, 2]. Braking system is essential for the traffic safety, providing controlled reduction of velocity in order to ensure stopping to a fixed point, reaching a certain lower speed or keeping it to an appropriate level when running on long and important slopes. For this purpose, the rolling stock has to be equipped with a system capable to ensure consistent and controllable retardation forces that can be efficiently applied on the entire range of the vehicles' designed speed domain.

Usually, vehicles designed to run with less than 160 km/h are equipped for tread braking, based on a relatively simple mechanism, which is efficient, failsafe and less expensive in operation [2, 3]. Such systems are based on the friction forces developed by the brake shoes applied and pressed against the wheels tread. So, during the braking action, the kinetic and the potential energy (when running on slopes) are dissipated in the form of heat generated at wheel/brake blocks interface and the velocity of the train decreases accordingly.

It is to notice that all systems relying on retardation torques generated directly on the wheelset are wheel/rail adhesion dependent and therefore the maximum brake force is limited to the actual available adhesion force. In particular, the brake shoes naturally grind and clean the wheel tread, favourable

acting to improve the wheel/rail adhesion conditions. However, the severe thermal regime of the friction couple can affect and even damage both wheels and brake shoes. As important components for the traffic safety, brake blocks have to fulfil certain requirements such as a high and stable friction coefficient, independent of speed, clamping force, specific pressure, temperature and environmental condition. Low wear rate, light weight, low noise and corrosion resistance, favourable thermodynamic properties are also qualities requested in operation for such materials. Of course, affordability and acceptable costs versus performance are nevertheless to be taken into account.

Composite materials for friction brakes

Composites represent a combination of two or more components, with different properties which, put together, produce a new material that reaches characteristics which cannot be provided by any of its constituents separately or not even by their mere sum. Each component can be distinctly found in the composite, maintaining its own physical and chemical properties, but the new material makes better use of their virtues, while diminishing to some extent the effects of their deficiencies. By certain synergistic effects, the composite material gets to have improved properties when compared with the individual constituent materials [4].

Basically, the different components of composite materials have two fundamental roles: to take over the external loads (the matrix) and to transmit the bulk of external loads (the reinforcement). The reinforcement is usually a discontinuous phase that provides strength and rigidity. The individual particles of the reinforcement are surrounded and bind together by the matrix, generally a continuous phase that provides protection against external influences. In order to obtain the targeted properties and characteristics, mainly a stable coefficient of friction and acceptable wear rate, the brake friction materials are composed of four main constituents - reinforcement, binder, friction modifier and fillers - so, in the composition, one may find more than 20 components [5, 6].

The usual structural materials in composite brake blocks are fibres of metal, glass, iron powder, aluminium and copper. These components provide hardness, the necessary rigidity, strength, wear resistance, thermal stability at high temperatures and, very important, the stability of the friction coefficient for the main body [7].

Typical binder materials – mostly phenolic or modified resins, eventually with the addition of rubber - have to keep together the rest of the ingredients and to maintain the structural integrity of the whole brake block under mechanical and thermal stress.

Fillers are generally used as an extender and, in particular for brake pads, may contribute to increase braking effectiveness, mechanical durability and hardness.

	Organic composite C180 type brake blocks	Phosphoric iron type P 10 brake shoes
Ambient conditions	Temperature: -50° C ... 60° C	Temperature: -40° C ÷ 45° C
for operation	Maximum relative humidity: 80% at 20° C	Average annual relative humidity: $\leq 75\%$
Functional, mechanical and physical characteristics	Mean friction coefficient: 0.25 Density: 2.6 g/cm ³ Specific pressure ≤ 150 N/cm ² Temperature sustained: 400° C Temperature momentarily: 600° C Plastic hardness HRX: 55 Specific heat capacity: 0.92 kJ/kg K	Brinell hardness: 197 < HB < 255 Impact test conditions: - mass of striker: M = 50...150 kg - distance between supports: L = 160 mm ... length of brake shoe - height H: in respect to H · L · M = 4.8 kg · m ²

Table 1
REQUIREMENTS REGARDING BRAKE BLOCKS FOR RAILWAY
VEHICLES

Normally they are low cost minerals such as clay, calcium carbonate and barites and serve also for improving thermal and frictional stability. By using appropriate fillers, positive influences are obtained regarding the density of the brake blocks and wear resistance, with beneficial effects on cost and production. Frictional modifiers are mainly used in order to enhance frictional stability and to control the wear rates of both brake blocks and wheel running surface. The amount of alumina and silica, typical abrasive particles, increase the friction coefficient, but also the wear, so the composition has to be carefully balanced in order to satisfy two important requests: high friction levels and low wear rates [8].

Composite and cast iron brake blocks

Mechanical, physical and chemical characteristics have to meet the requirements of [9] for composite, respectively [10, 11] in the case of phosphoric iron brake blocks. Some of them are presented in table 1. Common aspects refer to consistent performance under varying environmental conditions, without being dangerous to health and environment and without affecting the security, or the safety of work.

Regarding the specifications of the chemical composition, the organic composite brake blocks consist of numerous components such as phenolic and modified resins, iron and aluminium oxides, silica, brass as typically 62% Cu - 38% Zn alloy, barium sulphate, etc. [5] in various combinations and proportions. For the brake shoes of cast iron grade P 10, the content of phosphorus must be between 0.8 ... 1.1%, the manganese content has to be lower than 1%, but higher than a limit depending on the sulphur content of the iron, while the recommended total carbon and silicon contents are also clearly specified [11].

In accordance with UIC regulations, the brake blocks for trailed railway vehicles are characterised by a standard length of 320 (single block, Bg configuration), respectively 250 mm (double block, Bgu configuration). The preferred width is 80 mm and the preferred thickness is 60 mm. It is to notice that the contact surface between brake shoes, brake holder and cotter has to prevent the fitting by mistake of brake blocks from composite materials instead of cast iron ones [9-11].

Analytical aspects and modelling

The friction coefficient between brake blocks and wheel tread is essential in designing the brake system. The influence of certain parameters, such as velocity, friction element force (normal application force) and specific pressure exerted on the wheel tread/brake shoe contact surface is decisive for the braking capacity.

In this regard, the friction coefficient in the case of composite brake blocks μ_c is quite high and almost independent of the above mentioned parameters

$$\mu_c = 0.25 \quad (1)$$

In the case of cast iron P 10 brake shoes, the friction coefficient μ_s has a multiple dependency on all of these parameters. Increasing instantaneous running speed V and normal application force N determines lower friction capacity, while decrease of the specific pressure p_s engenders higher friction coefficient. In practical calculus, there are recommended different empirical relations, e.g. [12, 13]. One of the most frequently in use is (g stands for the gravitational acceleration):

$$\mu_s(V, N) = 0.6 \cdot \frac{V+100}{5V+100} \cdot \frac{16N/g+100}{80N/g+100} \quad (2)$$

More defining are the correspondent braking characteristics, as speed dependency of the maximum braking forces for a vehicle featured with n brake blocks:

$$F_b = \mu(V, N \dots) \sum_{j=1}^n N_j \quad (3)$$

These have to be associated to the limitations given by the wheel/rail adhesion forces F_a depending on the adhesion coefficient μ_a and on the mass m of the vehicle [12, 13]:

$$F_a = \mu_a(V) \cdot m \cdot g \leq F_b \quad (4)$$

Qualitative braking characteristics for identical vehicles equipped with composite, respectively cast iron brake shoes, are presented in figure 1.

Analysing figure 1, some important aspects have to be highlighted. For the same vehicle type, characterised by a certain mass and a maximum constructive velocity V_{max} , within identical wheel-rail adhesion conditions, in respect to (4), the braking force is generally higher in the case of composite (solid red line) than of cast iron (solid black line) brake shoes. More than that, it is to observe that at maximum velocity, cast iron as friction material determines much lower brake forces than composite brake blocks and this inequality is true on a large speed domain. Taking into account that a braking characteristic is more favourable as the braking force is closer to the adhesion force, it is clearly advantageous to use composite materials.

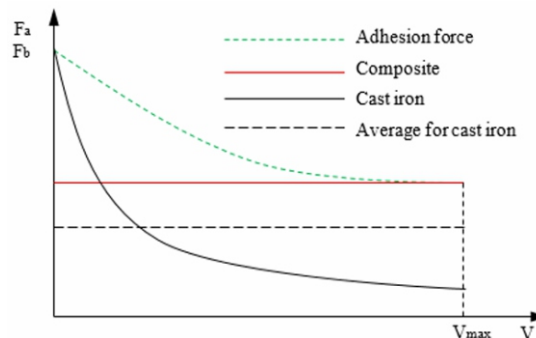


Fig. 1. Braking characteristics for composite and cast iron brake shoes

Considering the mechanical braking power as the product ($F_b \cdot V$) and the equivalent average braking force affordable by using cast iron shoes (dashed black line in fig. 1), the higher efficiency of composite brake blocks is practically revealed. At the same time, this will mean shorter braking distances and increased traffic safety.

It is however to notice that it is a low speed domain characterised by a higher efficiency of cast iron brake shoes. So, it is to expect that stopping distances have to be longer when braking actions are performed at low velocities for vehicles fitted with composite brake blocks. More than that, given the specific filling characteristics of the cylinders, the operation as slow acting braking system (type G - filling time 18-30 s) in current use on freight vehicles in long trains, is more sensitive than operating as fast acting system (type P - filling time 3-5 s), usually specific for passenger traffic or short freight trains operated with 100 km/h or more.

Numerical simulations were performed with the aim of a quantitative evaluation for the braking capacity of the same vehicle, in identical conditions, featured with composite, respectively cast iron brake blocks. The simulations were focused on the most problematic situations concerning the traffic safety: full loaded wagon, running on straight and horizontal track, respectively on important slopes. The braking process simulation programs for individual vehicles, developed under MATLAB environment (see for instance [13]), integrates the movement equation:

$$F_b(t, \dot{x}, p_c) + \frac{m_v g}{1000} w_p(t, \dot{x}^2) \mp \frac{m_v g}{1000} i + W_s = m_e \ddot{x} \quad (5)$$

There were considered x the travelled distance, F_b the braking force depending essentially on the air pressure p_c in brake cylinders and velocity [13], w_p the main specific resistance, i the declivity of the track, W_s other supplementary resistances (given by running in curves, wind etc. if case). While m_v is the vehicle's mass, the equivalent mass m_e takes supplementary into account the mechanical effects of the inertia of rotating masses [2].

Results and discussions

It was considered a typical four axles freight wagon, destined for 120 km/h maximum running speed, submitted to emergency braking action. It is featured with classical UIC air brake system [1], capable of operating both in fast acting (P type) and slow acting (G type) modes. The last case is common for long freight trains operated with less than 90 km/h. The vehicles have symmetrical brake rigging, in bilateral configuration, with two friction elements per shoe holder (2Bgu type – 32 brake shoes), as prescribed in such cases.

The main simulation data are summarised in table 2. In order to get results as accurate as possible, in the simulation programs were implemented experimental data acquisitioned on the computerized brake systems in the Laboratories of the Faculty of Transports in POLITEHNICA University of Bucharest. The air pressure evolution in brake cylinders up to the stabilisation at the maximum 3.86 bar, obtained with a KE 1c-SL air distributor, currently equipping freight vehicles in operation, is presented in figure 2.

The maximum normal forces N acting on each friction element were determined so that the braking forces respect condition (4): 17 kN/brake shoe in the case of cast iron equipment, respectively 13.95 kN/brake shoe when using composite brake blocks. By numerical simulations, there were determined the correspondent braking capacities, in terms of computed stopping distances versus initial braking

speed. The most relevant results are summarised in the diagrams presented in figure 3 for fastacting (P) mode, respectively in figure 4 for operation in slow-acting (G) mode.

Friction element type	Initial braking speed [km/h]		Slope [mm/m]	Filling time [s]		Vehicle mass [t]	
	P	G		P	G	Tare	Maxim
cast iron	120...20	90...20	0...30	3.4	22.32	25	80
composite							

Table 2
MAIN SIMULATION INPUT DATA

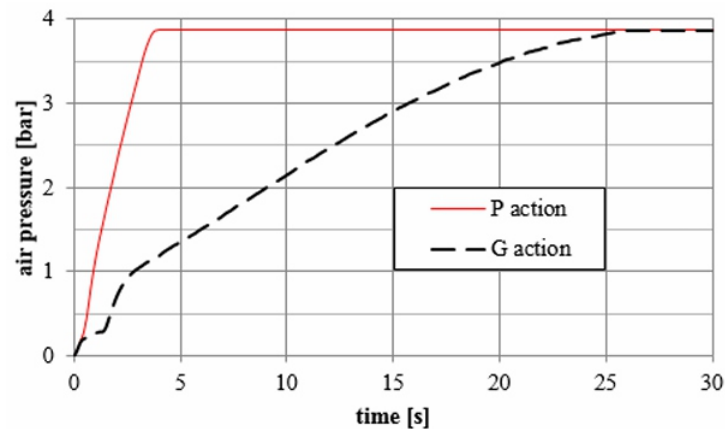


Fig. 2. Filling characteristics of brake cylinder determined experimentally

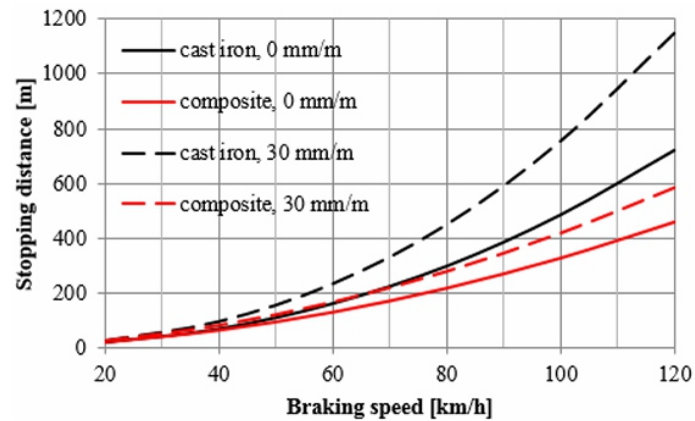


Fig. 3. Stopping distance dependency on braking speed for P mode action

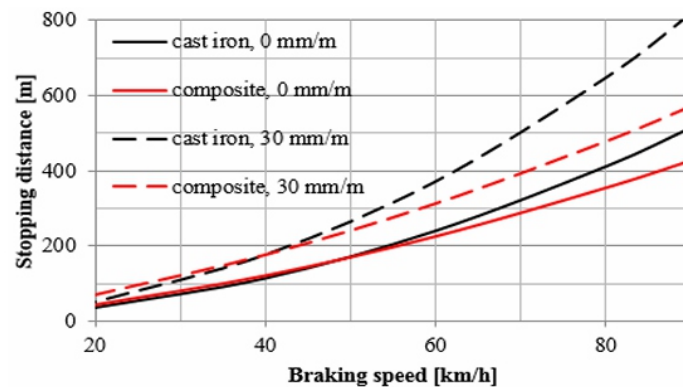


Fig. 4. Stopping distance dependency on braking speed for G mode action

Based on analysis of these diagrams, the most important aspect to reveal is that braking power is higher for composite brake blocks, even more as the initial braking speed is higher. For composite brake blocks, shorter stopping distances, up to 36%, respectively 50%, resulted for emergency braking in P mode from 120 km/h for running on horizontal, respectively on 30 mm/m slope track. If the system is set for G mode, it is still advantageous to rely on composite brake blocks, but the braking capacity is only 17%, respectively 30% higher compared with cast iron brake shoes for braking from 90 km/h in same conditions.

It is still to notice that in the case of braking actions performed at low velocities (under 40-30 km/h), the stopping distances become shorter for cast iron featured vehicles. This aspect becomes more obvious on important slopes, but it is to mention that, given the small velocities, braking distances are anyway shorter.

Relative to the normal forces acting on the friction elements, a decrease from 17kN/shoe to 13.995 kN/shoe in the case of composite brake blocks can be materialized in about 40% reduction in the diameter of the brake cylinders and a corresponding decrease in compressed air consumption. These aspects have to be also considered as contributions to a higher energetic efficiency of railway mode of transport.

Conclusions

Following the main target of the study, qualitative and quantitative evaluations of using composites instead of the classical cast iron for equipping the brake system of railway freight vehicles were presented. Considering the traffic safety as essential, the study refers mainly to the braking capacity by considering as parameter only the stopping distance, in various operational conditions.

The most important advantages of using composite brake blocks instead of the classical cast iron brake shoes can be synthesized as follows:

- noticeable increase of the braking capacity, which is more pronounced the higher the braking speed is and mainly in fast action (P) operational mode of UIC brake system;
- generally, more performing on important slopes, determining shorter stopping distances;
- smaller dimensions of brake cylinders with corresponding decrease in compressed air consumption.

As a possible drawback, the numerical simulations results indicate that for low braking actions initiated from low speeds, under 40...30 km/h, the braking capacity decreases, compared to cast iron brake shoes system. So, in operation, the recommendation in case of running with low velocities is to perform earlier and/or stronger braking actions than usual in classical cast iron equipment on rolling stock.

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Aspects of Heart Failure in Patients with Ischemic Heart Disease after Percutaneous Coronary Revascularization with Polymer-coated Drug-Eluting Stents versus Bare-Metal Stents

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ABSTRACT

Percutaneous coronary revascularization (PCR) with polymer-coated drug-eluting stents (DES) or baremetal stents (BMS) is considered the standard therapy in advanced ischemic heart disease (IHD). Despite revascularisation, many of these patients subsequently develop heart failure with reduced ejection fraction (HFrEF). We analysed 51 patients with IHD, treated by PCR and insertion of DES and/or BMS who later developed HFrEF. Patients with DES were more likely women, of younger age and a higher incidence of diabetes mellitus compared to patients with BMS who were generally men, of older age and had more frequently acute ST-elevation myocardial infarction (STEMI) as indication for PCR. Although patients with DES had more severe IHD, their EF was higher, possibly due to the benefits offered by the DES.

Keywords: ischemic heart disease, polymer-coated drug-eluting stent, bare-metal stent, heart failure with reduced ejection fraction

1. Introduction

Ischaemic heart disease (IHD) represents the most common cause of death and of HFrEF in the developed world [1]. The most effective treatment consists in a successful revascularization of the affected myocardium, realised either by PCR with insertion of stents, or by coronary artery by-pass graft (CABG) [2].

Heart failure secondary to IHD presents an increasing incidence because of the improved survival, attributed to the success of revascularisation by primary PCR in acute myocardial infarctions, but resulting often in left ventricular (LV) remodelling and chronic myocardial dysfunction. The best medical treatment of these patients represents a debated topic in the medical literature [3]. Despite best medical therapy of HFrEF according to guidelines [3], many patients remain symptomatic, with increased morbidity and mortality raising the issue of a new revascularization strategy. Currently, CABG is recommended over PCR for younger patients, with multivessel IHD and severely reduced LV function [1]. This procedure is associated with an increased perioperative risk. PCR involves a much lower risk and the development of more performant DES, treated with immunosuppressive and antiproliferative drugs, with an advanced polymer coating, could improve the evolution of these patients [4].

The aim of this study is to evidence with factors are associated with the presence of HF_rEF in patients with IHD treated by PCR and insertion of at least one stent and if there are differences between patients with DES versus those with BMS.

Experimental part

DES versus BMS

DES are considered superior to BMS for the treatment of IHD, most statistical analyses indicating lower rates of major adverse cardiac events [5, 6]. BMS consist only of a metal structure. DES consist of three parts - the stent platform, the polymer coating that binds the drug to the stent and releases drug and the drug with immunosuppressive and antiproliferative effects (paclitaxel, sirolimus and everolimus) which inhibits neointimal growth that would cause restenosis [4], (fig. 1).

One to three or more layers of polymer are used for the coating: a base layer for adhesion, a main layer that holds and elutes (releases) the drug into the arterial wall by contact transfer, and sometimes a top coat to slow down the release of the drug and extend its effect. The necessity of polymers on DES platforms is dictated by the need of an adequate amount and optimal release of the antiproliferative drugs for achieving ideal DES performance. Polymers selected to be used as a drug carrier should share following features: be biocompatible; do not interact with the drug; provide a platform for appropriate drug-eluting kinetics; behave biologically inert after the drug has been

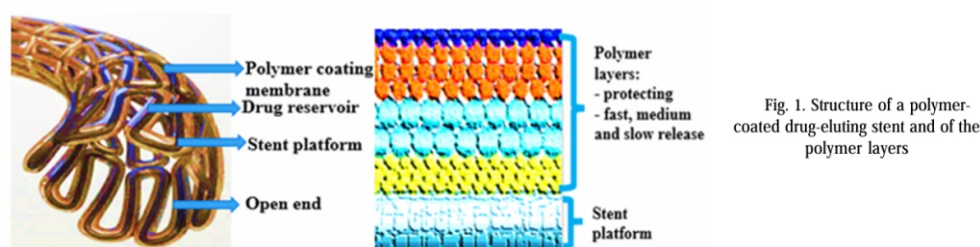


Fig. 1. Structure of a polymer-coated drug-eluting stent and of the polymer layers

Table 1
POLYMERS USED IN THE STENT COATING

Nonbiodegradable polymers		Biodegradable polymers	
Polymer	Proprieties	Polymer	Proprieties
Parylene C	Derivative of poly-paraxylylene, good barrier properties	Poly (L,D) - lactic- acid	Fully biodegradable, allows homogeneous dispersion of the drug
Poly-butyl methacrylate	Biocompatible with slow drug release kinetics	Poly-lactide-co-glycolide	Fully biodegradable due to ability of polymer crystallinity modification
Polyethylene-co-vinyl-acetate	Rapid drug-release kinetics	Poly(lactide-caprolactone)	Low biodegradability, facilitates drug diffusion

completely eluted, and be mechanically stable at longterm in the dynamics of coronary circulation milieu. Various permanent (biostable) and biodegradable polymers have been used on DES platforms with various results which are still in testing in clinical trials [7-11], (table 1).

Patients group

This study was conducted on 51 patients, aged between 50 and 75 years, mean age 63.74 ± 6.69 years, with angiographically confirmed IHD, treated by PCR and implantation of at least one stent. 28 of them were men and 23 women. Subsequently, they developed HF_rEF, treated with medication. During January-December 2018, they were either admitted for decompensated heart failure in the Cardiology Clinic or/and followed in the Ambulatory of our hospital.

They were divided in to group:

- Group A-the DES group; included 18 patients who received at least one DES during any revascularisation procedure, regardless of whether they had received another type of stent at any time;
- Group B-the BMS-group: included all patients with other types of stents except DES.

Cardiologic evaluation

The diagnostic of HFrEF was based on the presence of symptoms and clinical signs suggestive for heart failure and on the assessment of a reduced ejection fraction (EF) of under 39% by echocardiography. All echocardiographic examinations were performed with an Acuson Sequoia C 512 echocardiograph by the same echocardiographer in order to avoid inter-observer differences. On the echocardiography, after a regular exam of cardiac morphology and function, we assessed the ejection fraction (EF) of the LV by using the Simpson method (normal over 55%).

Statistical methods

Data analysis was performed using SPSS v.25 (Statistical Package for the Social Sciences, Chicago, IL, USA). Continuous variables were presented as mean and standard deviation (SD) or median and interquartile range (IQR), and categorical variables were presented as frequency and percentages. The results of the normality test (Shapiro-Wilk) showed a non-Gaussian distribution, reason why we continued to use nonparametric tests. To evaluate the proportion of stenting indication, associated conditions and risk factor in table 1 we used Fisher's exact test. To compare patients' characteristics in Table 2 we used the Mann-Whitney U test. A p value of less than 0.05 was considered to indicate a statistically significant difference.

The study was approved by the Ethics Committee of our hospital and all patients signed a written informed consent.

Results and discussions

All fifty-five patients included in our study had angiographically confirmed IHD and underwent one or more PCR with implantation of at least one stent. They were divided in two groups according to the type of stent. The main indications for PCR and stenting, associated diseases and risk factors, in both groups are illustrated in table 2 and the results of clinical and echocardiographic evaluations are presented in table 3.

On average, as compared to patients with BMS, patients with DES were younger ($p=0.004$) and more likely to be women (61.11%); they also had a higher prevalence of diabetes mellitus ($p<0.001$), systemic hypertension,

Table 2
PATHOLOGICAL CONDITIONS IN THE STUDY GROUPS

Characteristics of the study groups	Group A PCR and DES 18	Group B PCR and BMS 33	p value
Indication for stenting %			
Acute STEMI	5 (27.77%)	25 (75.75%)	0.001
Acute non-STEMI	3 (16.66%)	1 (3.03%)	0.120 - ns
Stable angina	2 (11.11%)	1 (3.03%)	0.282 - ns
Multivessel disease	8 (44.44%)	6 (18.18%)	0.057 - ns

Associated conditions and risk factors %			
Diabetes mellitus	16 (88.88%)	4 (12.12%)	<0.001
Systemic hypertension	14 (77.77%)	24 (72.72%)	0.750 - ns
CKD	8 (44.44%)	12 (36.36%)	0.394 - ns
Male gender	7 (38.88%)	21 (63.63%)	0.080 - ns
Smoking	11 (61.11%)	26 (78.78%)	0.153 - ns
Hypercholesterolemia	12 (66.66%)	11 (33.33%)	0.038
Alcohol	5 (27.77%)	10 (30.3%)	0.850 - ns

Legend: PCR - percutaneous coronary artery revascularisation; DES - drug eluting stent; BMS - bare-metal stent; STEMI - ST-elevation myocardial infarction; CKD - chronic kidney disease. Fisher's exact test

Table 3
CLINICAL CHARACTERISTICS OF THE STUDY GROUPS

Clinical characteristics	PCR and DES 18	PCR and BMS 33	p value
Age (years)	60 (55-65)	68 (60-70)	0.004
BMI (Kg/m ²)	27 (24.75-29.45)	27.5 (25-29)	0.906 - ns
Heart rate (b/min)	65 (60-70)	65 (60-70)	0.902 - ns
Number of stents	1 (1-2)	1 (1-1)	0.417 - ns
Time since last stenting (months)	12 (10-14.25)	19 (15.5 -21)	<0.001
Repeated PCR	5 (27.77%)	6 (18.18%)	0.417 - ns
LVEF (%)	27.04 (22.81-31.91)	23.72 (21.7-25.64)	0.056 - ns

Legend: PCR -percutaneous coronary artery revascularisation; DES - drug eluting stent; BMS - bare-metal stent; BMI - body mass index; LVEF-left ventricular ejection fraction. Mann Whitney U test.

hypercholesterolemia ($p=0.038$) and renal dysfunction. Multivessel disease and stable angina were the main indications for PCR. 27.77% of patients with DES had repeated PCR, and a higher number of stents, comparing to those with BMS. Patients with BMS were older, were more likely to be men (63.63%) and more often had primary PCR for acute STEMI as indication for stenting (75.75%). All patients included in our study had HFrEF. Those from group A, with PCR and DES, had a slightly higher EF, compared to the ones from group B, thus the difference was not statistically significant ($p=0.056$). This aspect could be explained by the fact that in the first group there were younger patients, but, on the other hand, they were more likely to have multivessel disease and diabetes mellitus, both conditions associated with HFrEF.

88.88% of our patients with DES were diabetics. In a study regarding outcomes of PCR with stenting in diabetic patients [12] concluded that the consequences of PCR are less favorable in diabetics compared with non-diabetic patients. New angioplasty techniques, such as DES, could improve the results of PCR in diabetic patients. Other authors debate upon the effectiveness of the new generation of DES on the LV systolic function [13, 14] and evidenced an improvement of LVEF after the use of Everolimus-eluting stents. Similar results were reported by Yee et al [15] in patients with severely reduced EF who underwent PCR with DES; however patients undergoing CABG showed greater gains in LVEF [16,17]. Other authors debate upon similar results in patients with multivessel disease [2, 15].

The prevalence of HFrEF and the outcomes of patients treated with DES versus BMS were analysed in several studies. For example, Lagerqvist in a study realised by using data from the Swedish Coronary Angiography and Angioplasty Registry, analyzed clinical particularities and mortality at 3 years of 6033 patients treated with DES and of 13,738 with BMS and concluded that the mortality was higher in patients with DES [5].

Several meta-analysis provides evidence that revascularization, irrespective of modality, compared with medical therapy, significantly improves survival and other outcomes in patients with EF $\leq 40\%$ and

significant CAD [1, 18]. CABG seems to be a more favorable option [18], although a network meta-analysis of 100 trials with 93 553 patients reported that PCR with new-generation DES resulted in better outcomes compared with initial medical treatment [1].

Conclusions

Although patients with HFrEF treated by PCR and DES had more severe IHD, with multivessel disease and a higher incidence of diabetes mellitus compared to those with BMS, EF was higher in the first group, possibly due to the benefits offered by the polymer-coated stents.

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Comparative Study on Plastic Materials as a New Source of Energy

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ABSTRACT

The pyrolysis can be an attractive way to reduce the plastic waste and, in the same time, to obtain alternative conventional fuels. In this respect, four polymers (low-density polyethylene, high-density polyethylene, propylene and polystyrene) were used in the pyrolysis process. The experiments were carried out by using an in-house plant, which allowed a maximum test temperature of 450 °C. The product oil and the derived gas from the pyrolysis process were evaluated using different techniques, such as elemental analysis (EA), calorimetry, gas chromatography (GC), gas chromatography coupled with mass spectrometry (GC-MS). Furthermore, for a comparative study two catalysts, zeolite and lignite, were also used for the pyrolysis process, in order to observe their influences on the final products. The higher heating value obtained for the oil was in the 40.17-45.35 MJ/kg range, acceptable for the use of these oil as an alternative fuel for diesel engine. Also, the sulphur content from the obtained oil does not cause environment problems, being lower than the allowed limits (10 mg/L). In addition, the pyrolysis derived gas was rich in hydrocarbons, conducting to a high calorific value, in the 73.42 – 121.18 MJ/kg range.

Keywords: catalyst, lignite, plastic, pyrolysis, waste

1. Introduction

Nowadays, with a world production of 335 million tonnes in 2016, the plastics play an important role in various areas such as, food, chemical, construction, automotive, agriculture, electronic and fashion, due to their properties: easier processability, durability or corrosion resistance. The last two properties turn the advantages of these materials into a serious environmental problem, because the plastic waste accumulation and their low degradability property resulted in the occupation of a large storage area [1, 2].

In Europe, comparing with the statistics reported in 2012, in 2016 the plastic waste amount increased with approximately 2 million tons, from 25 million tons, while the percentage sent to the landfill decreased from 38% to 27.3%. In the same time, in the case of recycle and energy recovery the statistic was better, the percentages increasing from 26% and 36% to 31.1% and 41.6%, respectively [2, 3].

The incineration is not an environment solution to decrease the plastic waste quantity, due to carbon dioxide release into atmosphere, but the pyrolysis can be. Many researchers turned their attention to waste plastic pyrolysis, highlighting the advantages of this process by converting the waste into high calorific power oil or gaseous products [4-8]. Their studies were focused on the pyrolysis of i) virgin plastic materials, ii) plastic wastes and co-pyrolysis of plastic-wood composite (woody biomass), using different reactor configurations [3, 9-15]. The obtained oil products can be comparable with petroleum [16], in terms of heat value and emission factor, thus being tested in diesel engines. Furthermore, the by-product gas presents also a high heat value and the residue is obtained in low quantity. A serious drawback in the plastics pyrolysis is the requirement of high temperature, but this can be an energetically sustainable process considering the high heat values of the oil and gas products [17, 18].

Various parameters, such as temperature, time and catalyst, influence the quality of gaseous and liquid products resulted from the pyrolysis process [4-8].

It was demonstrated that the most important pyrolysis parameter, the temperature, influences the properties of the obtained oil and gaseous products, due to thermally degrading polymer chain [8]. Thus, at a temperature of about 600 °C it was obtained a liquid with higher content of aromatic hydrocarbons than at a temperature of about 450 °C. Also, it was evidenced an optimum reaction time interval, between 15 and 30 min, when a total conversion is achieved [8]. The use of various catalysts is expected to reduce the required temperature of plastic degradation but, on the other hand, their use can increase the process cost. Therefore, the introduction of a cheaper catalyst into the process (found in abundance in nature, such as natural zeolite), as an alternative for the commercial catalysts (such as zeolite-Y, ZSM5, Al-MCM-41) can be the key to reduce the costs [19-21].

Taking into account all the above-mentioned aspects, this study focused on the investigation of the pyrolysis process of virgin plastics (obtained from low-density polyethylene, high-density polyethylene, polypropylene, and polystyrene) with and without catalysts (lignite and zeolite), in order to observe the difference of pyrolysis products.

Experimental part

Materials and methods

The used polymers were commercially available products, such as: low-density polyethylene (LDPE) and polypropylene (PP) were procured from SABIC (Riyadh, Saudi Arabia) and polystyrene (PS), high-density polyethylene (HDPE) were purchased from Versalis S.p.A (Santo Donato Milanese, Italy).

One of the used catalysts was lignite, due to the high content of lignin. This was purchased from a local mine (Berbesti mine, Valcea county, Romania). Another type of catalyst, the LMS (Linde Molecular Sieves) zeolite, was obtained from Linde Romania (Bucharest, Romania).

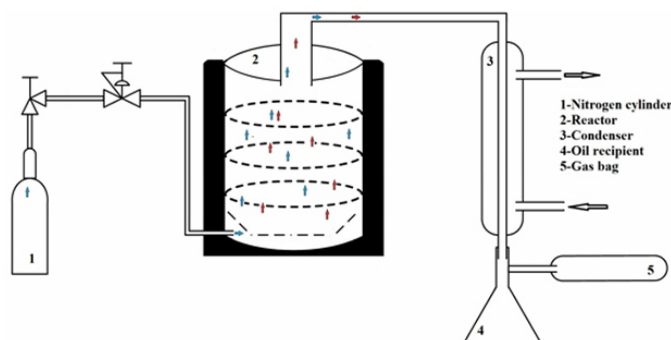


Fig. 1. Pyrolysis experimental setup

High purity nitrogen (99.999% Vol) was purchased from SIAD Romania (Bucharest, Romania).

The pyrolysis products were examined using an EA 2000 Flash elemental analyser (Thermo Scientific, Waltham, MA, USA) in order to obtain information about the gaseous emissions resulted after the combustion of liquid oil product. The analyser had a thermal conductivity detector (TCD) and two chromatographic columns (SM5A and Porapack Q) purchased from Sigma Aldrich (Steinheim, Germany).

The heat value, the most important quality characteristic, was established through an IKA 5000 calorimeter (IKA, Staufen im Breisgau, Germany).

For the analysis of non-condensable gases, a Varian CP 3800 gas chromatograph (Varian Instruments, Palo Alto, CA, USA) was used. It was equipped with thermal conductivity and flame ionization detectors and three columns, such as CP-Al2 O₃ /KCl (25 m x 0.32 mm internal diameter), CP-PoraBOND Q-HT (27.5 m x 0.32 mm internal diameter), CP-Molsieve 5 Å (50 m x 0.53 mm internal diameter) (Agilent Technologies Inc., Santa Clara, CA, USA). The chromatographic method was previously developed [22].

Furthermore, a Varian 450 gas chromatograph (Varian Instruments, Palo Alto, CA, USA) coupled with a Varian 240 mass spectrometer (Varian Instruments, Palo Alto, CA, USA) was used for the qualitative analysis of the pyrolysis liquid oil. The chromatograph was equipped with a Thermo Scientific TG-WAXMS capillary column (60 m x 0.32 mm x 0.25 µm) (Thermo Scientific, Waltham, MA, USA) for the separation of oil compounds and a split injection valve (1:10 split ratio) heated at 150 °C for volatile compounds. Also, this chromatographic method was described in a previous work [23].

Experimental setup

The pyrolysis process was carried out using the experimental setup presented in figure 1. The installation consists in a pyrolysis reactor made from stainless steel with an internal diameter of 100 mm and a height of 450 mm. Inside the reactor there are placed two stainless-steel supports, one for the tested materials and the second one for the catalyst. The reactor is isolated with basaltic wool to maintain a constant temperature and it is thermostated through a ceramic bracelet that ensure a temperature up to 450 °C. Prior to the experiments, a nitrogen flow of about 100 mL/min was provided by a gas cylinder in order to ensure an inert atmosphere.

Also, the reactor is equipped with a water condenser, in order to separate the products into condensable and noncondensable products, which were collected in an oil recipient and a gas bag, respectively.

The tests were performed using, in the first step, the polymers (PP, PS, HDPE and LDPE) without the catalysts. The necessary polymer quantity was 55 g and the temperature ranged between 24 and 450°C, with a step increment ratio of 50 °C/5 min. After the maximum temperature was reached, this was held for 30 min. In the second step, the polymers in presence of catalysts (zeolite or lignite) were used with a 1/10 (zeolite/polymer) ratio, in order to observe the changes in the quality products. The catalysts were placed above the polymer sample in their support to offer time and space for a better interaction. The pyrolysis processes were carried out in the same conditions and every experiment was repeated for 4 times and the results were averaged.

Results and discussions

The effect of the plastic types and also of the catalyst on the pyrolysis product yields (oil-PPO, gas-PPG and wastePPW) is presented in figure 2. It can be seen that the highest liquid fraction was obtained from the PS in the presence of lignite (79 %), followed by pyrolysis without catalyst of PS (76 %), PP (53 %) and LDPE (41%). On the other hand, the lowest liquid fraction resulted from the LDPE (38%) and HDPE (40%) pyrolysis with zeolite. The addition of the zeolite catalyst conducted to the decrease of the liquid fraction for all the plastic samples, the most noticeable difference being observed for PS pyrolysis. However, there were not observed significant differences once the lignite was used as catalyst. Liquid oil products obtained from LDPE, HDPE and PP pyrolysis without and with catalysts showed mainly the presence of paraffinic and olefinic groups (fig. 3). The aromatic compounds ratio is insignificant, being in the 6.50- 10 % range. The catalysts did not significantly influence the oil content of these polymers.

Instead, the PS pyrolysis oil is dominated by aromatic and paraffins compounds, the content of olefins being negligible. The higher ratio of aromatic compounds was due to its high stability and it was found for the PS / Lignite oil (45.15 %), followed by the PS / Zeolite oil (44.18 %) and the PS oil (42.20 %). Also, in the case of the oil obtained from the PS pyrolysis with catalysts, no changes were noticed. The data obtained from the elemental and calorimetric analysis of the pyrolysis oil (elemental content, higher heating value – HHV and emission factor-EF) are presented in table 1 [24-26]. The sulphur contents in the samples are below the method quantification limit (10 mg/L), in this respect, the possibility of sulphur compounds formation is very reduced, making the pyrolysis oil environmental friendly. Also, the nitrogen content is very low, and it was slightly influenced by the catalyst presence. On the other

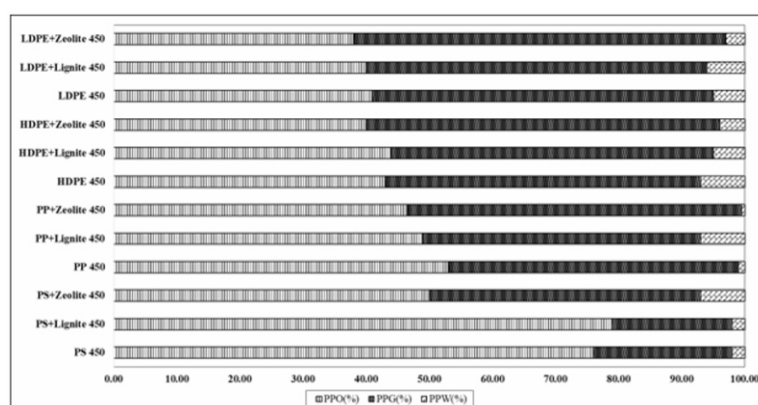


Fig. 2. Effects of the plastic type and catalyst on the product yields

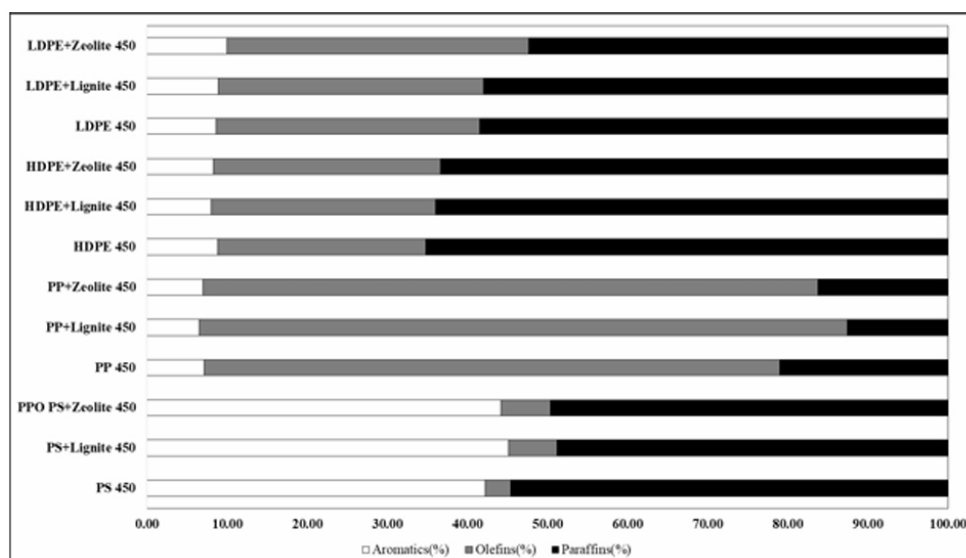


Fig. 3. Comparison of volume fraction obtained using lignite and zeolite catalysts

hand, the highest contents of carbon and hydrogen were 87.92 wt.% and 13.24 wt.% for the oil obtained from PS and HDPE, respectively, without catalysis. The oxygen content was very low in the oil obtained from PS pyrolysis, namely 3.90 wt.%, and it increased to 9.26 wt.% and 9.09 wt.% due to zeolite and lignite, respectively. The highest oxygen content was obtained in PP pyrolytic oil, 19.39 wt.%, but the presence of zeolite and lignite conducted to its decrease to 16.07 wt.% and 13.95 wt.%, respectively. The oil higher heating values (HHVs) were in the 40.1745.35 MJ/kg range, showing their potential as an alternative fuel. The zeolite slightly increased the higher heating value of the LDPE pyrolytic oil. Also the same trend was observed in the case of oil obtained from PS pyrolysis with both catalysts.

Noticeable emission factor value was registered for the oil produced from PS. The use of zeolite and lignite conducted to the improvement of its emission factor. The gas chromatography results for the gas samples are presented in table 2 and table 3. Furthermore, a typical chromatogram of the obtained PPG from PS pyrolysis is presented in figure 4.

Among the significant quantities of methane, ethane, ethylene, propane, propylene, n-butane, neopentane, in the pyrolysis derived gases, there were also presented permanent gases such as hydrogen, carbon monoxide and carbon dioxide (table 2 and table 3). The gas composition depended on the composition of the tested material, therefore the styrene and toluene are the main components of PS.

After the identification and quantification of the components from the pyrolysis gases, the higher heating value and the emission factor were calculated and summarized in table 4 [27].

The gases resulted from the pyrolysis process had significant higher heating values. The gas produced from the PS pyrolysis had the highest HHV (121.18 MJ/m³) and the use of lignite in its pyrolysis conducted to the highest EF (123.71 t/TJ).

The use of catalysts conducted to a decrease of the heat value and to an increase of the emission factor, excepting the case of using lignite for PP pyrolysis.

According to the values presented in table 4, the resulting gas has the potential to be used in the pyrolysis or the turbine process.

Feed material*	N (wt.%)	C (wt.%)	H (wt.%)	S (wt.%)	O (wt.%)	HHV (MJ/kg)	EF (t/TJ)
HDPE	0.34	80.71	13.24	0.005	5.71	44.50	67.25
LDPE	0.46	78.69	12.93	0.005	7.915	44.22	65.98
PP	0.3	68.83	11.47	0.005	19.395	44.63	57.18
PS	0.31	87.92	7.86	0.005	3.905	40.17	81.25
HDPE / Zeolite	0.13	71.75	11.49	0.005	16.63	44.29	60.06
LDPE / Zeolite	0.26	77.47	12.85	0.005	9.415	45.35	63.32
PP / Zeolite	0.25	71.72	11.95	0.005	16.075	43.64	60.95
PS / Zeolite	0.23	83.01	7.49	0.005	9.265	41.26	74.66
HDPE / Lignite	0.46	73.40	9.13	0.005	17.01	42.99	63.33
LDPE / Lignite	0.17	67.63	11.37	0.005	20.825	44.49	56.37
PP / Lignite	0.49	76.16	9.39	0.005	13.955	42.62	66.29

*The pyrolysis temperature was 450°C for all feed materials

Tabel 1
ELEMENTAL COMPOSITION, HIGHER HEATING VALUE AND
EMISSION FACTOR OF PPO

Composition (%Vol)	HDPE	LDPE	PP	PS
Methane	3.93	4.26	6.56	0.31
Ethylene	8.83	11.07	7.25	2.09
Ethane	5.17	4.23	1.84	5.41
Propane	19.54	19.32	4.53	1.77
Propylene	20.03	17.20	43.03	3.79
i-Butane	0.15	0.23	0.41	0.10
n-Butane	12.17	13.97	1.75	1.50
neo-Pentane	10.94	13.79	10.72	0.58
i-Pentane	0.24	-	-	1.68
n-Pentane	3.74	0.24	19.91	2.95
n-Hexane	1.42	1.26	0.22	5.55
2,3-Dimethylbutane	4.80	-	0.96	10.28
2-Methylhexane	-	-	0.64	4.88
3-Ethylpentane	-	-	-	-
3-Methylhexane	-	-	-	-
2,2,3-Trimethylbutane	-	-	-	-
Methylcyclohexane	2.04	-	-	-
n-Heptane	-	-	-	-
Benzene	-	-	-	-
i-Octane	-	-	-	-
n-Octane	-	-	-	-
Toluene	-	-	-	27.11
Styrene	-	-	-	23.77
Hydrogen	2.19	1.97	0.57	0.57
Carbon monoxide	0.65	3.41	0.37	0.37
Carbon dioxide	4.16	0.64	1.25	1.25

Table 2
COMPOSITION OF DERIVED GAS FROM NON-CATALYSED PLASTIC PYROLYSIS

Table 3
COMPOSITION OF DERIVED GAS FROM CATALYSED PLASTIC PYROLYSIS
COMPOSITION OF DERIVED GAS FROM CATALYSED PLASTIC PYROLYSIS

Composition %Vol	HDPE/ zeolite	LDPE/ zeolite	PP/ zeolite	PS/ lignite	HDPE/ lignite	LDPE/ lignite	PP/ lignite	PS/ lignite
Methane	3.93	6.55	6.76	0.10	14.59	7.11	18.65	3.00
Ethylene	8.84	6.81	9.10	10.54	12.97	11.75	10.01	9.25
Ethane	5.18	13.60	1.32	1.51	24.81	6.88	11.33	17.68
Propane	19.57	19.01	8.55	1.30	5.16	18.32	3.40	1.85
Propylene	20.07	19.93	40.65	2.15	29.37	18.83	29.59	12.43
i-Butane	0.15	0.34	0.97	1.00	0.11	0.27	0.63	0.10
n-Butane	12.19	10.83	2.37	2.41	1.63	10.20	0.34	0.46
neo-Pentane	10.95	7.73	11.94	1.70	0.07	11.21	16.21	2.64
i-Pentane	0.24	0.01	0.20	0.27	0.02	1.01	2.31	0.05
n-Pentane	3.75	0.85	13.54	2.57	3.44	0.38	1.53	1.07
n-Hexane	1.42	3.12	0.12	3.57	0.04	0.60	0.13	0.15
2,3-Dimethylbutane	4.81	3.89	0.56	0.56	-	-	0.01	1.83
2-Methylhexane	-	0.74	1.12	0.25	-	-	0.74	0.25
3-Ethylpentane	-	-	-	-	-	-	-	-
3-Methylhexane	-	-	-	-	-	-	0.46	0.55

Table 3
CONTINUED

2,2,3-Trimethylbutane	-	-	-	0.34	0.29	-	0.08	0.82
Methylcyclohexane	2.05	-	-	0.32	-	-	1.19	0.31
n-Heptane	-	-	-	0.10	-	-	-	0.31
Benzene	-	-	-	29.26	-	-	-	2.95
i-Octane	-	-	-	-	-	-	-	0.45
n-Octane	-	-	-	0.02	-	-	-	0.03
Toluene	-	-	-	2.26	-	-	-	0.29
Styrene	-	-	-	36.15	-	-	-	40.01
Hydrogen	2.19	4.59	0.96	2.23	3.76	3.63	1.37	2.49
Carbon monoxide	0.65	0.72	0.85	0.93	0.94	2.33	1.20	0.61
Carbon dioxide	4.17	1.28	0.99	0.44	2.80	1.24	1.41	0.43

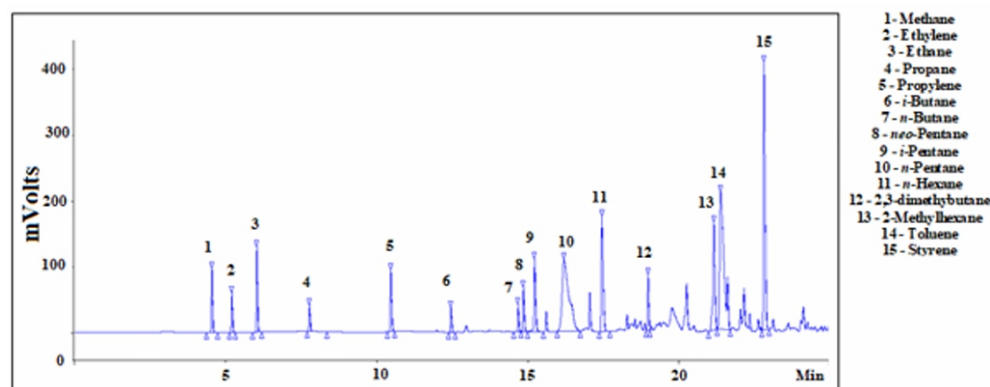


Fig. 4. Typical GC-FID chromatogram for the gas derived from PS pyrolysis

Feed material	HHV, at 0 °C (MJ/kg)	EF (t/TJ)
HDPE	99.83	69.44
LDPE	99.46	69.62
PP	105.04	70.11
PS	121.18	95.53
HDPE / Zeolite	92.09	70.19
LDPE / Zeolite	93.03	69.69
PP / Zeolite	100.77	70.39
PS / Zeolite	105.01	112.23
HDPE / Lignite	73.42	83.59
LDPE / Lignite	92.57	70.02
PP / Lignite	92.64	68.66
PS / Lignite	76.46	123.71

Table 4
HIGHER HEATING VALUE AND EMISSION FACTOR
OF DERIVED GAS FROM PYROLYSIS PLASTIC

Conclusions

This study evaluated the pyrolysis process of various plastics in the presence of zeolite or lignite as catalysts, in terms of product yields and composition, higher heating values and emission factors. The results shown that the introduction of zeolite in the pyrolysis processes affected the oil fraction by decreasing it. The lowest oil fraction was obtained for LDPE pyrolysis in the zeolite presence (38%) and the highest oil fraction was obtained from PS pyrolysis in the presence of lignite (79%). Significant contents of aromatic compounds were found in the oil produced from PS with and without catalyst, due to its high stability. The highest ratio of aromatics was observed in the oil resulted from PS pyrolysis in the presence of lignite (~45 %). The low sulphur content (under the European legislation limit for diesel fuels) make the pyrolysis oil an environmentally friendly alternative for conventional fuels.

The HHV for the resulted oils varied in the 40.17-45.35 MJ/kg range. Furthermore, the derived gases presented also significant heat values, between 73.42 – 121.18 MJ/m³.

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The Advantages of Bioresorbable INION® Implants in Traumatology Design, polymer composition and preliminary results

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ABSTRACT

Some disadvantages of traditional metallic implants used in orthopedics and traumatology prompted the development of bioresorbable polymer devices. The aim of this experimental study is to emphasize the characteristics of INION® resorbable implants (regarding design and polymers compositions), as well as to evaluate the results when using these innovative implants in two trauma cases. The polymers used in manufacturing INION® devices (Trimethylene Carbonate/TMC; L-Polylactic acid/LPLA; D,L Polylactic acid/ DLPLA; Polyglycolic acid/PGA) degrade in alpha-hydroxy acids, gradually losing their hardness in 18-36 weeks with a complete bioresorption of 2-4 years. The clinical cases demonstrated the advantages of INION® plates (adapted shape, low profile, polyaxial screws, acceptable strength) or pins (allowing the alignment and fixation of fracture, no migration). Among our patients, we found excellent results concerning the maintaining of primary reduced fracture, active range of motion, minimal pain with improving everyday comfort, no tissue or implant complications. Bioresorbable fracture fixation INION® devices are a viable alternative to traditional metallic implants, offering same significant advantages over them: the avoidance of long-term interference with gliding structures, keeping their strength long enough to support bone healing, no need to remove the implants, less pain, radiolucency, elimination of stress shielding and a lower risk of complications.

Keywords : bioresorbable, polymers, bioresorption, polyaxial screws, stress shielding.

1. Introduction

Internal fixation devices in orthopedic surgery such as plates, screws, pins, staples and suture anchors

manufactured from stainless steel, titanium or other materials have been used for many years. [1]. However, despite their global use, some complications or disadvantages were identified such as longterm migration, deterioration of the osteosynthesis material, reaction to the osteosynthesis material, interference with standard and MRI imaging techniques, stress shielding with bone resorption and weakening, growth restriction in young patients, necessity of elective removal of implants after fracture healing [2-4]. One of the challenges related to medical research is the manufacturing of some biomaterials (biodegradable and bioresorbable) with the necessary characteristics to help with healing of various medical pathologies [2,5]. The first biodegradable material used for sutures was collagen which degraded proteolytically and disappeared due to phagocytosis, causing a local inflammation of the tissue [6,7]. Many macromolecular compounds are biodegradable but few of them have the necessary properties to be used as internal bone fixation devices. The most used materials in medical practice due to their excellent biocompatibility with the human body are polyglycolic acid (PGA), polydioxanones (PDS) and polylactic acid (PLA) [8-10].

The characteristic of an ideal bioresorbable material must be: reproducible synthesis, versatility (amendable to a variety of polymer processing techniques) retaining sufficient strength over the time, no inflammatory reactions that necessitate removal [2]. Bioresorbable implants are increasingly used in trauma, orthopedic and cranio-maxillofacial surgery [2, 3, 11-13]. The aim of this experimental study is to emphasize the characteristics of INION® resorbable implants (regarding design and polymers compositions), as well as to evaluate the results when using these innovative implants in two trauma cases.

Experimental part

INION® bioresorbable plates and pins

The INION® bioresorbable plates and pins are preferable in complex fractures of the proximal and distal humerus, fractures of peroneal malleolus, fractures of the forearm, fractures of the distal radius, knee osteochondral lesions, surgery of the forefoot and hand, fixation of bone grafts or bone substitutes [3, 11, 13-16]. Their characteristics comprise: the possibility to cut the plates at the necessary length and shape depending on the patient's anatomy, the possibility of "low profile" mounting by cutting the heads of the screws, the possibility of inserting some polyaxial screws as well as radiotransparency (fig. 1). [17] The advantages of the bioresorbable plates compared to classic plates are the possibility to be used in the most difficult anatomical cases, they have a low risk of irritation of tissues and allow the complete visualization of the fracture. The polymers used in manufacturing the plates, screws and pins (Trimethylene Carbonate/TMC; L-Polylactic acid/LPLA; D,L Polylactic acid/DLPLA; Polyglycolic acid/PGA) degrade in alpha-hydroxy acids, gradually losing their hardness in 18-36 weeks with a complete bioresorption of 2-4 years [18,19].

The INION® bioresorbable pins allow the alignment and fixation of fractures (forefoot, wrist or radial head fractures), osteotomies, arthrodeses or bone grafts in the presence of the necessary additional immobilizations (other rigid fixations, cast). Regarding their advantages, the pins do not migrate externally, have a lower risk of infections and are more comfortable for the patients. Although according to biomechanical tests, the Kirschner pins are 16 N (equivalent of 1.6 kg) more firm than the bioresorbable pins, from a clinical point of view, they are similar [18-19].

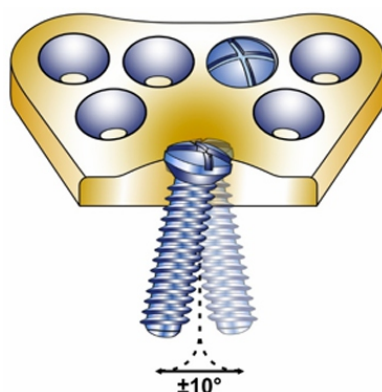


Fig. 1. The bioresorbable INION® plates allow the insertion of polyaxial screws (the screw position can be changed with 10° in any direction inside a solid cone); Adapted image from [18,19]

Synthesis of polymers for application in INION® bioresorbable devices

A polymer is a substance consisting of molecules with a high molecular mass formed from a high number of small identical molecules called monomers [20-21]. The lactic acid (acid 2-hydroxipropionic) is a monomer consisting of 2 enantiomers (L and D), considered to be the monomer with the highest potential in chemical conversions due to the carboxylic and hydroxylic group (fig. 2)[21-24].

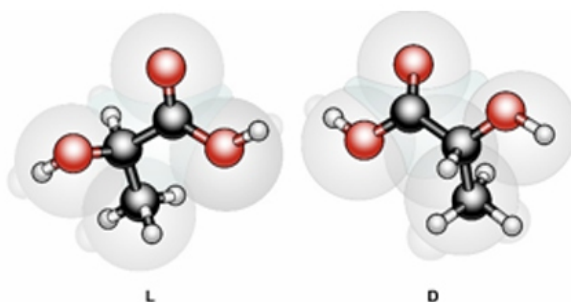


Fig. 2. L-and D- Lactic acid. Adapted image from [21]

Obtaining lactic acid by fermentation differs depending on the bacteria type used. In the heterofermentative process by hexose equimolar quantities of carbon and ethanol are produced while in the homofermentative process via the hexoses metabolism only lactic acid is produced. Due to its features, the lactic acid may protrude through the lipid membrane serving as an energetic sublayer and may enter in cells via the protein transport system, the monocarboxylate transporter (MCT). [21] In the cell, the lactic acid is transformed in glucose serving as an energetic and protecting layer against the damages generated by the free radicals due to its anti-oxidizing properties [21,23-25]

The polylactic acid is a chiral polymer produced by processing and polymerization of lactic acid monomers and is formed from asymmetrical carbon atoms with a helicoid structure. The term polylactic acid represents a family of polymers: pure poly-L-lactic acid (PLLA), pure poly-D-lactic acid (PDLA) and poly-D,L-lactic acid (PDLLA). Depending on the composition of L-enantiomers, the polylactic acid can be crystalized in three forms (α , β , and γ) [21,26-29] The polymerization process from lactic acid to polylactic acid can be made through different methods including: polycondensation,

ring opening polymerization and directly by azeotropic dehydration or enzymatic polymerization (fig. 3)[21,30]

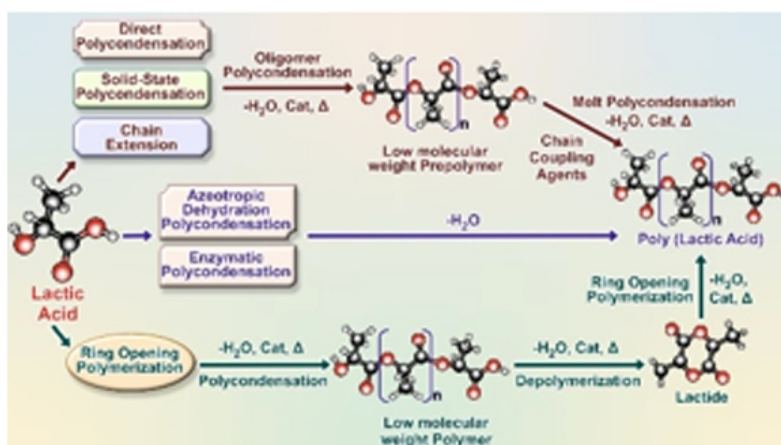


Fig. 3. Synthesis methods for Poly(lactic acid) .Adapted image from [21]

Properties of polymers

The crystallinity and properties of the polylactic acid largely depend on the stereochemistry and thermal history. The polylactic acid with a content of over 90% pure poly-L-lactic acid (PLLA) tends to be crystalline compared with the amorphous aspect of the polylactic acid with an inferior pure optical content. The melting temperature and the glass transition temperature of the polylactic acid decrease together with the level of poly-L-lactic acid in the composition. The physical characteristics of the polylactic acid such as density, thermal capacity and mechanical capacity depend on the transition temperatures [21, 29, 31-32].

The glass transition temperature is one of the most important parameters since the changes in the mobility of the polymeric chain occur at and over this temperature (T_{table 1})[21, 31-33]

Table 1
PROPERTIES OF LACTIC ACID POLYMERS ADAPTED IMAGE FROM [21]

LACTIC ACID POLYMERS	DENSITY (G/CM ³)	MELTING TEMPERATURE (°C)	GLASS TRANSITION TEMPERATURE (°C)
PLLA	1.290	173 – 178	55 – 80
PDLLA	1.25	120 – 170	43 – 53
PDLA	1.248	120 – 150	40 – 50

Resorption of bioresorbable implants

The degradation of the polylactic acid takes places mainly by hydrolysis after months of exposure to humidity. The breaks of the non-enzymatic chains of the ester links lead to a gradual decrease of molecular weight until the molecular weight of the lactic acid and oligomers allows their metabolism by microorganisms in carbon dioxide and water [21, 34-36].

The materials used in INION® bioresorbable implants are amorphous and degrade in vivo by hydrolysis and later on they are metabolized by the body in CO₂ and H₂O. The degradation profiles were adapted in order to assure initial stability and then the progressive charging of the bone in order to stimulate regeneration. The implants gradually lose their resistance after 18-36 weeks in vivo with a complete resorption in 2-4 years [18,19].

Clinical cases

Case 1

A 36 years old female with polytrauma and a right distal radius fracture; open reduction and internal fixation with a bioresorbable INION® plate and screws is performed (fig. 4).



Fig. 4.A-H Osteosynthesis with a INION® resorbable plate for a distal radius fracture A.Initial radiographs of the wrist; B. Postoperative control radiographs with implant radiolucency, good reduction and screw holes visualization; C. Postoperative control radiographs at 3 months; Fracture healing, implant radiolucency and holes visualization D. Intraoperative image with reduced distal radius fracture site; E. Aspect of the INION® bioresorbable plate; F. Intraoperative plate positioning; G - H Insertion of the bioresorbable polyaxial screws;

Case 2

A 18 years old patient with a trauma due to falling from the same level. He is admitted with the diagnosis of bilateral radial head; open reduction and internal fixation with INION® bioresorbable pins is performed on the right side (fig. 5).



Fig. 5A-J - Osteosynthesis with INION® resorbable pins for a radial head fracture;A - B - Right radial head fracture;C -D -Left radial head fracture;E - Intraoperative image within insertion of the INION® bioresorbable pins; F -G - Postoperative radiographs with good reduction of the articular fracture and radiolucency of the pins; H J- Postoperative CT with 3D reconstruction; good reduction and visualization of the tip of the pins

Results and discussions

Among our patients operated with INION® bioresorbable implants, we found excellent results concerning the maintaining of primary reduced fracture, active range of motion, minimal pain postoperative with improving everyday comfort, no tissue or implant complications.

The most common biomaterials used in medical practice due to their excellent compatibility with the human body are polyglycolic acid (PGA), polydioxanone acid (PDS) and polylactic acid (PLA) [8-10]. The crystallinity and characteristics of polylactic acid depends mostly on stereochemistry and thermic history (melting temperature and glass transition temperature) as well as the level of poly-L-lactic acid in its composition. Polylactic acid degradation occurs mainly by hydrolysis after months of exposure to moisture. The fracture of the nonenzymatic chains of ester linkages lead to a gradual decrease in molecular weight until molecular weight of lactic acid and oligomers allow their metabolism by microorganisms into carbon dioxide and water [33, 3536].

INION® bioresorbable implants made of Trimethylene Carbonate TMC, L-Lactide LPLA and D,L-Lactide DLPLA, degrade in vivo by hydrolysis, subsequently being metabolized by the organism in CO₂ and H₂O. Degradation profiles were adapted to provide initial stability and then progressive bone loading to stimulate regeneration. The implants gradually lost their resistance after 18-36 weeks in vivo with complete resorption between 2 and 4 years [18-19]. The studies showed the fact that the healing time in case of bioresorbable implants is almost equal with that of the classic implants. With a success rate of 96.88%, besides the excellent biocompatibility with the body, the bioresorbable implants have the advantages that they do not irritate the surrounding tissues, a secondary surgical intervention is not necessary for the ablation of the osteosynthesis material, they allow micro movements at the fracture focus level favoring a faster consolidation and healing. Although the bioresorbable implants are more expensive, the final price is lower compared with classic implants which need two surgical interventions [34, 3738].

Previous experience and a significant learning curve is mandatory for obtaining the best results with bioresorbable implants [3]. At the same time, some complications can be attributed to the bioresorbable implants such as a failure rate of the internal fixation device of 1.2%, an infection incidence of 1.7% and an incidence of the aseptic inflammation which needs surgical drainage of 7.8% [30, 37-38]. Today there is a limitation and a low confidence in using biodegradable implants due to their mechanical properties and polymer strength (which are lower than the traditional metallic implants) [5]. In the same time, the interfragmentary compression is not well realized with the miniscrews and biocompatibility is still an insufficient solved problem [5, 7].

For sure, the future implant design will overcome the limits of polymer strength [2] and the combination of bioabsorbable implants with therapeutic agents or osteogenic substances will improve the bone healing [3].

Conclusions

From collagen bioresorbable suture wires, the development of bioresorbable and biocompatible materials such as polyglycolic acid (PGA), polydioxanone acid (PDS) and polylactic acid (PLA) represents a medical advancement with use in the healing of different pathologies.

Bioresorbable fracture fixation INION® devices are a viable alternative to traditional metallic implants, offering same significant advantages over them: the avoidance of long-term interference with gliding structures, keeping their strength long enough to support bone healing, no need to remove the implants, less pain, radiolucency, elimination of stress shielding and a lower risk of complications.

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