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Epoxy resins and low melting point alloy composites

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ABSTRACT

Purpose: The goal of this work was to describe manufacturing process of polymer matrix composite materials reinforced with Wood's alloy particles and to observe changes of structure.

Design/methodology/approach: Polymer matrix composite materials reinforced with the Wood's alloy particles fabricating method was developed during the investigations, making it possible to obtain materials with good mechanical, electrical and thermal properties . Microscopic examination of samples cross- sections in order to search structure of prepared composite materials was done.

Findings: The influence of the processing conditions on structure of Wood's alloy-epoxy composite was observed using microscopic images.

Research limitations/implications: Presented research was limited to composites in the form of thin film.

Practical implications: Conducted research programmes concerning these materials show their applications possibilities. Polymer composites with low content of a metallic filler can form materials with high thermal conductivity and mechanical strength higher than polymeric matrix.

Originality/value: Polymer composites with metallic, low-melting alloys constitute poorly explored group of polymer composites. Most literature describe composites of low-melting-temperature alloys and thermoplastics matrix. Authors of this paper made an attempt to develop composite with thermosetting matrix. Heating was applied to melt metallic alloy but in this same time to cure epoxy resin.

Keywords: Engineering Polymers; Composites; Low-melting-point alloy; Wood's alloy; Epoxy resin

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MATERIALS

1. Introduction

Designing composites , being a joint of two or more materials different from each other and distinct in ready compound, is the most common way of creating new engineering materials. Structural or chemical composition in macro scale gives unlimited possibilities of designing their properties and simultaneously allows to broaden their application. [1,2]. The idea of new composite materials designing was the base for finding new materials with unique physical properties for the many kind of industries.

Polymer composites with metallic, low-melting alloys constitute poorly explored group of polymer composites. Conducted research programmes concerning these materials show their many applications possibilities. Usually polymer matrix was filled with metal particles for magnetic, electric or shielding properties [3-5]. Polymer composites with low content of a metallic filler can form materials with high thermal conductivity and mechanical strength higher than polymeric matrix. Especially metallic fibres are expected to improve mechanical properties.

In the common filled polymer systems, especially composites containing metal powder have emerged as a new-generation materials and are of interest for many domains of engineering, because they offer a wide range of possible applications including electromagnetic interference shielding, prevention discharging of static electricity, heat conduction, conversion of mechanical to electrical signals, and so forth [6,7,8].

The presence of rigid metal powders greatly decreases processing ability of the polymer matrix. In addition, the metal powders, especially those in nanoscale, are easily oxidized during mixing process which increases the electrical resistivity of the composites. To solve those problems, Zheng and coworkers [9-12] developed a new type of polymer composite by mixing low-melting-point metal alloy particles and polymer as a matrix.

Low-melting-point alloy consist of eutectic and non-eutectic combinations of metallic elements that, in themselves, melt at a much higher temperature. They have been known for many years and have been called by many different names. Many of these have more than one name, but usually we used inventor's name - like Woods, Lipowitzs, Onions, Newtons, Roses and so on metals or alloys. On the other hand, many of these alloys are sold under either trade names or proprietary numbers. This situation protected the manufacturer that developed a specific composition of material. With today's chemical facilities, it is easy to break down the ingredients of such materials if the information is really essential. With a reputable manufacturer, however, this system has an advantage in as much as manufacturers sell a product with specific properties and specific characteristics, which they advertise and which they promise to supply. This practice, widespread in the steel, aluminium, and copper industries, can easily be carried into the region of low melting-point alloys [13].

One should remember that some low-melting-point alloys become partially or fully molten at temperatures below that of boiling water. This is unique, especially as the parent metals in the pure state have their melting points high above alloy’s, as presented in Table 1 [13].

This can be explained by the same considerations used in explaining the phase diagram. Many metals form eutectic compositions with a melting point much lower than that of the parts of metals composition. Therefore, if we have a binary alloy system, we can achieve relatively low melting temperatures, which can be lowered even further by the use of ternary and quaternary eutectic compositions with melting points as low as those shown in Table 2 [13].

As it is presented in Tables 1 and 2, the most traditional low-melting point alloys are based on bismuth.

The use of bismuth in metallurgical applications increased greatly in the 1990s. With the many eco concerns, bismuth has been found to be a competitive replacement for lead in many areas of application. As an example, bismuth is used to replace the lead in some brass water fittings. In alloy with tin, bismuth is used in replacing lead in bronze bearings. It is also used in place of lead in heat-treating applications and in galvanizing operations [14,15].

Because bismuth expands during solidification and its alloys with certain other metals give low-melting alloys, bismuth is particularly well suited for a number of uses. Bismuth can be compounded with other elements in such alloys that can grow, reduce, or be unchanged dimensionally and stable during solidification. Because of this, bismuth alloys have found wide range of very demanding and specific industrial applications [15].

Significant and frequent industrial applications of bismuth alloys are following [14]:

- Anchoring - bismuth alloys that grow on solidification are particularly useful for aligning and setting of forming die. It is much easier to melt and pour an alloy around two parts of forming split-die at the same time. This method also makes it easier to relocate parts or change dies. The low temperatures involved do not cause distortion of setting system.
- Radiation shielding - bismuth, like lead, absorbs electromagnetic radiation. Therefore, bismuth alloys are widely used in the medical industry for shielding during radiation therapy.
- Electromagnetic shielding - because bismuth is highly diamagnetic, its alloys are very useful in applications where electronic equipment must be protected from outside interference or where our equipment can generate damaging electromagnetic-waves. These alloys can be easily cast into or sprayed onto the surface of the area needed for maximum shielding.
- Tube bending. The search for high-strength, low-weight structural materials demands the use of hollow tubes of many metals and alloys as structural components. These materials must often be forming to fit given design. Bending of empty tube may cause deformation of the shape of the tube by flattening or wrinkling. Such tubes can be filled with a low-melting bismuth alloy that allows the tube to be bent without any distortion. After that the alloy can be easily melted out of the tube and used again.
- Fusible safety devices. Low-melting bismuth alloys, especially those that are eutectic, have found numerous uses in safety devices. These alloys can be cast into any shape necessary in order to be used as a plug or switch that must function at a given temperature. High-pressure or temperature valve fittings are among the devices that contain low-melting bismuth alloys.
- Lens blocking. Low melting point alloys have become useful in the optical industry for securing lenses during grinding processes. Bismuth alloys are excellent conductors of heat, so provides that the lenses may be polished without overheating. The alloys have high strength so that good control is maintained during the grinding process. The weight of the alloy provides for a dampening of the vibrations caused by the grinding. After processing, the lenses are immersed in relative low temperature bath to remove the alloy, which can be used again.
- Fusible core technology. This is currently the fastest growing area of bismuth alloy application today. Low melting bismuth alloys make it possible to produce items having complex shapes with internal voids that cannot be produced using conventional investment casting technology. These alloys are being used in the electroforming industry as well as the plastics industry, where cost and weight reduction have become critical. Once moulding or electroforming is complete, the part is immersed in a heat water bath that melts out the alloy for use again. This process is useful for the polymeric materials industry.

- Proof casting of dies and moulds. Low-melting alloys make the process of die making faster and easier. The low-temperature alloys can be used in rapid tooling technology. This application is especially important for prototype-tools where we can't use polymeric materials because we need characteristic properties of metals. These alloys allow to produce a casting that is exact in detail, requiring no curing time. The casting can then be inspected and measured to gauge the accuracy of the dies. After life time of tool-prototype, it can be melted and is completely usable again.
- Lead-free waterfowl shot. Waterfowl poisoning from lead shot has been a ecologists concern for years. Research has indicated that a large percentage of waterfowl have been poisoned by ingestion of lead shot. This prompted the search for an alternative to lead shot.

Compositions of low-melting point alloys and polymers can create new kind of materials.

Most literature describe compositions of low-melting-point alloys and thermoplastics matrix [6-9]. This compositions are interesting because their easy manufacturing process. First step is melting the alloy. The second one is thermoplastic material plastification. As a results two quasi-fluids are obtained which are mixed in different technology processes, mainly in extrusion. After cooling a new composite material is produced, with new electrical, mechanical, thermal and other properties.

Authors of this article undertook an effort to create a thermosetting matrix composite. Heat was applied for alloy melting but in this same time for thermosetting resin curing. As a result two opposite processes had to be controlled.

Table 1.
Tin-bismuth with addition of other elements (Fussible Alloys). Solidus, and liquidus [13]

Composition %					Freezing range °C	
Sn	Bi	Pb	Cd	Others	Solidus	Liquidus
43	14	43	…	...	143	163
33	34	33	…	…	95	143
26	54	20	…	…	102	…
25	50	25	…	…	93	…
20	35.5	35	9.5	…	67	90
17	67	16	…	…	95	149
16	52	32	…	…	94	…
15	39	31	15	…	68	85
13	50	27	10	…	70	…
13	48.5	26.5	10	2 Tl	68	…
13	49	27	10	1 In	68	69
12.5	50	25	12.5	…	68	73
11.5	45	24	9.5	10 Tl	67	81
11,5	45	24	9.5	10 Tl	52	55
11.5	57	23	8.5	…	67	73
11	42.5	38	8.5	…	70	90
10.5	40	21.5	8	20 In	48	50
10	28	27.5	34.5	…	71	120
9.5	50	34.5	6	…	70	176
9	33	18	7	33 In	56	138

Table 2.
Melting temperature, toxcity and price of solder elements in order of increasing melting points [13,16]

Metal (element)	Melting point °C	Price $/kg (2010)	Toxcity	Availability
Indium (In)	155.0	565	Not estab.	Rare
Tin (Sn)	231.9	18.20	Nontoxic	Yes
Bismuth (Bi)	271.0	18.10	Nontoxic	Limited
Cadmium(Cd)	321.0	3.90	Toxic	Yes
Lead (Pb)	327.4	2.34	Toxic	Yes
Antimony (Sb)	631.0	8.15	Toxic	Yes
Silver (Ag)	960.5	570	Nontoxic	Limited
Copper (Cu)	1083.0	7.53	Nontoxic	Yes

2. Material and methods

The experiments were made with the Wood's alloy supplied by “Innovator” Company, Poland. Measured melting point was about 70ºC. Particles were dispersed in a two different resins systems. Chips of the Wood's alloy were made by the milling 2 kg billet (Fig. 1). At this stage of experiment no particles segregation was performed

Two epoxy resin systems were applied as polymeric matrix. First resin system was solid-state thermally cured epoxy resin Epidian 100 by “Organika Sarzyna” Company (Poland). Second epoxy resin system was cured at ambient temperature with hardener help - epoxy resin Epidian 6 and hardener IDA (mixed in weight proportion 2:1), both by “Organika Sarzyna” Company (Poland).

Compositions of all compounds are presented in Table 3. Composites with solid-state epoxy resin were prepared according to the following procedure: Pieces of solid resin were milled byhand using porcelain mortar and pestle. It was possible because this kind of resin is easily to grind. Next powdered metal and powdered resin were mixed together. Composites with liquid matrix were prepared by thoroughly mixing in glass beaker. Ready mixtures were placed on the top of microscopic glasses and heated up in the dryer to temperature specified in the Table 3. Times of samples melting and curing are also presented in Table 3. Obtained final samples of epoxy-Wood’s alloy composites were observed in light microscope.

3. Results

In Fig. 2 samples with Epidian 100 (solid-state) as matrix are presented. In Fig. 3 composites based on Epidian 6 plus IDA are shown. Optical inspection without magnification suggested that metallic chips were not molten at all. Also many agglomerates are visible in obtained samples. Another mixing methods are now tested to achieve better composites homogenization.

To reach detailed examination of composites all samples were submitted to microscopic inspection.

Microscope examinations were made with the Zeiss Discovery.V12 light microscope equipped with the computer image analysis system at the magnification of 100x. Figures 4-11 show the structure of all epoxy - Wood’s alloy composite materials.

Fig. 1. Wood's alloy shavings

The composites with low concentration of the Wood's alloy particles have very unevenly distributed filler particles (Figs. 4, 5 and 8). Almost all metallic particles are grouped into agglomerates. Shear stresses applied during mixing were not sufficient to disintegrate this agglomerates. It has to be taken into consideration that for Epidian 100 systems particles were mixed only in solid state. For Epidian 6 systems poor homogenisation is the result of low viscosity of epoxy matrix. Another method of mixture preparation is needed. Higher shear stresses levels can be obtained when at the beginning concentrates will be prepared. Afterwards homogeneous concentrates can be diluted with pure resin to specified concentration. For Epidian 100 systems additional mixing in liquid state can improve homogeneity. Results obtained for the highest filler concentration confirm this suggestion. Homogeneous composite structures for the highest filler concentrations are presented in (Figs. 7 and 11). Even for 60% of metallic particles good distribution of filler in polymeric matrix was achieved.

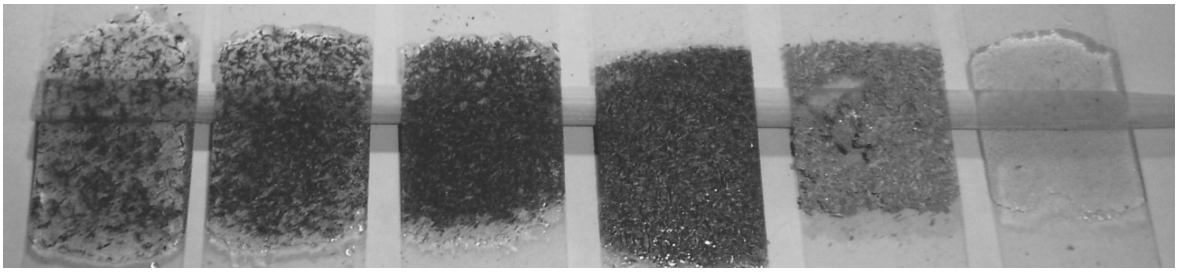

Fig. 2. Composites of Epidian 100 and Wood's alloys. From left: 20, 40, 60, 80, 100, 0% parts of Wood’s alloy

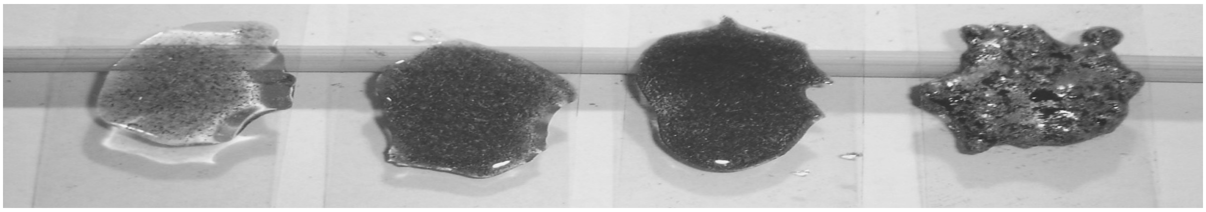

Fig. 3. Composites of Epidian 6+IDA and Wood's alloys. From left: 20, 40, 60, 80% parts of Wood’s alloy

Table 3.
Proportions of compositions

Sample	Resin system proportions		Part of resin system %	Part of Wood's alloy %	Temperature ºC	Time h
	Epoxy resin	Hardner				
1	Epidian 100		80	20	180	1
2			60	40		
3			40	60		
4			20	80		
5	Epidian 6	IDA	80	20	95	4
6			60	40		
7			40	60		
8			20	80		

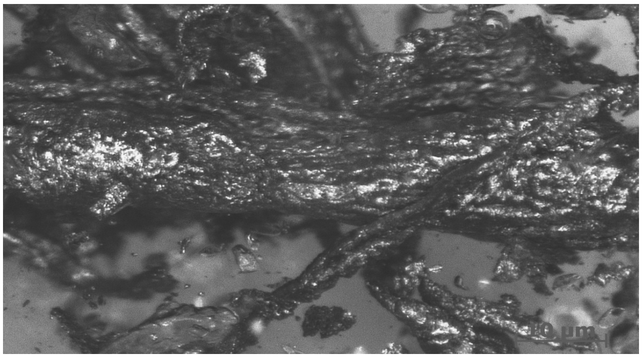

Fig. 4. Epidian 100 (80%) - Wood’s alloy (20%) composite

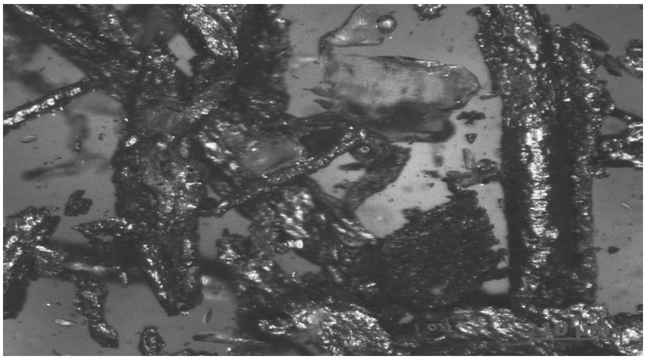

Fig. 5. Epidian 100 (60%) - Wood’s alloy (40%) composite

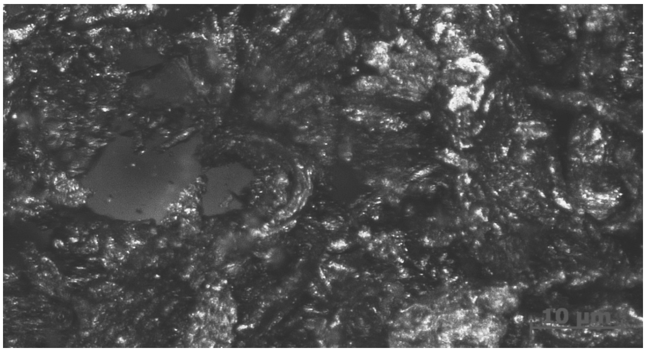

Fig. 6. Epidian 100 (40%) - Wood’s alloy (60%) composite

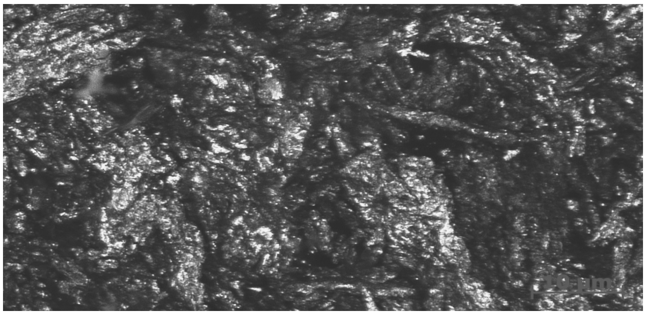

Fig.7. Epidian 100 (20%) - Wood’s alloy (80%) composite

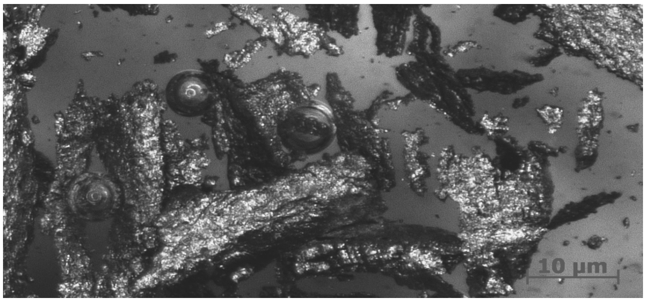

Fig. 8. Epidian 6 +IDA (80%) - Wood’s alloy (20%) composite

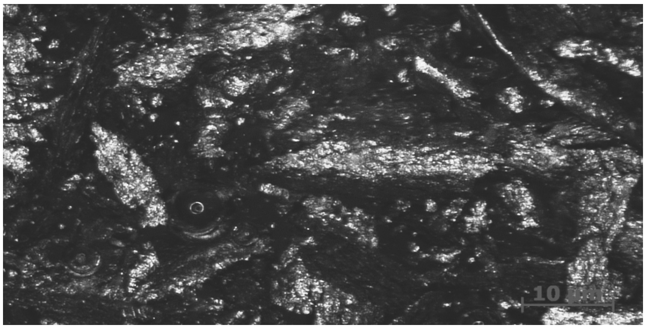

Fig. 9. Epidian 6 +IDA (60%) - Wood’s alloy (40%) composite

Microscopic studies showed also that for low concentrations the structure of composites have defects visible as gas bubbles (Figs. 4,5 and 8). In the case of solid particles it is the result of air trapped in mixture and not able to escape after melting due to high viscosity of Epidian 100. In the case of Epidian 6 systems it is the air trapped in polymeric matrix or filler powder that was not removed in mixture preparation procedure. In future experiments degassing is planned to avoid these imperfections. Figs. 5 and 6 show that cracking of polymer matrix happened in regions without filler particles. It was the result of shrinkage differences between regions with high and low concentration of metallic particles and in this way stresses generation. The second reason is that polymeric matrix exhibits low thermal conductivity and heat generated in hardening process leads to additional stresses formation.

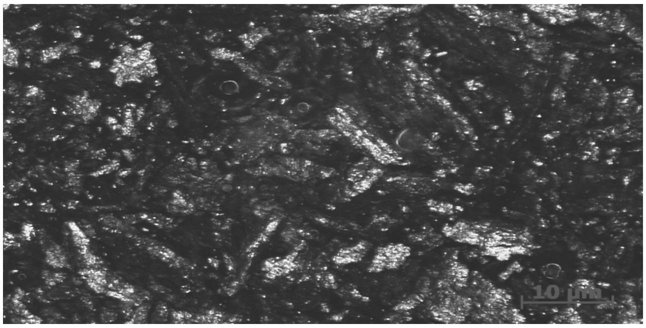

Fig. 10. Epidian 6 +IDA (40%) - Wood’s alloy (60%) composite

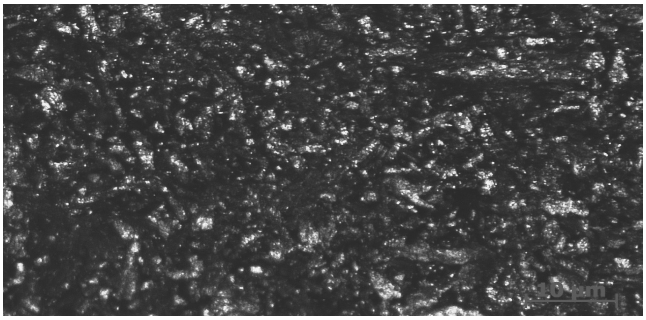

Fig. 11. Epidian 6 +IDA (20%) - Wood’s alloy (80%) composite

The differences between composites based on different matrixes can be observed for compounds containing 60% of the polymer and 40% of the Wood's alloy particles. Microscopic photographs suggest a better filler distribution in polymeric matrix for composites with Epidian 6 and hardener IDA (Figs. 5 and 9). It can be explained by preparation procedure. Systems based on Epidian 6 were mixed in liquid state and more homogeneous structure was achieved. Systems with Epidian 100 were mixed only before melting.

In composites filled with the largest quantity of the Wood's alloy particles, polymer matrix is difficult to be seen. This composites gives the impression of a coherent and rough substance (Figs. 11 and 7). No air bubbles and voids are also visible so this amount of polymeric matrix is sufficient to wet and join all metallic particles ant to form homogeneous composite. Microscopic observations with higher magnifications are planned to verify this conclusion. Also adhesion between metallic particles and polymeric matrix have to be checked.

Figs. 4, 5 and 8 show that despite the high curing temperature, much higher then melting point of Wood's alloy, some of the filler particles have sharp edges. Even metallic chips whose surface was molten did not change their shape. This may indicate that applied melting temperatures and times were insufficient to achieve metal liquefaction. For composite formation it is advantages. Full metallic particles liquefaction can lead to their fusion and formation of big metallic volumes and high composite heterogeneity. Research is planned to test the influence of metallic particles melting on adhesion between polymer matrix and metallic particles. It is possible that different processing parameters are needed to achieve the best coupling between this different materials.

Results achieved for high concentrations of filler particles show that it is possible to manufacture homogeneous epoxy-Wood's alloy composites with low level of typical composites imperfections. Such composites may be applied in many different industry fields such as electrical, electronic and mechanical engineering. Further research is needed to confirm it and to better recognize crucial properties. The proper research projects are planned in near future

4. Conclusions

This work gives valuable insight into the behaviour of epoxy composite materials reinforced with Wood's alloy in mixing and curing processes.

Results show that it is possible to manufacture homogeneous epoxy-Wood's alloy composites with low level of typical composites imperfections. Such composites may be interesting for many industry branches.

The study results showed that even though the temperature of the resin cross-linking was much higher than melting point of alloy, melting of metallic chips process was only initiated. Presented images show that metallic chips were melted during resin curing only on their surface and in minimal extend. It is advantages because completely melted metallic particles are able to join forming big composites heterogeneities.

The results obtained for both epoxy resins system were similar despite that different temperature and preparation times were used.

Presented research was only preliminary. In the future, researches with a smaller alloy particles and more bulky samples are planned. In the next step mechanical, electrical and thermal properties will be tested.

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