

Conductive Composites of PVC and Wood's Metal with Interpenetrating Network Structure

Monika Trojanowska-Tomczak,¹ Ryszard Steller,¹ Jarosław Janukiewicz,² Jan Ziaja,³
Grzegorz Szafran³

¹Polymer Engineering and Technology Department, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

²Institute of Telecommunication, Radiocommunication and Teleinformatics Department, Teleinformatics and Acoustics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

³Institute of Electrical Engineering Fundamentals, Electrotechnology Department, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Correspondence to: M. Trojanowska-Tomczak (E-mail: monika.trojanowska-tomczak@pwr.wroc.pl)

ABSTRACT: This work presents composite materials with interpenetrating network structure based on thermoplastic polymer and low melting metal alloy. Composites with various alloy content were prepared by PVC powder sintering to obtain polymer matrix with open pores. Then, liquid Wood's metal was intruded into the matrix using a pressure autoclave. Obtained composites have been studied with respect to microstructure, mechanical, thermal, and electrical properties. SEM micrographs revealed good dispersion of metal in the matrix but at low loading levels it is incomplete. Addition of metal improved mechanical properties, especially flexural strength. Electrical resistivity of samples varies from 10^{-4} to 10^{-5} Ω m and these values are typical of conductors. The measurements of electromagnetic interference shielding effectiveness (EMI SE) shows that generally PVC/Wood's metal composites have a good ability to shield electromagnetic waves. Composites containing more than 15 vol % Wood's metal exhibited EMI SE above 40 dB in the major part of frequency range. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: composites; mechanical properties; morphology; poly(vinyl chloride); porous materials

Received 21 November 2012; accepted 1 February 2013; published online

DOI: 10.1002/app.39115

INTRODUCTION

Polymers as the inherently insulating materials are often filled with metals to increase their electrical properties. Such composites have one or a combination of excellent mechanical, chemical, thermal, or electrical properties at lighter weights than their predecessors. First investigations took place decades ago and now conducting polymer composites have many technical applications e.g., electromagnetic interference shielding, sensors, circuit elements in microelectronics, antistatic protection.^{1,2} Usually, metal particles are in the form of fibers, powders or flakes which are randomly dispersed within the polymer matrix. The most popular metal fibers are made of steel, titanium, aluminum, tungsten, while copper, iron, nickel, aluminum, and silver are mostly used as powder fillers. A wide range of these metal particles were examined and presented in many publications.^{3–6}

Another, not so well-known class of metal containing materials are polymer-low melting metal alloy composites. Yi et al. have studied electrical properties of Sn-Pb alloy powder-filled polysty-

rene composites.⁷ Room-temperature resistivity of the samples varied from 1 to 10^{17} Ω m. For the samples which were molded below the melting point of the alloy a sudden drop in resistivity with filler content up to about 20 vol % was observed. At an average content of 23 vol % the material changes from an insulator to a conductor as the conductive pathways through the whole material are formed. However, when the composites were processed above the melting point of the alloy, the percolation did not take place. In addition, composites molded below the T_m of the alloy shows positive temperature coefficient of resistance (PTCR) transition at about 200°C.

Polystyrene loaded with eutectic metal (Bi-Sn alloy) and nickel particulate filler was reported by Mrozek et al.⁸ The incorporation of 10 vol % nickel prevented coalescence of the liquid metal and made it possible to maintain eutectic dispersion. Composite consisting of 70 vol % PS/30 vol % eutectic/10 vol % nickel exhibited conductivity of 0.1 S/cm. At 50 vol % loading of eutectic metal conductivity increased to 350 S/cm.

Similar investigations were made by Bormashenko et al.⁹ The resistivity of composites based on polyethylene and low melting metal alloy containing Sn – 45% (by weight), Zn – 20%, Cd – 35% was measured. The resistivity of composites was very high, as it varied within the range 10^9 – 10^7 Ω m. The percolation threshold was not yet achieved even at 30 wt % loading of metal.

Włodarczyk et al.¹⁰ did research work about polyamide 6 compositions with Wood's metal (3 vol %) and sodium (0.1 vol %) as a specific compatibilizer. Electrical properties were measured by thermally stimulated depolarization (TSD). Results testified to an insufficient spatial dispersion of the alloy particles; conductive paths within PA 6 matrix were not created.

Many other properties of different polymer/LMPA systems were also studied, e.g., thermal and mechanical behavior of unsaturated polyester resin/Wood's metal, rheological properties of polystyrene/Sn-Pb alloy, transient viscoelastic properties, and crystallization kinetics of poly(phenylene sulfide)/Sn-Pb alloy.^{11–13} Moreover, a doctoral thesis about polymer-low melting metal alloy systems was written by Włodarczyk.¹⁴ As a matrix thermoplastic polymers were used (PA 6, PA 12, PP, PP-g-MA) and as a filler different metal alloys with the melting temperature range from 70°C to 200°C. Influence of polymer/metal content and sample preparing conditions on composite properties and structure was studied. It was established that properties depend strongly on polymer whereas type of low melting metal alloy does not have such great importance.

All materials described above are composites in which metal filler is randomly dispersed in polymer matrix. Thus, when the filler content is low, the mean distance between metal particles is large and the conductance is limited by the polymer matrix because conducting phase is discontinuous. To create a conducting polymer composite the filler content has to be sufficiently high because the concentrated metal particles get closer and finally form a conducting path through the whole system.¹

A preferable structure with respect to lowering of the percolation threshold in polymer/metal composites seems to be a structure of interpenetrating network type created by polymer and metal co-continuous phases. Sorensen has described the preparation way of such composites.³ However, his method has some disadvantages e.g., it is necessary to modify polymer viscosity because the constituents must have similar rheological properties.

In this work a new preparation method of polymer/metal composites with interpenetrating network structure is presented. The other objective of the research is also to characterize the morphology, mechanical, thermal, and electrical properties of poly(vinyl chloride)/Wood's metal composites.

The preparation technique used in this work employs the sintering method for preparation of polymer matrix with open pores which are filled with liquid metal. When liquid metal contacts with the solid polymer surface it is not spontaneously absorbed by the pore system due to poor wettability. However, it is possible to intrude a non-wetting low melting liquid metal alloy into pore structure by using pressure because enough high pressure

overcomes capillary forces. The higher is pressure the smaller pores can be filled up. After cooling a sample metal solidifies and remains trapped in the pores. The relation between pressure required to force liquid metal into pores and a pore radius is given by the Washburn equation.¹⁵ Basing on the foregoing rule Wood's metal was used to analyze the porosity of sandstones, cement, cracks in marble structure under load, and microstructure of mudstones.¹⁶

EXPERIMENTAL

Materials

The low melting point metal alloy used was the Wood's metal (Bi₅₀ Pb₂₅ Sn_{12.5} Cd_{12.5}) provided by the POCH S.A (Poland) in the form of pellets. The melting temperature range of the alloy is approximately from 70°C to 72°C and a specific gravity of 9.7 g/cm³. The polymer used was the suspension poly(vinyl chloride) (Polanvil S-67 HBD) supplied by Anwil S.A. (Poland) which has the density 1.38 g/cm³ and the particle size from 0.088 to 0.25 mm.

Preparation of Polymer Matrix

The PVC matrices with open pores were prepared by sintering method. Pores can be treated as a second phase and the whole sample as a system of two interpenetrating continuous phases. For that reason if the pores are fill up with liquid metal alloy, the structure of interpenetrating polymer-metal network is created. The optimum sintering temperature was close to 170°C. PVC powder was loaded into a stainless-steel mold and after preliminary densification by vibration was put into a laboratory oven for 20 min. Then the mold was closed tightly for 15 min in room temperature. In this time the cap of the mold exerted pressure on the powder. Pressure enhances particles deformation and bonding. The obtained sinters had a form of discs (4.5 mm in thickness, 32 mm in diameter) and the porosity of ca. 10, 15, 20, and 30%. Different porosities was obtained by changing density of sample, it means different amounts of powder was placed in the mold. Knowing density of solid PVC (0% porosity) and volume of sinter disc we were able to count weight of powder correlated to particular porosity. Respectively porosity of 10%, 15%, 20%, and 30% was obtained by following weight of PVC powder: 4.5 g, 4.25 g, 4.0 g, 3.5 g.

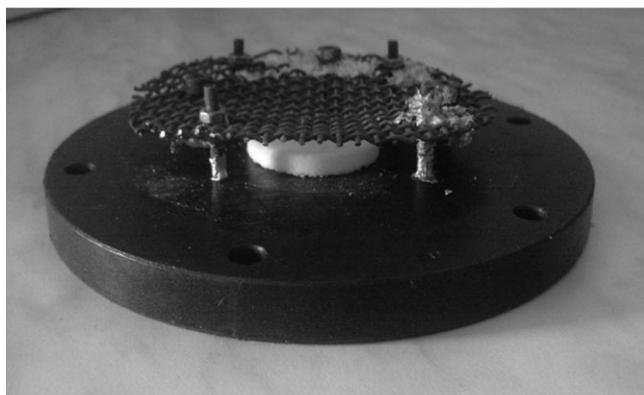
Preparation of Composite

The experimental assembly to intrude the Wood's metal into the polymer matrix is composed of an autoclave with a stand, a pressure nitrogen gas tank and a vacuum pump. The special autoclave made of stainless-steel and coated with Teflon is shown in Figure 1(a). Vessel is closed by a cap with screws and a heat resistant seal provides an adequate tightness. The autoclave has two valves for applying separately the vacuum and pressure.

The fabrication of the composite involves the following steps. The autoclave with Wood's metal inside is heated to 110°C until metal is fully molten. Then the autoclave is closed by the cap with attached polymer matrix [Figure 1(b)] and the heating is continued to increase the temperature of the sinter. If polymer sample is cold, liquid metal solidifies too rapidly in contact with the sample during intrusion. Next the air is evacuated and the autoclave is 180° turned on the stand and the molten metal



(a)



(b)

Figure 1. Autoclave for preparation of polymer-low melting metal alloy composites a) vessel inside b) cap with net for sinter placing.

floods the sample. The sample location between interior surface of a cap and a mesh attached to the cap prevents its immersion in liquid metal during intrusion. To intrude metal into pores the nitrogen pressure of 0.4 MPa is applied for 5 minutes. The pressure used in experiment allows to fill up the basic pores between sintered PVC grains with the diameter larger than ca. 1 μm , i.e. the constituents do not interpenetrate in nanoscale but in microscale. After intrusion autoclave is turned to the initial position.

Measurements

The average pore size, porosity, and pore size distribution of the polymer matrices were measured by mercury pressure porosimetry using the porosimeter Micrometrics Autopore II.

SEM images of the composite microstructure were obtained with the Zeiss EVO MA25 scanning electron microscope. The samples were polished and coated with carbon to avoid charging and imaged with 20 kV accelerating voltage in high vacuum mode.

Following mechanical and thermal properties were determined: hardness (Brinell method), impact strength (Dynstat method),

flexural strength (Dynstat method), and Vicat temperature in accordance with the recommendations of appropriate standards. Mechanical tests were done at room temperature.

Electrical resistance of the samples was measured at room temperature using a standard 4-wire method. The samples were placed in a climatic chamber which was equipped with Peltier device. Multi range high resolution current source Ipaco was used. Voltage drop across the electrode was measured by digital multimeter Agilent Technologies 34401 A. The resistance values were normalized to obtain the volume resistivity in $\Omega \text{ m}$. The sample dimensions were $30 \times 10 \times 5 \text{ mm}^3$ and the distance between voltage electrodes was 10 mm. Electrical resistance of polymer matrix was determined from voltage-current characteristic and values were normalized to obtain the volume resistivity. High resistance electrometer Keithley 6430 was used. The samples had a thickness of 4.5 mm and diameter of 32 mm.

Electromagnetic interference shielding was measured using ASTM D7449 and ASTM D5568 standard methods because a single method for such small samples does not exist. Measurements were carried out with Agilent Technologies E5071C network analyzer. The range of frequency was 300 kHz–6.5 GHz. The samples used for characterization had a form of ring (internal diameter 6 mm, external diameter 14 mm).

RESULTS AND DISCUSSION

Composite Structure

Figure 2(a) presents the pore size distributions of PVC matrices with different porosity values within the range from 10% to 30%. It is clear that the samples of higher porosity contain smaller amount of pores with size below 1 μm . For that reason the value of mean pore diameter increases with the rise of sample porosity. Median pore diameter for all matrices is shown in Figure 3.

Differential distribution curves [Figure 2(b)] show three maxima at ca. 4, 300, and 8000 nm independently of the porosity. The smallest pores and partially the mean pores results probably from the porous structure of the grains of suspension PVC, while the larger pores were created during PVC sintering in form of empty spaces between grains. The existence of the smallest pores should be treated as advantageous with respect to the improvement of adhesion between polymer and metal. Such pores make it possible the mechanical anchoring of the metal at the grain surface. It increases the adhesion and consequently the properties of the polymer—low melting alloy system.

Figure 4 shows the SEM micrographs of the composites with various loading levels of Wood's metal. Generally, a good distribution of the metal alloy within the composite can be observed. However, at low filler loading [10 vol % Wood's metal, Figure 4(a)] the metal network is created only at the edge of the sample whereas in its middle only neat PVC appears. It can be also seen that metal alloy inclusions have irregular shapes and different size from a few μm up to 100 μm , which obviously results from pore size dimensions in the matrix. Such irregular structures can facilitate the formation of conductive networks. However, at low metal loading the metal network is not complete. This situation arises from the fact that matrices with the

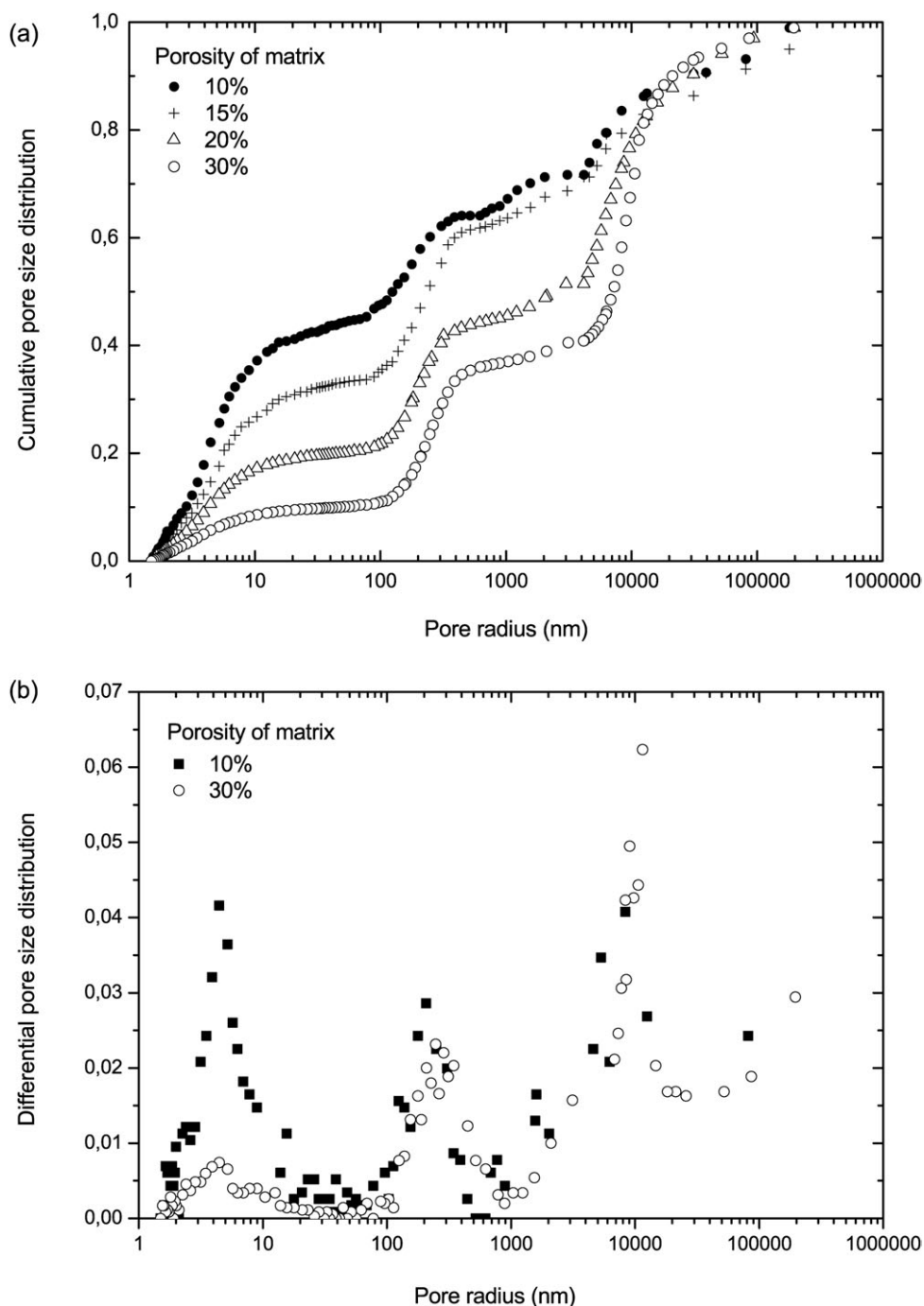


Figure 2. Pore size distribution for PVC matrices of different porosity a) cumulative distribution b) differential distribution.

porosity 10% or 15% have many small pores, the part of which may be also closed. Mercury porosimetry shows that for matrices with 10% porosity pores with diameter from 1 nm to 1 μm contain even 47% of all pores. Higher pressure should be applied to fill such small pores.

The created metal network can be more clearly observed after extraction of PVC phase. The composite containing 20 vol % of metal was placed in cyclohexanone until PVC dissolved totally. Gentle stirring was used during the process. SEM photography

of remaining metal phase is shown in Figure 5. It shows unequivocally that the metal phase is continuous and forms the network of branched paths. Connecting grains of suspension PVC form second continuous phase and in the result the composite has a structure of interpenetrating network (Figure 4).

To gain an additional insight into the metal phase within the composite a fragment of Wood's metal was mapped by means of the energy dispersive x-ray spectroscopy (EDX). For all composites EDX maps indicate that cadmium and tin are located

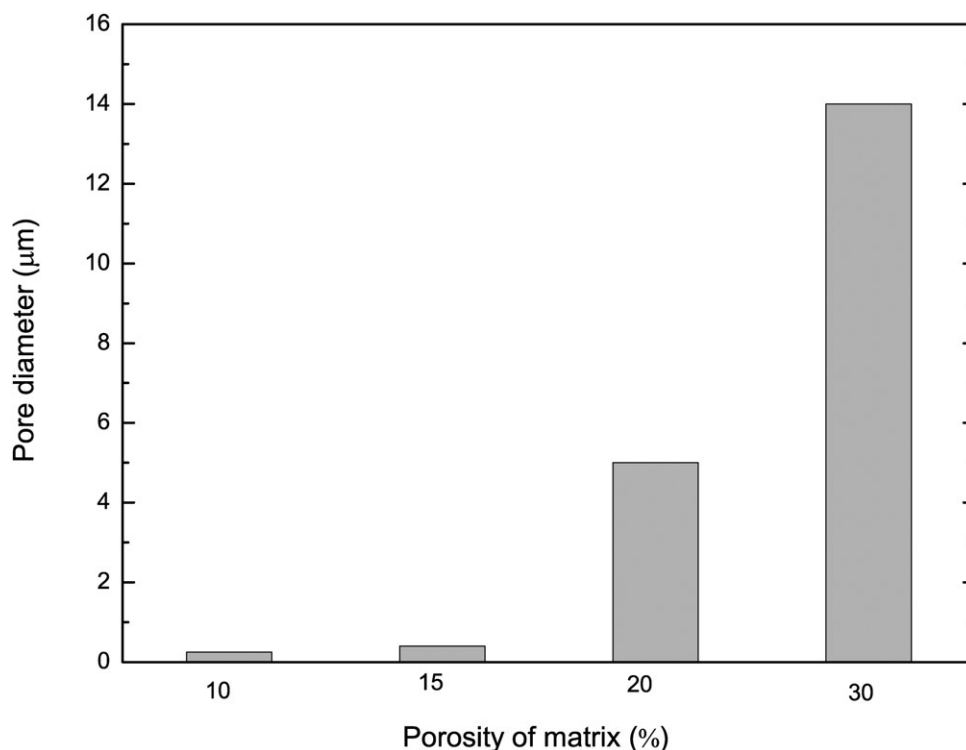


Figure 3. Median pore diameter at different porosity of matrix.

only in some areas of alloy, whereas bismuth and lead are found uniformly. It is interesting that cadmium has a form of strips. Because the composites are created in the atmosphere of nitrogen there are no metal oxides. Figure 6. shows EDX map for 20 vol % metal loading sample.

Mechanical and Thermal Properties

The mechanical properties for all composites are better than for corresponding polymer matrices and strengthening effect of alloy is obvious. However, improvement of mechanical strength is not very substantial. It is a consequence of Wood's metal properties e.g., low hardness caused by the lead presence in the alloy. Another reason might be a poor adhesion between polymer and metal surface. On the other hand, positive effect could have grains of suspension PVC which are porous and they let metal to anchor on polymer, that was already mentioned previously. Figures 7–10 show the Brinell hardness, impact and flexural strength and Vicat temperature dependence on filler content, respectively. It is also shown the comparison between properties of polymer matrices and corresponding composites. The largest changes in all mechanical properties are observed if the filler content is 30%. Impact strength value increases three times and flexural strength increases even five times for this metal content. Somewhat smaller changes are observed for composite containing 20% of metal filler. An opposite trend can be seen in the case of Vicat temperature. Generally, the softening point of composites decreases slightly. Only the sample with 30 vol % of metal concentration has almost the same value of Vicat temperature as the polymer matrix. It is due to the low melting temperature of Wood's metal because the alloy occurs

in the liquid state at the temperature resulting from the measurement principle of the composite softening point.

Electrical Resistivity

The results of resistivity measurement show that the composites conduct electrical current well. The resistivity of samples varies from $3.3 \cdot 10^{-4}$ to $1.5 \cdot 10^{-5} \Omega \text{ m}$ and this values are typical of electrical conductors. For comparison, Wood's metal exhibits specific resistivity of $8 \cdot 10^{-7} \Omega \text{ m}$ and sintered PVC matrix $1.5 \cdot 10^{14} \Omega \text{ m}$.¹⁷ It is clear that specific resistivity decreases as the concentration of metal alloy increases (Figure 11). All samples demonstrated a linear current-voltage relationship that means they follow Ohm's Law. The typical current-voltage plot is presented in Figure 12.

The systems polymer-low melting metal alloy, which are prepared by melt blending in extruder and metal is dispersed in matrix, do not have such a good conductivity at similar composition as the composites presented here. As an example can be mentioned the composite polystyrene/tin-lead alloy described by X.Zhang.¹⁸ At 20 vol % metal loading this composite does not conduct electrical current. The material changed from an insulator to a conductor at an average metal content of 23 vol %. Similar situation is in the Mrozek et al. work.⁸ The composites exhibited conductivity at 30 vol % metals loading (10 vol % Ni/20 vol % eutectic) of 0.1 S/cm which approximately corresponds to resistivity of 1 $\Omega \text{ m}$. Foregoing examples are the evidences that the interpenetrating phase structure of components created already during preparation of the composite matrix decreases the percolation threshold. For that reason our composites have a low resistivity even at 10 vol % of Wood's metal loading.

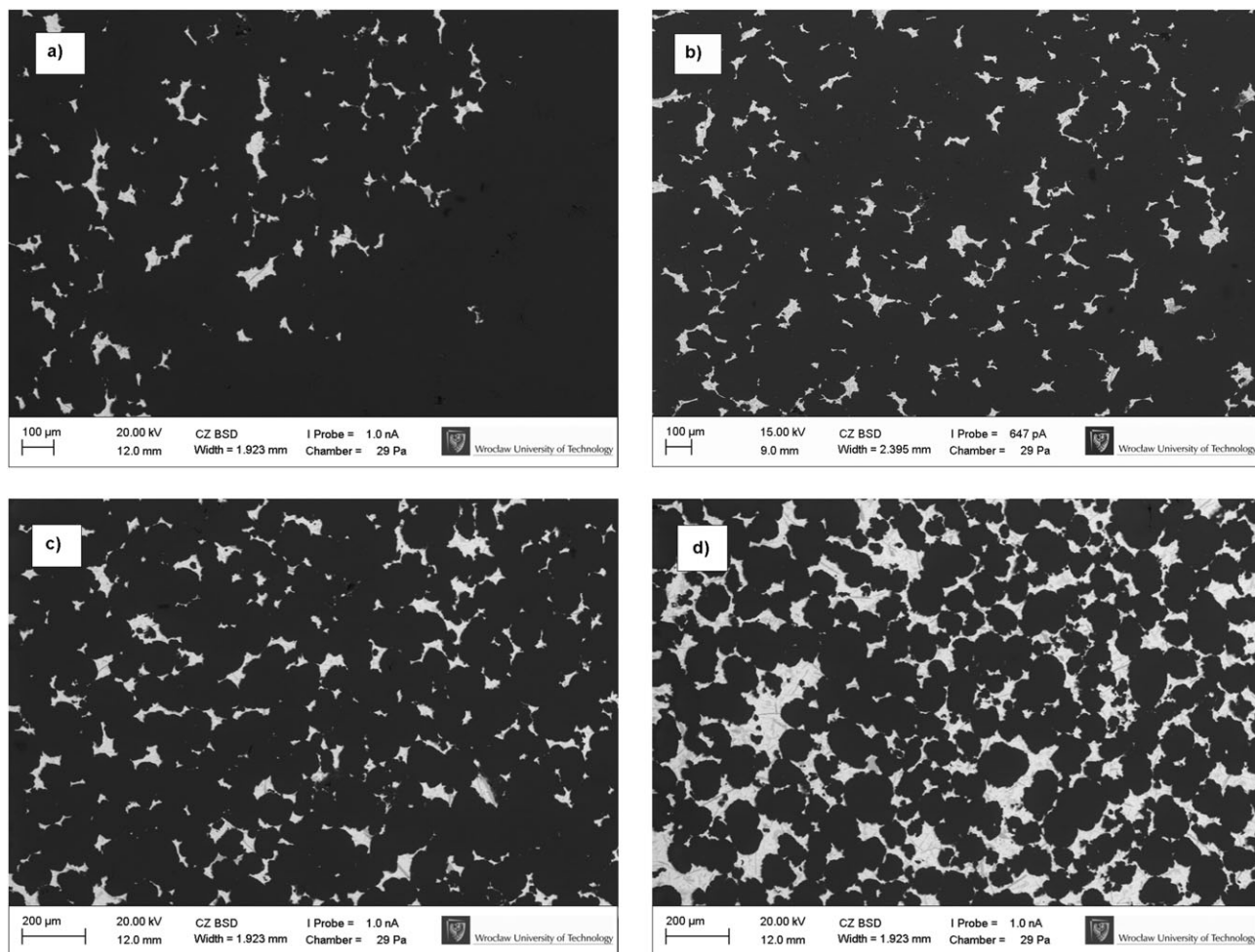


Figure 4. SEM images of composite samples with Wood's metal concentration: a) 10 vol% b) 15 vol% c) 20 vol% d) 30 vol%.

Shielding Effectiveness of Electromagnetic Interference

EMI SE is a measure of the material's ability to attenuate electromagnetic waves intensity. The materials block the amount of

power by absorption, reflection, and multiple-reflection. The higher the SE value, the better the attenuation. Shielding effectiveness is defined as the ratio of the electric field strength (modulus of the vector) \vec{E}_i obtained in the selected position in the absence of the shield and the field \vec{E}_t at the same location

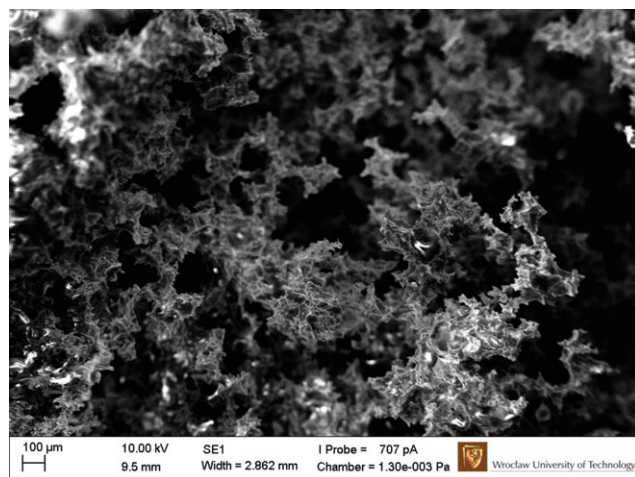


Figure 5. SEM image of metal phase after extraction of PVC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

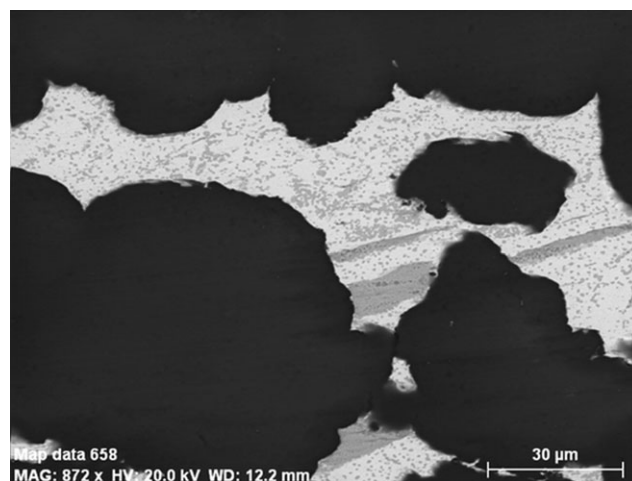


Figure 6. X-ray map for 80% PVC + 20% Wood's metal composite.

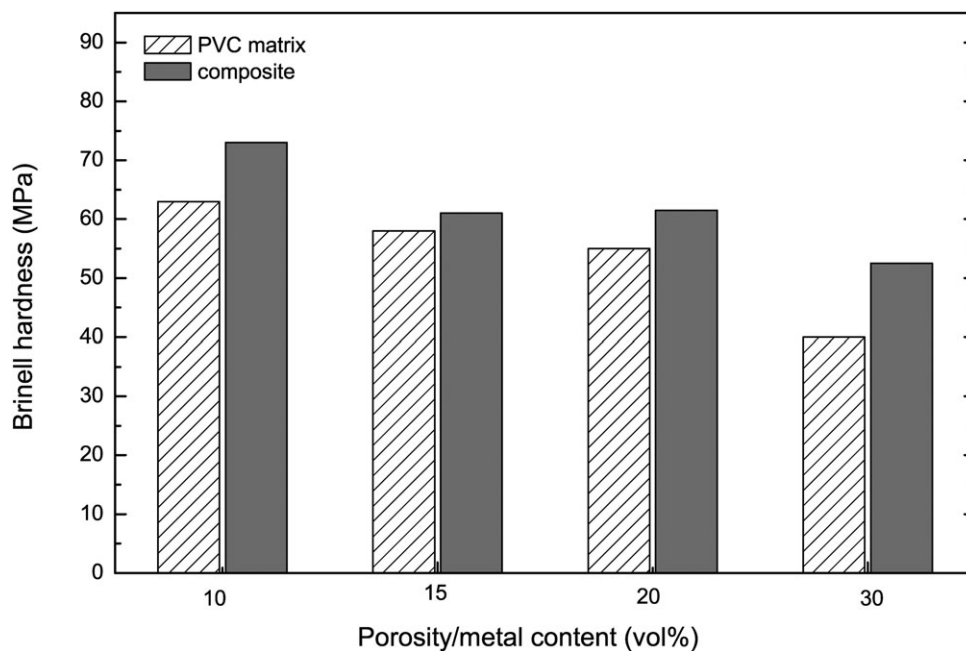


Figure 7. Brinell hardness of PVC/Wood's metal composites.

with the shielding enclosure.^{19,20} It is expressed in logarithmic units (dB)

$$SE(\text{dB}) = 20 \log_{10} \left(\frac{|\vec{E}_i|}{|\vec{E}_t|} \right). \quad (1)$$

It is well known that the target value of EMI SE needed for commercial applications is around 20 dB. This value corresponds to blocking 99% of electromagnetic waves.²¹

Results of measurements obtained in this study show that for the composites which contain 20 vol% and 30 vol% of Wood's metal EMI SE value is very good. But the samples at 10 vol% and 15 vol% metal loading exhibit significantly lower level of shielding. However, a large influence on EMI SE values has an air gap between specimen and coaxial transmission line. This free space of air reduces contact surface. For that reason all values obtained here are lower than the real ones. Despite the

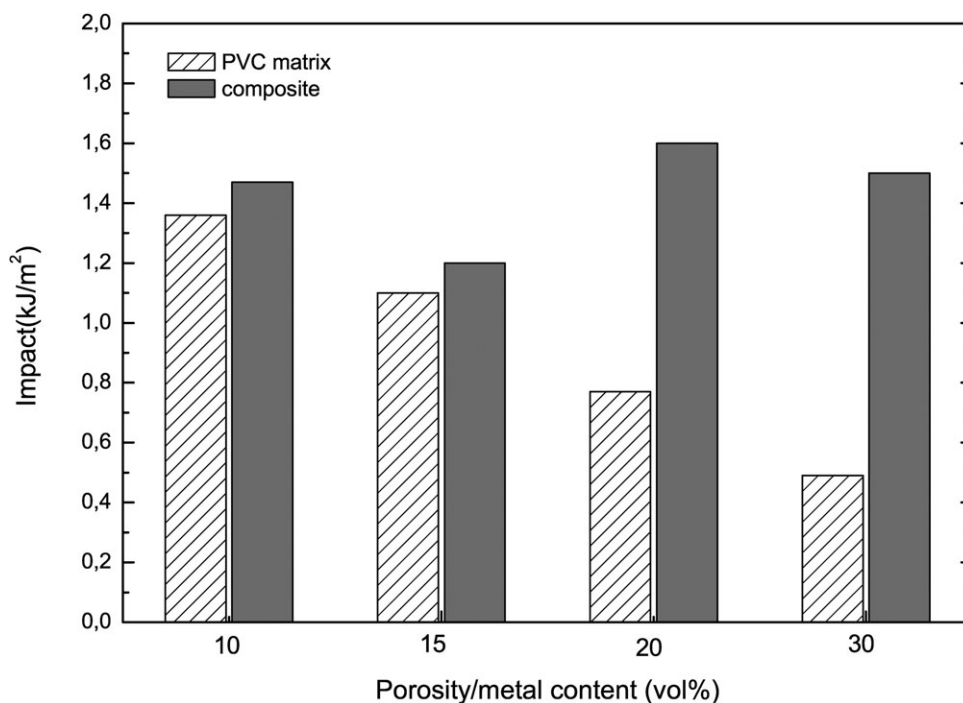


Figure 8. Impact of PVC/Wood's metal composites.

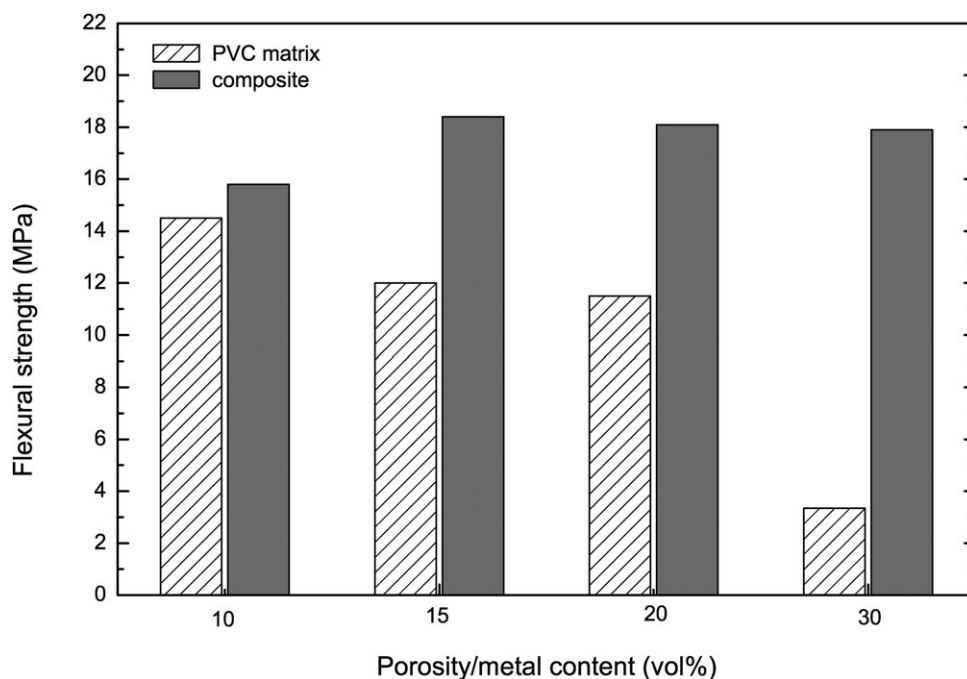


Figure 9. Flexural strength of PVC/Wood's metal composites.

problems with specimen adjustment to a test specimen holder we can unequivocally state that PVC/Wood's metal composites show ability to shield electromagnetic waves. It was expected because bismuth is highly diamagnetic and, like lead, absorbs electromagnetic radiation.

Figure 13 illustrates the variation of EMI SE within the measured frequency range from 300 kHz to 6.5 GHz for the PVC/Wood's metal composites. It is evident that the EMI SE

increases with the increasing filler content. It is also known, the improvement of shielding effectiveness is primarily ascribed to the improvement of the entire conductivity of composite. The composite with 30 vol % of metal, which has the lowest resistivity, exhibits SE up to 66 dB. The attenuation effectiveness strongly depends on frequency only for composites which contain 20 and 30 vol % of Wood's metal. The rest of composites change the SE value slightly after crossing 3 GHz and achieve the ultimate SE around 15 dB.

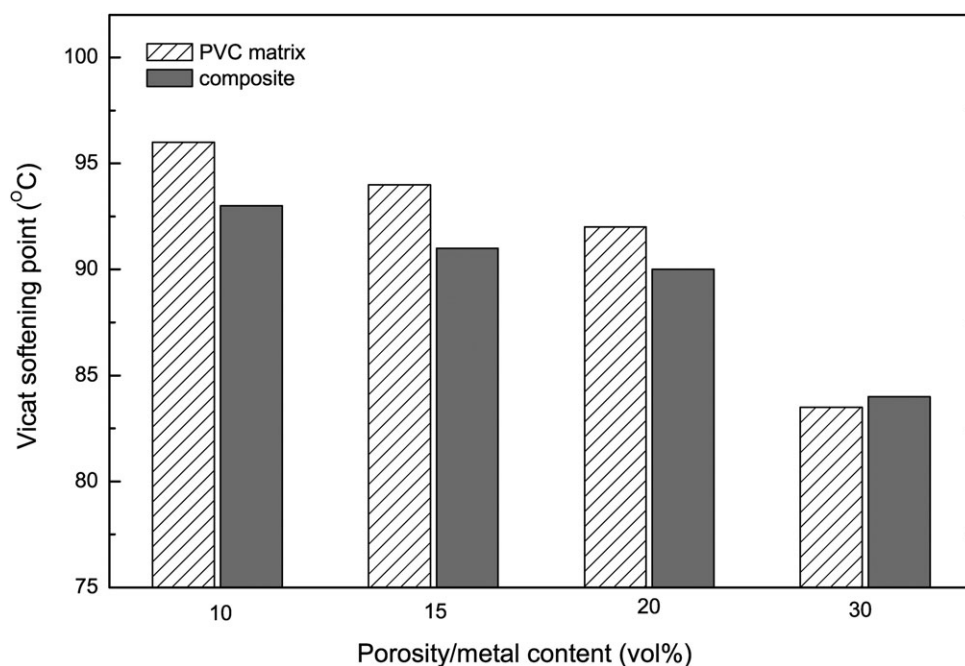


Figure 10. Vicat temperature of PVC/Wood's metal composites.

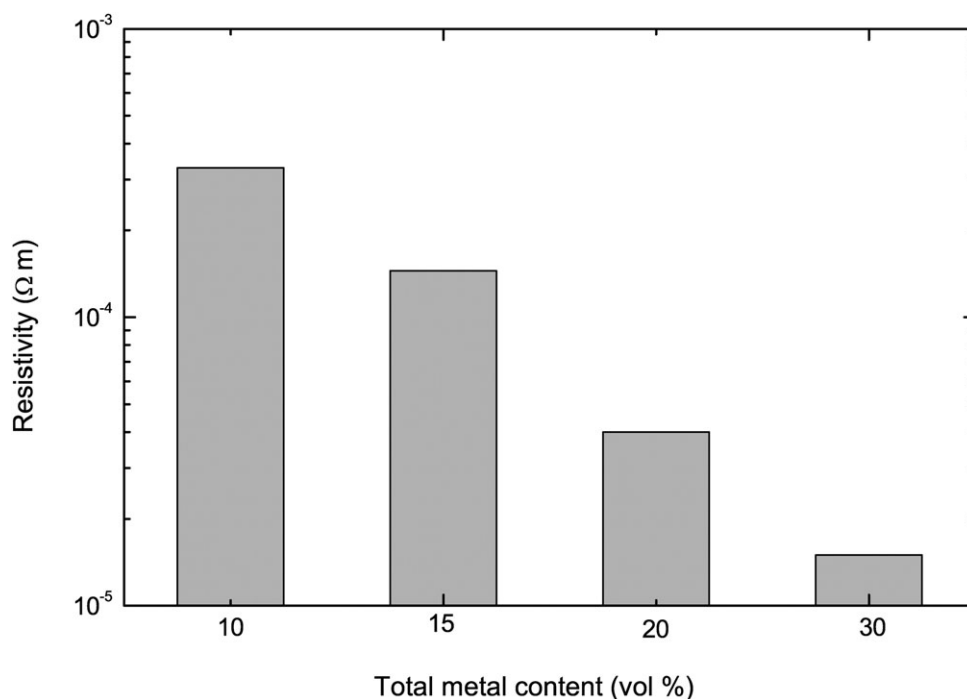


Figure 11. Resistivity of PVC/Wood's metal composites.

CONCLUSIONS

Using the method of intrusion of a liquid metal alloy into a porous polymer matrix, composite materials based on poly(vinyl chloride) and Wood's metal alloy were prepared. This method allowed to obtain novel composites with interpenetrating network (phase) structure which was confirmed by scanning electron microscopy.

It was found that the mechanical properties vary with the alloy content. Wood's metal does not cause a significant improvement in impact and flexural strength at low-metal content. Brinell hardness increases only slightly for all compositions as a result of low hardness of Wood's metal. Small lowering of Vicat softening point of composites was observed. It is due to low melting temperature of the alloy, i.e., 70°C.

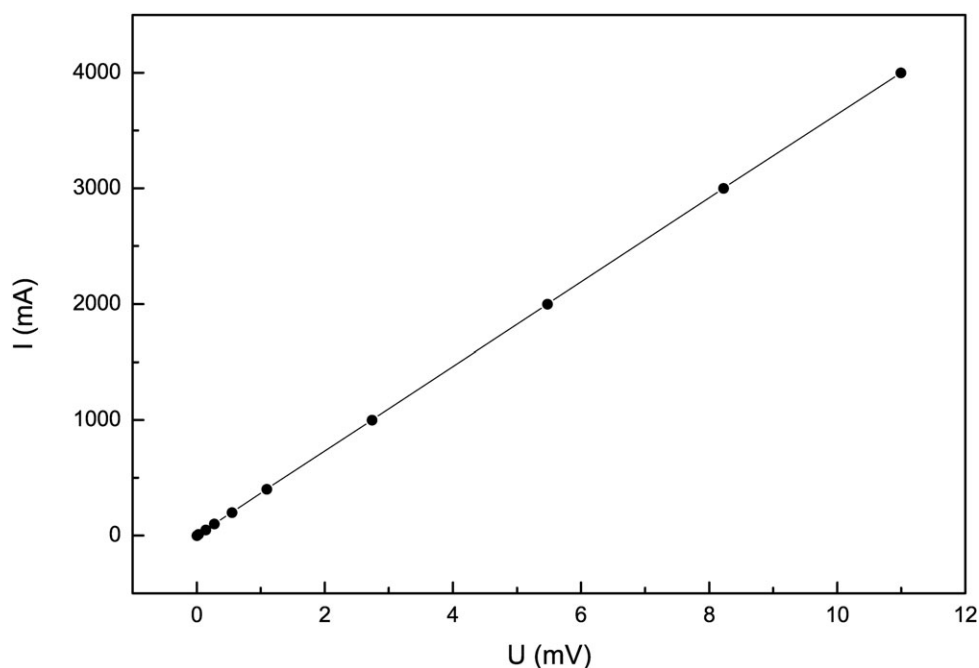


Figure 12. Current-voltage dependence for 70% PVC + 30% Wood's metal composite.

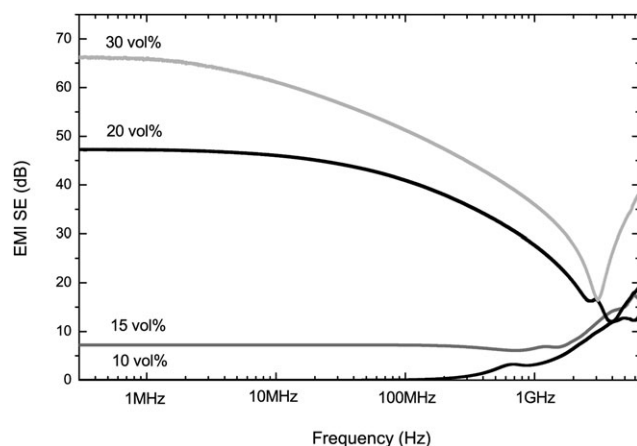


Figure 13. X-band EMI SE of PVC/Wood's metal composites as a function of electromagnetic wave frequency.

The results of electrical resistivity measurement show that the materials conduct electrical current well, even at 10 vol % metal alloy loading. PVC/Wood's metal composites also exhibit EMI SE capabilities and these which contain more than 15 vol % of filler can be effectively used in advanced applications requiring shielding of EMI. The resistivity was found to decrease with increasing metal content. Since shielding effectiveness is connected with conductivity, samples with higher metal loading level have a greater EMI SE which reaches even 60 dB.

Generally, it can be stated that the addition of Wood's metal have more advantageous influence on electrical properties than on mechanical ones and optimal properties shows composite containing 20 vol % of metal alloy.

Obtained results showed that interpenetrating network structure allows to reduce essentially the metal content, i.e. the percolation threshold, to form conducting paths. However there are still open problems connected with such materials that require explanation, such as. the effect of preparation conditions, e.g. pressure, on the properties of these composites comprising also other thermoplastics and low melting metal alloys.

ACKNOWLEDGMENTS

This work was co-financed by the European Union as part of the European Social Fund.

REFERENCES

1. Strümpfer, R.; Glatz-Reichenbach J. *J. Electroceramics* **1999**, *3*, 329.
2. Qureshi, A.; Mergen, A. *J. Macromol. Sci. Part A* **2008**, *45*, 462.
3. Sorensen, I. W. European Patent, 0 163 058, April 12, (1985).
4. Bhattacharya, S. K. *Metal-Filled Polymers*; Marcel Dekker: New York, **1986**.
5. Holbrook, A. L. *Int. J. Powder Metal.* **1986**, *22*, 41.
6. Pritchard, G. *Conducting Fillers for Plastics 1: Plastics Additives*; Chapman & Hall: London, **1998**.
7. Xiao-Su, Y.; Xiangwu, Z.; Lie, S.; Yi, P. *Polym.-Plast. Technol. Eng.* **2000**, *5*, 829.
8. Mrozek, R.A.; Cole, P. J.; Mondy, L. A.; Rao, R. R.; Bieg L. F.; Lenhart, J. L. *Polymer* **2010**, *51*, 2954.
9. Bormashenko, E.; Sutovski, S.; Pogreb, R.; Sheshnev, A.; Bormashenko, J. *J. Thermoplast. Compos. Mater.* **2004**, *17*, 245.
10. Włodarczyk, E.; Steller, R.; Gubański, A. *e-Polymers* 2006, P-012, International Polymer Seminar Gliwice **2005**.
11. Gökhan, C.; Küsefoğlu, S. *J. Appl. Polym. Sci.* **2006**, *100*, 832.
12. Wu, D.; Wu, L.; He, J.; Zhang, M.; Yan, C. *J. Polym. Sci.: Part B: Polym. Phys.* **2008**, *46*, 677.
13. Wang, J.; Fu, J.; Xiong, C. *J. Wuhan University of Technology - Mater. Sci. Ed.* **2002**, *17*, 93.
14. Włodarczyk, E. Thermoplastic blends of polymer and low melting alloy. Ph.D. Thesis, Wrocław University of Technology, Wrocław, **2009** (in polish).
15. Washburn, E. W. *Physics* **1921**, *7*, 115.
16. Willis, K. L.; Abell, A. B.; Lange, D. A. *Cement Concrete Res.* **1998**, *28*, 1695.
17. Shalaby, R. M. *J. Mater. Sci. Technol.* **2009**, *25*, 449.
18. Zhang, X.; Pan, Y.; Shen, L.; Zheng, Q.; Yi, X. *J. Appl. Polym. Sci.* **2000**, *77*, 1044.
19. Lozano-Guerrero, A. *J. Microwave Opt. Technol. Lett.* **2010**, *52*, 2476.
20. Al-Ghamdi, A. A.; El-Tantawy, F. *Compos. Part A* **2010**, *41*, 1693.
21. Markham, D. *Mater. Des.* **2000**, *21*, 45.