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ELECTRICAL AND THERMAL PROPERTIES OF COMPOSITES BASED ON THERMOPLASTIC POLYMER AND LOW MELTING METAL ALLOY

The paper concerns composite materials based on a thermoplastic polymer and low melting metal alloy. Composites with various alloy content were prepared by the sintering of PMMA or PVC powder to obtain a matrix with open pores. Then, liquid Wood's alloy was intruded into the matrix using a pressure autoclave. The obtained systems consist of co-continuous, interlaced 3D networks. The microstructure, electrical and thermal properties have been investigated. SEM micrographs revealed good dispersion of the filler in the matrices. The metal alloy inclusions have irregular shapes and different sizes from a few μm up to 100 μm. The results of the resistivity measurements showed that both composites conduct electrical current well. The resistivity of the samples varies from $4.2 \cdot 10^{-4}$ to $1.5 \cdot 10^{-5}$ Ω·m and the type of matrix does not have an influence. In contrast to electrical conductivity, the concentration dependence of thermal conductivity did not show percolation behaviour. The thermal conductivity of the composites increased but only slightly and its value is still closer to the polymers than to the metals. A slight reduction in the Vicat softening point of the composites was observed. It is due to the low melting temperature of the alloy, i.e. 70°C.

Keywords: polymer matrix composites, low melting alloy, electrical resistivity, thermal conductivity

ELEKTRYCZNE I TERMICZNE WŁAŚCIWOŚCI KOMPOZYTÓW POLIMER TERMOPLASTYCZNY - - NISKOTOPLIWY STOP METALI

Głównym celem towarzyszącym wytwarzaniu kompozytów polimer-metal jest otrzymanie materiałów dobrze przewodzących prąd przy jak najmniejszej zawartości metalu. Jednak większość kompozytów, w których metal jest rozproszony w matrycy polimerowej w sposób przypadkowy, wymaga stosunkowo dużej zawartości napełniacza. Niesie to ze sobą trudności różnego rodzaju, np. wzrost lepkości układu, powstawanie aglomeratów. W niniejszej pracy przedstawiono kompozyty o innej strukturze, tj. strukturze wzajemnie przenikających się składników, gdzie polimer i metal tworzą dwie ciągłe fazy. Porowate matryce polimerowe o otwartych porach wytworzono za pomocą techniki spiekania. Następnie napełniano je ciekłym stopem niskotopliwym przy użyciu ciśnienia azotu. Jako osnowy użyto suspensyjnego polichlorku winylu oraz polimetakrylanu metylu, a jako napełniacza stopu Wooda. Otrzymano kompozyty o zawartości metalu 10, 20 i 30% obj. Zaprezentowano wyniki obserwacji mikrostruktury zbadanej za pomocą skaningowego mikroskopu elektronowego. W ramach pomiarów właściwości elektrycznych i termicznych określono rezystywność skrośną, przewodnictwo cieplne oraz temperaturę mięknienia wg Vicata. Na podstawie mikroskopii SEM stwierdzono, że matryca nie ma wpływu na strukturę kompozytów. Między złączonymi ziarnami polimeru występuje ciągła faza metaliczna, przy czym ziarna PMMA mają bardziej regularny, kulisty kształt niż ziarna PVC. Mikroskopia wykazała również stosunkowo równomierny rozkład cząstek napełniacza. Wszystkie kompozyty dobrze przewodzą prąd elektryczny. Rezystywność skrośna rośnie wraz z zawartością metalu i mieści się w przedziale wartości od $4{,}2 \cdot 10^{-4}$ do $1{,}5 \cdot 10^{-5}$ Ω·m. Pomimo, że rezystancja PVC jest o rząd mniejsza od rezystancji PMMA, kompozyty nie wykazują znacznych różnic w zależności od rodzaju matrycy. Wbrew oczekiwaniom przewodnictwo cieplne nie ulega znacznemu zwiększeniu. Jego wartość wzrasta w porównaniu do matryc, ale pozostaje nadal bliższa materiałom polimerowym niż metalom. Dla zawartości stopu Wooda 30% obj. przyjmuje najwyższą wartość 1,5 W/(Km), a więc jest około trzykrotnie większa od przewodnictwa czystych PVC i PMMA. Odporność cieplna kompozytów uległa niewielkiemu zmniejszeniu. Jest to prawdopodobnie wynik występowania stopu Wooda w stanie ciekłym w warunkach pomiaru ze względu na jego niską temperaturę topnienia (ok. 70°C).

Słowa kluczowe: kompozyty o osnowie polimerowej, stop niskotopliwy, rezystywność, przewodnictwo cieplne

INTRODUCTION

Polymer-metal composites are primarily created to produce polymeric materials which exhibit electrical conductivity and the main aim is conductivity approaching pure metals.

The most common metal fillers are: nickel, aluminium, copper, iron or silver in the form of a powder, fibres or flakes. Thermoplastics such as polyethylene, polypropylene, polystyrene are typically used as matrix

material [1, 2]. To obtain electrical conductivity, a high amount of filler is required. It causes an increase in viscosity, poor degassing behaviour and sometimes reduces the mechanical properties, for instance impact strength. Moreover, polymers and metals are highly incompatible. It is difficult to mix a great amount of metal particles into the polymer matrix without the formation of agglomerates [3]. The electrical properties of these composites are directly related to the conductivity and the permittivity of the constituent phase. Obviously, they depend critically on the volume content of filler. The size and shape of the filler, spatial arrangement of the metal particles and adhesion between the metal and polymer also have an important influence [4].

Usually, polymer-metal composites described in publications are systems in which metal particles are randomly dispersed in the polymer matrix. This article presents a composite with another structure, i.e. a structure of an interpenetrating network type created by a polymer and metal co-continuous phases. The preparation technique used in this work employs the sintering method for preparation of the polymer matrix with open pores which are filled with a liquid, low melting metal alloy. When the liquid metal comes into contact 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 the pore structure by using pressure because a high enough pressure overcomes the capillary forces. After cooling, the sample metal solidifies and remains trapped in the pores. The relation between the pressure required to force liquid metal into the pores and the pore radius is given by the Washburn equation [5]. Connecting the grains of polymer powder forms a continuous phase. The metal phase is also continuous and forms a network of branched paths which was confirmed by SEM microscopy.

In the present study, the electrical and thermal properties of PVC and PMMA composites loaded with Wood's metal were discussed. The metal fillers volume fractions differ from 0 to 0.3.

EXPERIMENTAL PROCEDURE

Materials

As the polymer matrices suspension, poly(vinyl chloride) (PVC) and polymetryl methacrylate (PMMA) were used. PVC (Polanvil S-67 HBD) supplied by Anwil S.A. (Poland) has a density of 1.4 g/cm^3, PMMA (Metapleks SO) has a density of 1.2 g/cm^3.

The low melting point metal alloy used was Wood's metal (Bi_{50} Pb_{25} $Sn_{12,5}$ $Cd_{12,5}$) provided by STANLAB (Poland) in the form of pellets. The melting temperature range of the alloy is approximately from 70 to 72°C and with a specific gravity of 9.7 g/cm^3.

Preparation of composites

The PVC and PMMA matrices with open pores were prepared by the sintering method. The optimum sintering temperature for both polymers was close to 170°C. The polymer powder was loaded into a stainless-steel mold and after preliminary densification by vibration, was put into a laboratory oven for 20 minutes. Then the mold was closed tightly for 15 minutes at room temperature. During this time the cap of the mold exerted pressure on the powder. Pressure enhances particle deformation and bonding. The obtained sinters had the form of discs (4.5 mm in thickness, 32 mm in diameter) and a porosity of ca. 10, 20 and 30%. Different porosities were obtained by changing the sample weight (density). A precise porosity value was verified by mercury porosimetry. Fabrication of the composite involves the following steps. The autoclave with Wood's metal inside was heated to 100°C until the metal was fully molten. Then the polymer matrix was placed inside and the autoclave was closed with the cap with an attached extender which prevents matrix immersion in the liquid metal, and the heating was continued to increase the temperature of the sinter. If the polymer sample is cold, the liquid metal may solidify in contact with the sample during intrusion. Next the air was evacuated and a nitrogen pressure of 0.4 MPa was applied to intrude the metal into the pores. The pressure used in the experiment allows one to fill up the basic pores between the sintered grains with a diameter larger than ca. 1 μm, i.e. the constituents do not interpenetrate on the nanoscale but on the microscale.

Measurement methods

SEM images of the composite microstructure were obtained with a 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 the high vacuum mode. The electrical resistance of the composites was measured at room temperature using a standard 4-wire method. The samples were placed in a climatic chamber which was equipped with a Peltier device. An Ipaco multi-range, high-resolution current source was used. Voltage drop across the electrode was measured by a digital multimeter, Agilent Technologies 34401 A. The resistance values were normalized to obtain a volume resistivity in Ω·m. The sample dimensions were 30 x 10 x 5 mm and the distance between the voltage electrodes was 10 mm. Electrical resistance of the polymer matrix was determined from the voltage-current characteristics and the values were normalized to obtain the volume resistivity. A high resistance electrometer, Keithley 6430, was used. The samples had a thickness of 4.5 mm and diameter of 32 mm.

The Vicat temperature was determined in accordance with PN-54/C-04260 using a standard measuring device.

Thermal conductivity was measured using a device constructed at the Wrocław University of Technology. It consists of three independent systems: the power supply of a heater, thermocouple and a Metex multimeter. A quartz standard sample was used to determine the power of the heater. The samples were in the form of a disc with a thickness of 1÷2 mm and diameter of 20 mm. Knowing the power of the heater, the dimensions of the sample and temperature difference between both sides of the sample, thermal conductivity λ was calculated according to the following equation:

$$\lambda = \frac{P \cdot t}{A \cdot \Delta T} \qquad (1)$$

where P is the power of the heater, t is the thickness of the sample, A is the area of the cross-section and ΔT is the temperature difference.

RESULTS AND DISCUSSION

SEM microscopy

Figure 1 shows the SEM micrographs of the composites with PVC and PMMA matrix for 20 vol.% metal loading. The dark zones present the polymer whereas the bright ones present the metal phase.
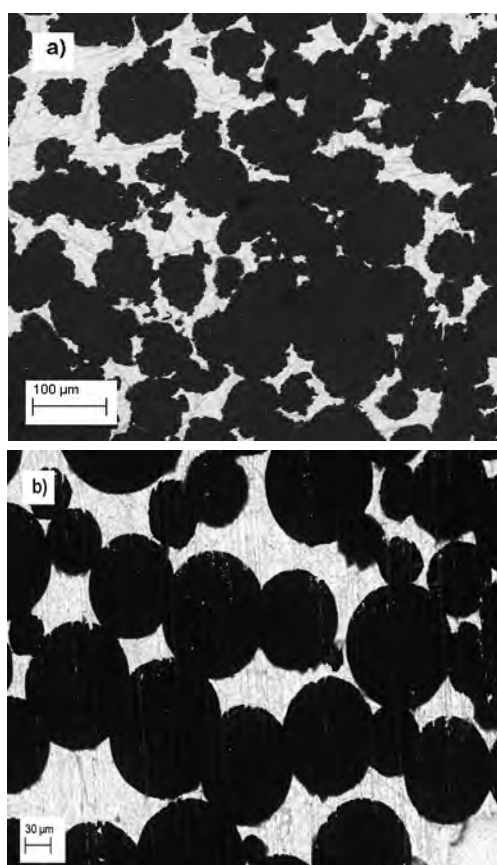

Fig. 1. SEM images of composites containing 20 vol.% Wood's metal: a) PVC matrix, b) PMMA matrix

Rys. 1. Obrazy SEM przekroju kompozytów zawierających 20% obj. stopu Wooda: a) matryca PVC, b) matryca PMMA

There are no significant differences between composites based on PVC or PMMA. However, the PMMA grains are rounder and have a regular edge. Between the bonding grains there is a continuous phase of metal. Quite good distribution of Wood's metal within the composite can be observed. It can be also seen that the metal alloy inclusions have irregular shapes and different sizes from a few µm up to 100 µm, which obviously results from the pore size of the matrix. Such irregular structures can facilitate the formation of conductive networks. McQueen et al. [7] studied the percolation threshold in polymer/filler composites. Their experimental results supported the theory that irregular filler shapes, especially elongated ones, reduce the percolation threshold. Our results confirmed this theory that is presented beneath in the section *Electrical resistivity*. Energy dispersive x-ray spectroscopy (EDX)gives additional insight into the metal phase within the composite. For both, the PVC and PMMA composites, EDX maps indicate that cadmium and tin are located only in some areas of the alloy, whereas bismuth and lead are found uniformly. It is interesting that cadmium is in the form of strips. Because the composites are created in the atmosphere of nitrogen there are no metal oxides.

Electrical resistivity

The results of resistivity measurement show that both composites conduct electrical current well. The resistivity of the samples varies from $4.2 \cdot 10^{-4}$ to $1.5 \cdot 10^{-5}$ Ω·m and the type of matrix does not have an influence. These values are typical of electrical conductors. For comparison, Wood's metal exhibits a specific resistivity of $8 \cdot 10^{-7}$ Ω·m, the sintered PVC matrix $1 \cdot 10^{14}$ Ω·m and the PMMA matrix $1 \cdot 10^{15}$ Ω·m. It is clear that specific resistivity decreases as the concentration of the metal alloy increases (Fig. 2). All the samples demonstrated a linear current-voltage relationship, that means they follow Ohm's Law.
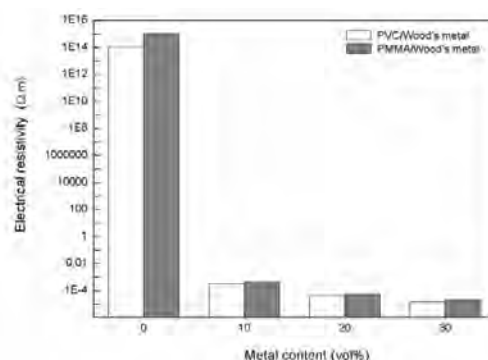

Fig. 2. Electrical resistivity of composites: PVC/Wood's metal and PMMA/Wood's metal

Rys. 2. Rezystywność skrośna kompozytów: PVC/stop Wooda, PMMA/stop Wooda

The polymer-low melting metal alloy systems which are prepared by melt blending in an extruder and then the metal is dispersed in the matrix, do not have as

good conductivity with a similar composition as the composites presented here. For comparison, the polystyrene composite filled with a Sn-Pb alloy powder described by Yi et al. [6] can be mentioned. The room-temperature resistivity of the samples varied from 1 to 10^{16} $\Omega \cdot m$. For the samples which were molded below the melting point of the alloy, a sudden drop in resistivity with a 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 conductive pathways through the whole material are formed. A foregoing example is the evidence 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.% Wood's metal loading.

Thermal properties

Figures 3 and 4 show the Vicat temperature and thermal conductivity dependence on the filler content. A comparison between the properties of the polymer matrices and the corresponding composites is also shown. Generally, the softening point of the composites decreases slightly or 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.
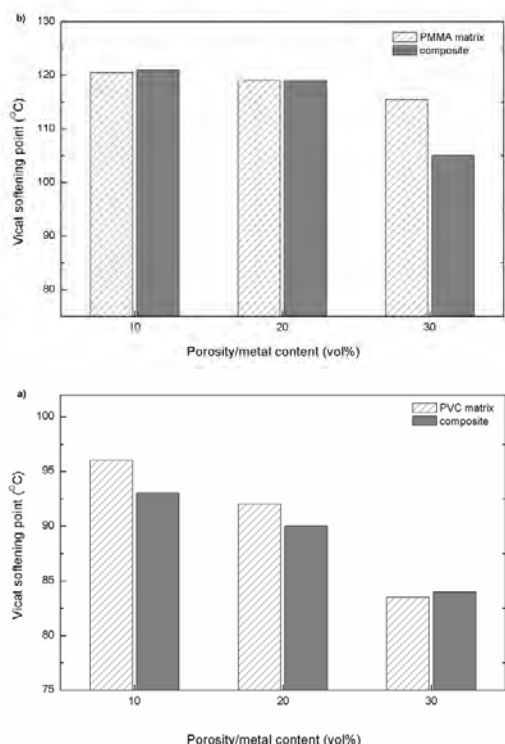

Fig. 3. Vicat temperature of composites: a) PVC/Wood's metal, b) PMMA/Wood's metal

Rys. 3. Temperatura mięknienia wg Vicata kompozytów: a) PVC/stop Wooda, b) PMMA/stop Wooda

In contrast to electrical conductivity, the concentration dependence of thermal conductivity does not show the percolation behavior. Wood's metal exhibits a thermal conductivity of 18 W/Km, PVC and PMMA ca. 0.5 W/Km. Composites containing 30 vol.% metal alloy exhibited a maximal thermal conductivity of 1.5 W/K·m. The thermal conductivity of the composites increases but only slightly and its value is still closer to the polymers than to the metals. This situation was unexpected and further investigations are necessary.
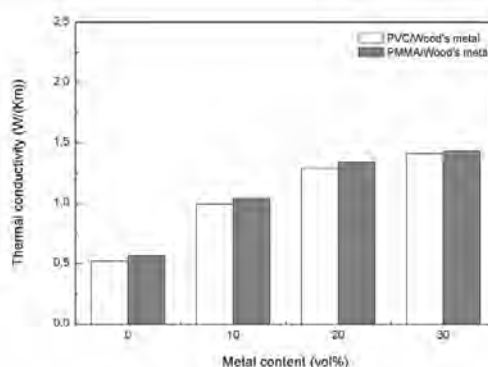

Fig. 4. Thermal conductivity of composites: PVC/Wood's metal and PMMA/Wood's metal

Rys. 4. Przewodnictwo cieplne kompozytów: PVC/stop Wooda, PMMA/ stop Wooda

SUMMARY

Composite materials based on a thermoplastic polymer and low melting metal alloy were prepared by filling the PVC or PMMA porous matrix with Wood's metal in a liquid state. Such systems consist of two continuous, interlaced 3D networks. The network phase structure was proved by scanning electron microscopy. The results of electrical resistivity measurement show that the materials conduct electrical current well, even at 10 vol.% metal alloy loading. The resistivity value varies from $4.2 \cdot 10^{-4}$ to $1.5 \cdot 10^{-5}$ $\Omega \cdot m$ and depends on the Wood's metal content. The type of matrix has almost no influence although the resistivity of PVC and PMMA differs by one order of magnitude.

Although the electrical conductivity of composites is very high, the thermal conductivity improved only slightly. Composites containing 30 vol.% of metal alloy exhibited a thermal conductivity of 1.5 W/K·m which increased 3 times in comparison to pure polymer.

A slight reduction in the Vicat softening point of the composites was observed. It is due to the low melting temperature of the alloy, i.e. 70°C.

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