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Selected electrical and thermal properties of polylactide/graphite composites

RAPID COMMUNICATION

Summary — The influence of graphite on volume and surface resistivity as well as on some thermal properties of composites containing a polylactide matrix was studied. The graphite content was up to 50 wt. %. It was found that the volume and surface resistivity decreased with the increasing graphite content and the percolation threshold appeared at the level of the filler content of 30–40 wt. %. No essential influence of graphite on phase transition temperatures was observed. However, the phenomenon of cold crystallization appeared. The sample mass loss upon heating started at *ca.* 270 °C.

Keywords: polylactide/graphite composites, electrical properties, phase transition temperature of polymer matrix, thermal stability.

WYBRANE WŁAŚCIWOŚCI ELEKTRYCZNE I CIEPLNE KOMPOZYTÓW POLILAKTYD/GRAFIT

Streszczenie — W pracy badano wpływ grafitu na rezystywność skrośną i powierzchniową oraz na niektóre właściwości cieplne kompozytów z osnową polilaktydową. Zawartość grafitu w tych kompozytach wynosiła od 0 do 50 % mas. Stwierdzono, że wraz ze wzrostem zawartości grafitu maleją rezystywność skrośna i powierzchniowa, a próg perkolacji występuje na poziomie 30–40 % mas. zawartości napełniacza (rys. 1, tabela 1). Nie stwierdzono w badanych kompozytach istotnego wpływu dodatku grafitu na wartości temperatury przejść fazowych, natomiast zaobserwowano występowanie zjawiska zimnej krystalizacji (rys. 2, tabela 2). Badania termogravimetryczne wykazały, że rozkład termiczny przejawiający się ubytkiem masy rozpoczyna się w temp. ok. 270 °C (rys. 3).

Słowa kluczowe: kompozyty polilaktyd/grafit, właściwości elektryczne, temperatura przejścia fazowego osnowy polimerowej, stabilność termiczna.

Polymeric composites containing graphite are being applied in various areas of engineering since many years. They are also a subject of intensive scientific investigations that have been inspired to a great extent by many new possible applications. Unique combinations of various physical and chemical properties of graphite, being an allotropic form of carbon, are advantageous in this aspect. Many features of that filler used as a dispersed phase of the composites are of a great practical importance. These are: high conductivity of electric current and heat, low thermal expansion coefficient, high thermal stability, relatively low specific gravity, high resistance to aggressive chemical compounds, and valuable tribologi-

cal properties (self-lubrication). In recent years, a rapid increase in the significance of polymeric nanocomposites is observed. The nanoparticles of graphite enable improvement of mechanical properties of these nanocomposites, including tensile strength and modulus of elasticity in tension (Young's modulus). General properties of various products obtained from polymeric composites and nanocomposites containing graphite are relatively well recognized [1–4].

Polymeric composites and nanocomposites containing graphite are used to produce materials:

- conducting electric current,
- exhibiting antistatic properties (*i.e.*, preventing from accumulating electric charge),
- acting as shields of various kinds, including elements of military equipment, against electromagnetic radiation.

They are also of a great interest as materials to manufacture capacitors and electrodes [5, 6]. They are the sub-

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ject of many studies, including investigation of the percolation threshold appearing while conducting the electric current. This threshold mainly depends on the kind of a polymer matrix, the method of graphite preparation, and the size of its particles [7, 8].

The thermally exfoliated graphite, introduced in the amount of 5–70 wt. % into organic polysiloxanes, makes the composites conduct electric current. They exhibit high anisotropy of volume resistivity in two mutually perpendicular directions and may be used as detectors in various measuring systems. The percolation threshold of these materials appears at the graphite contents of 4 wt. % [7]. In order to determine this threshold, one may use an analytical model presented by Li and Kim [8]. It enables to investigate the effect of a mean distance between the graphite plates as well as their thickness, diameter, and specific surface area on the percolation threshold.

The electric field induced in these materials substantially affects electric conductivity of the polymeric composites containing graphite as well. It causes orientation of graphite nanoplates, consistent with the field lines, which in turn increases electric conductivity [9]. Application of the methods for intercalation and/or exfoliation of graphite enables to diminish volume and surface resistivity, to increase both the thermal conductivity coefficient and the tensile strength of polymeric materials containing that filler, and to use these materials as coatings for metal products [10–12].

The purpose of the present work was to examine the influence of graphite on some electrical, and thermal properties of composites with a polylactide matrix. So far, the authors have not found any results of such studies in the available literature. Nevertheless, the need to perform these investigations is justified by expectations of a rapid growth of polylactide applications.

EXPERIMENTAL

Materials

The studied composites contained the following components:

– Poly(lactic acid) (PLA), type 2002D (NatureWorks®, USA) used as a polymer matrix, characterized by the melt mass-flow rate (*MFR*) equal to 4.3 g/10 min (2.16 kg, 210 °C), density $d = 1.24 \text{ g/cm}^3$, number-average molecular weight $\bar{M}_n = 79\,000$, and content of D-mers equal to 3.5 %.

– Graphite, type 231-955-3 (POCH S.A., Poland) used as a filler, characterized by the 325 mesh fraction equal to 85 %.

Sample preparation

A co-current twin-screw extruder, type TSK 20 (Bühler, Germany), equipped with segmented screws of diameters of 20 mm and length/diameter ratio of 40, was

used to produce granulated materials: PLA and PLA/graphite composites with 5, 10, 20, 30, 40, and 50 wt. % content of graphite, denoted as L, LG5, LG10, LG20, LG30, LG40, and LG50, respectively. The temperatures of barrel heating zones I, II, III, and IV and of the extruder die were set to 190, 195, 195, 195, and 195 °C, respectively.

The rectangular samples $6 \times 6 \times 1 \text{ mm}$ in size were prepared from these granulated materials, using a laboratory injection molding press type Battenfeld Plus 35/75 (Battenfeld GmbH, Germany). The samples were denoted the same way as the extruded materials. The temperatures of barrel heating zones I, II, and III and of the die of the injection molding press were set to 190, 190, 200, and 200 °C, respectively.

Methods of testing

The measurements of volume resistivity (ρ_V) and surface resistivity (ρ_S) were performed with Model 8009 electrodes and Model 6517A electrometer (Keithley Instruments Inc., USA), according to the ASTM D256-07 standard. The examinations were carried out using a constant voltage of 100 V and the measurement time before a change in the voltage polarization was 30 s. The assumed values of ρ_V and ρ_S for individual samples are arithmetic means of ten measurements.

The differential scanning calorimetry (DSC) measurements were performed with a Q 200 calorimeter (TA Instruments, USA) under nitrogen flow, according to the PN-EN ISO 11357-1:2002 standard. About 4 mg of the polymer were placed on an aluminum pan for sampling. The samples were successively quenched to 0 °C, heated to 250 °C at the rate of 5 °C/min, annealed at 250 °C for 3 min, cooled to 0 °C at the rate of 5 °C/min, and reheated to 250 °C at the rate of 5 °C/min. There were determined glass transition temperature (T_g), change in the specific heat (Δc_p) during the glass transition, cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), melting temperature (T_m), and enthalpy of the melting (ΔH_m).

The mass changes of the samples due to decomposition of PLA were measured by a Q 500 thermogravimetric analyser (TA Instruments, USA), according to the PN-EN ISO 11358:2004 standard. Investigations were performed under nitrogen flow with the heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Volume and surface resistivity

Results of the ρ_V and ρ_S measurements are shown in Figure 1. As can be seen, resistivity of both kinds decreases steadily as the graphite content increases up to 40 wt. %. The detailed numerical data on these quantities, compiled in Table 1, allow for a precise analysis of variation of the resistivity. It follows from the table, that within

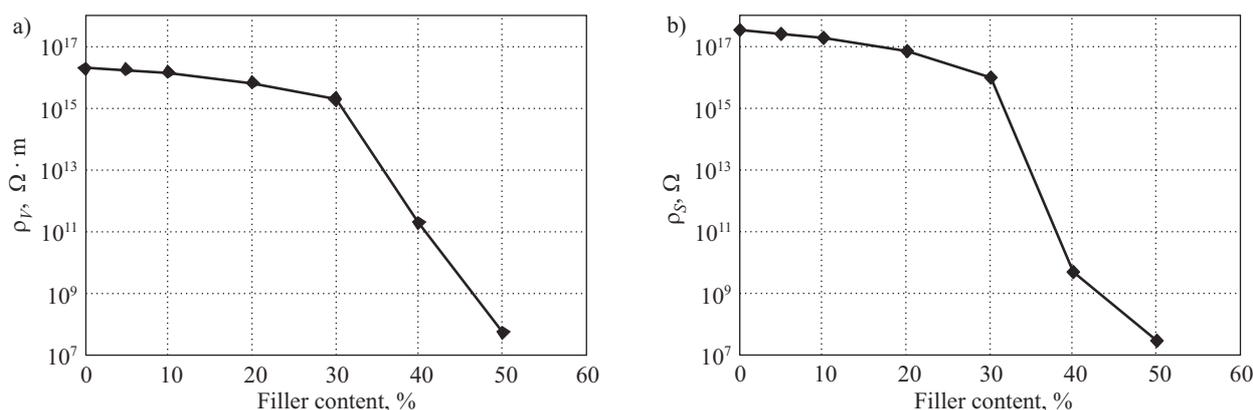


Fig. 1. Effect of the graphite content on the resistivity of PLA/graphite composites: a) volume resistivity (ρ_V), b) surface resistivity (ρ_S)

three successive ranges of the graphite content, *i.e.*, 0–30, 30–40, and 40–50 wt. %, the values of ρ_V and ρ_S decrease respectively 9- and 35-fold (from $18 \cdot 10^{15}$ to $2 \cdot 10^{15}$ $\Omega \cdot m$ and from $35 \cdot 10^{16}$ to $1 \cdot 10^{16}$ Ω), $1 \cdot 10^4$ - and $2 \cdot 10^6$ -fold (from $2 \cdot 10^{15}$ to $2 \cdot 10^{11}$ $\Omega \cdot m$ and from $1 \cdot 10^{16}$ to $5 \cdot 10^9$ Ω), and $3.3 \cdot 10^3$ - and $1.7 \cdot 10^2$ -fold (from $2 \cdot 10^{11}$ to $6 \cdot 10^7$ $\Omega \cdot m$ and from $5 \cdot 10^9$ to $3 \cdot 10^7$ Ω). This means, that in the range of the graphite fraction up to 30 wt. %, a relatively slow decrease in the values of ρ_V and ρ_S occurs. A further growth of the graphite content (in the range of 30–40 wt. %) causes a dramatic decrease in the ρ_V and ρ_S values, which continues for the graphite fraction rising from 40 to 50 wt. %.

Table 1. Volume resistivity (ρ_V) and surface resistivity (ρ_S) of PLA/graphite composites

Symbol of sample	Graphite content, wt. %	$\rho_V \cdot 10^{-15}$ $\Omega \cdot m$	$\rho_S \cdot 10^{-16}$ Ω
L	0	18	35
LG5	5	17	25
LG10	10	14	18
LG20	20	6	7
LG30	30	2	1
LG40	40	$2 \cdot 10^{-4}$	$5 \cdot 10^{-7}$
LG50	50	$6 \cdot 10^{-8}$	$3 \cdot 10^{-9}$

The data indicate also, that in the range of the filler content up to 40 wt. %, ρ_V decreases slower than ρ_S while, in the range of 40–50 wt. %, ρ_V decreases more rapidly than ρ_S . Such large and rapid variations in the values of ρ_V and ρ_S , occurring in the range of the graphite content from 40 to 50 wt. %, indicate that the phenomenon of percolation appears in the studied samples.

Phase transition temperatures

Figure 2 illustrates the DSC curves associated with the second stage of heating of the samples L and LG50. The

DSC curves for the remaining samples are similar in shape and the measurement results for all the samples are summarized in Table 2.

Table 2. DSC data of the investigated composites

Symbols of sample	T_g $^{\circ}C$	Δc_p $J/g \cdot ^{\circ}C$	T_{cc} $^{\circ}C$	ΔH_{cc} J/g	T_m $^{\circ}C$	ΔH_m J/g
L	58.1	0.60	120.2	25.6	150.0	25.7
LG5	58.1	0.43	122.6	15.4	150.1	17.9
LG10	58.0	0.41	122.5	17.3	149.8	18.7
LG20	57.7	0.36	119.0	18.6	149.0	19.1
LG30	58.0	0.30	118.7	15.1	149.1	15.7
LG40	58.3	0.31	116.7	16.7	148.9	17.5
LG50	57.8	0.30	118.6	16.8	149.2	17.9

The results show that the glass transition temperature (T_g) of the studied composites does not essentially vary with the increasing graphite content and is confined to the range of $\Delta T_g = 0.6$ deg, *i.e.*, from 57.7 to 58.3 $^{\circ}C$ (Table 2). No regularity in this small variation was observed. Thus, it can be concluded that graphite does not affect the T_g values of individual composites. On the other hand, the value of specific heat change (Δc_p) steadily decreases from 0.6 to 0.3 $J/(g \cdot ^{\circ}C)$ with the graphite content increasing up to 30 wt. % (Table 2), which is associated with the transition of the PLA matrix from the glassy state to the viscoelastic one. This is caused by reduction in the fraction of the amorphous phase in the composites due to the decreasing content of PLA. For the composites with a higher graphite content (samples LG30, LG40, and LG50), the values of Δc_p do not vary and remain equal to *ca.* 0.3 $J/(g \cdot ^{\circ}C)$.

The phenomenon of cold crystallization observed during heating of the studied composites, occurred in the temperature range of 116.7–122.6 $^{\circ}C$ (Table 2). However, no clear relation between the temperature of cold crystallization (T_{cc}) and the graphite fraction of the composites was found. This indicates that graphite does not influ-

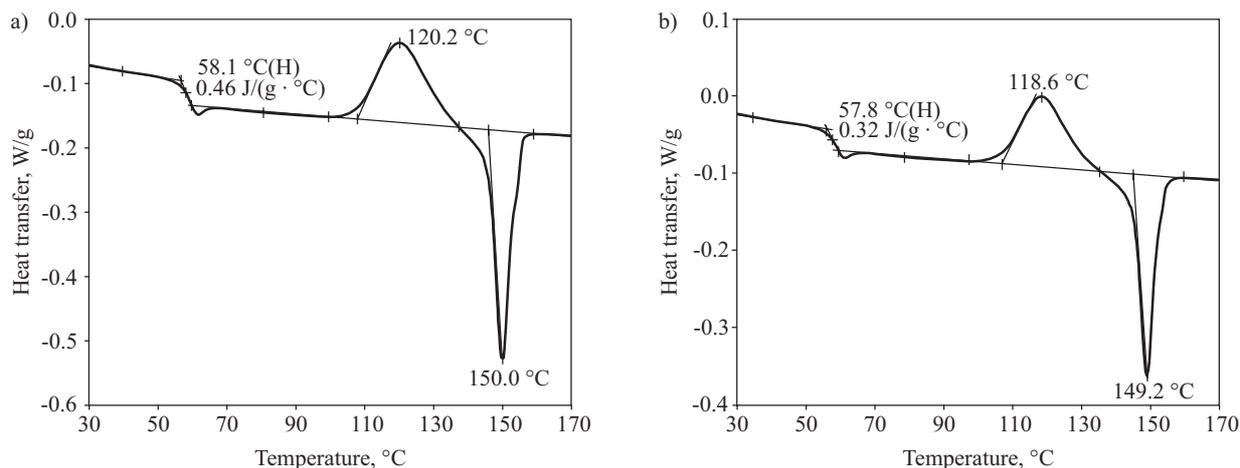


Fig. 2. DSC curves corresponding to the second heating of the samples: a) L, b) LG50

ence the value of T_{cc} , which is due to the fact that graphite does not crystallize within this temperature range. Nevertheless, the cold crystallization enthalpy (ΔH_{cc}) varies (Table 2). It is equal to 25.6 J/g for PLA (sample L) while it decreases to 15.4 J/g for PLA with 5 wt. % of graphite (sample LG5). For the remaining samples, the ΔH_{cc} values range from 15.4 to 18.6 J/g. This suggests that graphite is not a beneficial nucleant for PLA crystallites appearing during the process of cold crystallization.

The melting temperature (T_m) of the studied composites ranges from 148.9 to 150.1 °C (Table 2). However, the changes in T_m do not refer to the graphite content variation. This indicates that graphite does not affect the T_m value, which is due to the fact that graphite does not melt in the temperature range applied in the discussed measurements.

Thermal stability

Figure 3 shows the data from thermogravimetric analysis (TGA curves), including the curves of mass and mass derivative (dm/dT , where m and T are the sample mass and temperature, respectively), which characterize the loss of

mass in samples L and LG50 within a wide range of temperature. The curves for the remaining samples are similar in shape, the only difference is the amount of mass loss at *ca.* 370 °C. Above that temperature, mass losses were not detected for any of the samples, since the latter contain graphite that does not decompose.

When comparing the TGA curves for all the studied composites, one can state that the sample mass losses start at *ca.* 270 °C, independently of the graphite content. The temperatures corresponding to the mass loss of 5% ($T_{5\%}$) and to the mass loss of 50% ($T_{50\%}$) occur within a narrow range (310–316 °C) and (346–352 °C), respectively. The temperatures corresponding to the mass loss of 90% could not be determined because graphite does not decompose in the temperature range applied in the discussed measurements.

CONCLUSIONS

— The volume and surface resistivity of the composites with the PLA matrix decreases as the graphite content increases. The percolation threshold for these materials occurs at a relatively large graphite fraction (*ca.*

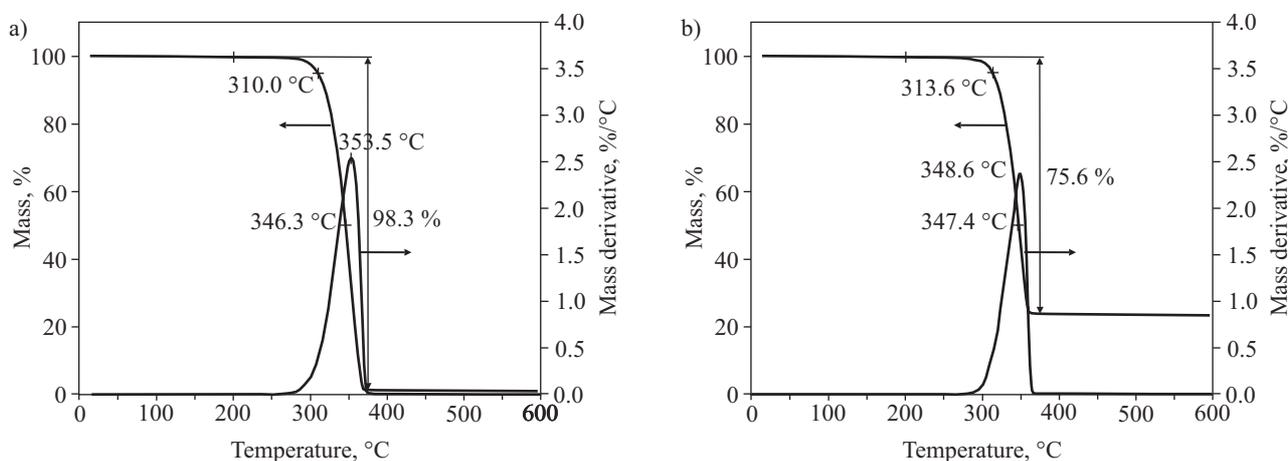


Fig. 3. TGA curves of samples: a) L ($T_{5\%} = 310$ °C, $T_{50\%} = 346.3$ °C), b) LG50 ($T_{5\%} = 313.6$ °C, $T_{50\%} = 347.4$ °C)

30–40 wt. %). This indicates that graphite has to be modified (exfoliated) in order to reduce the filler content, at which the percolation threshold appears.

– Graphite does not essentially influence the phase transition temperatures of the composites with the PLA matrix. It seems that this filler is not beneficial as a nucleant of the crystalline phase. The phenomenon of cold crystallization is observed in the studied composites.

– Independently of the graphite content, the mass losses due to heating of the composites with the PLA matrix start at *ca.* 270 °C.

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