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Processing and mechanical properties of poly(ε-caprolactone)/graphite composites

RAPID COMMUNICATION

Summary — Influence of graphite microparticles on the static tensile strength (σ_M, σ_B, ε_M, ε_B and E), impact strength (u_C), and mass melt flow rate (MFR) of composites including a poly(ε-caprolactone) matrix was investigated. The composites with graphite content from 0 to 50 wt. % were prepared. It was found that the increase in the graphite fraction caused the increase in both the static tensile strength (σ_M) and the longitudinal modulus of elasticity (E) and the decrease in the tensile strain at break (ε_B), Charpy impact strength (u_C), and melt mass-flow rate (MFR).

Keywords: poly(ε-caprolactone)/graphite composites, mechanical properties, impact strength, melt mass-flow rate.

WŁAŚCIWOŚCI PRZETWÓRCZE I MECHANICZNE KOMPOZYTÓW POLI(ε-KAPROLAKTON)/GRAFIT

Streszczenie — W pracy zbadano wpływ mikrocząstek grafitu na właściwości mechaniczne przy statycznym rozciąganiu (σ_M, σ_B, ε_M, ε_B and E), udarność (u_C) i masowy wskaźnik szybkości płynięcia (MFR) kompozytów o osnowie z poli(ε-kaprolaktonu). Przygotowano próbki kompozytów z zawartością grafitu od 0 do 50 %. Stwierdzono, że wraz ze wzrostem zawartości grafitu wzrastają: wytrzymałość przy statycznym rozciąganiu (σ_M) i współczynnik sprężystości wzdłużnej (E), a maleją: wydłużenie względne przy zerwaniu (ε_B), udarność (u_C) i masowy wskaźnik szybkości płynięcia (MFR).

Słowa kluczowe: kompozyty poli(ε-kaprolakton)/grafit, właściwości mechaniczne, udarność, masowy wskaźnik szybkości płynięcia.

For many years, graphite microparticles have been an important filler of composites comprising a polymeric matrix. They change volume resistivity, surface resistivity, and magnetostrictive properties of various polymeric materials. They can also improve some mechanical properties, which enable to apply these materials to manufacture many different articles: shielding against the effects of electric and magnetic fields, protective coatings against accumulation of electrostatic charges, measurement sensors, thermistors and heating elements. The polymer/graphite composites reveal beneficial tribological properties, including self-lubrication [1, 2].

Polymeric nanocomposites containing graphite nanoparticles as fillers are a subject of intensive research and application works as well. This creates unique possibilities to produce new materials of advantageous functional qualities that are unavailable by the use of other methods. Natural graphite exhibits a layer structure; thus, it may be a source of nanoparticles in the form of single plates less than 100 nm thick. At present, such nanoparticles may be produced with three main methods [3—6]:

— oxidation of graphite to obtain graphite oxide, or graphene oxide;

— intercalation of graphite by introduction of atoms or molecules of suitable chemical compounds between the graphite layers;

— expansion of graphite by heat treatment, including microwave irradiation.

The influence of the graphite particles on the properties of a polymer/graphite composite is usually being described by nonlinear functions, frequently including step changes, *e.g.*, in the case of analytical description of the percolation phenomenon. The form of these functions essentially depends on the manufacturing conditions, size, shape and specific surface area of the graphite particles. Therefore, the effects of the interaction between these particles and the polymer matrix should be determined experimentally for each individual composite [7—10].

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The present work was aimed at the investigation of the influence of graphite microparticles on some mechanical and processing properties of composites containing a poly(ε-caprolactone) (PCL) matrix. In recent years, researchers took a new interest in this polymer due to its excellent rheological properties, relatively low production costs and biodegradability. This creates real possibilities to broaden the application area of PCL, especially in relation to the demands of the natural environment protection and to the economical problems of the contemporary world [11]. By now, the authors of this paper have found in the available literature no reports on the results of studies similar to those presented here. The necessity to perform such investigations is justified by expectations of a fast growth of the PLC applications in various areas of technology and economy.

EXPERIMENTAL

Materials

Poly(ε-caprolactone) (PCL), type CAPA® 6800 supplied by Solvay Caprolactones (UK) was characterized by number-average molecular weight $\overline{M}_n$ = 80 000 and melt mass-flow rate *MFR* = 2.6 g/10 min (2.16 kg, 160 °C). This polymer was meant to be extruded or injected and to be used as a matrix.

Graphite, type 231-955-3, of the 325 mesh fraction equal to 85 %, to be used as a microfiller was delivered by POCh S.A. (Poland).

Sample preparation

A concurrent twin-screw extruder, type TSK 20 (Bühler, Germany), equipped with segmented screws 20 mm in diameter and length/diameter ratio of 40, was used to prepare samples of PCL and PCL/graphite composites with 5, 10, 20, 30, 40 or 50 wt. % of graphite, denoted as C, CG5, CG10, CG20, CG30, CG40, and CG50, 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 specimens (dumbbell-shaped) designed to examine mechanical properties by static tension and those (bar-shaped) to perform Charpy impact strength tests were prepared by injection molding with the use of an injection molding press, type Battenfeld Plus 35/75 UNILOG B2 (Battenfeld GmbH, Germany), with the screw diameter of 22 mm, shot volume of 38 cm^3 and specific injection pressure of 200 MPa.

In order to ensure uniform experimental conditions to all the samples, the C samples were prepared using granulated PCL that was previously extruded once with the TSK 20 extruder. The PCL/graphite composites were additionally extruded in connection with the introduction of graphite.

Methods of testing

A tensile testing machine, type TIRATEST 27025 (TIRA GmbH, Germany), was used to examine the specimen mechanical properties under static tension, according to the standards PN-EN ISO 527-1:1998 and PN-EN ISO 527-2:1998. The tensile rate was set to 50 mm/min. The following quantities were determined: tensile strength (σ_M), tensile stress at break (σ_B), tensile strain at tensile strength (ε_M), tensile strain at break (ε_B), and longitudinal modulus of elasticity (Young's modulus denoted as E).

A hammer, type IMPats-15 (ATS FAAR, Italy), was utilized to determine Charpy impact strength (u_C), according to the standard PN-EN ISO 179-1:2004. The energy applied was set to 2 J. Specimens with a notch type A made by a notching machine type 6816000 (CEAST, Italy) were examined.

A melt indexer, Model MP 600 (Tinius Olsen, USA), was used to measure the melt mass-flow rate (*MFR*), according to the standard PN-EN ISO 1133:2006. The piston load was 2.16 kg and measurement temperature 160 °C.

The values of σ_M, σ_B, ε_M, ε_B, E, and u_C were determined using 12 specimens of each composite, while two extreme results were neglected and the arithmetic mean of 10 remaining ones as well as standard deviation of the mean were derived.

RESULTS AND DISCUSSION

Mechanical properties under static tension

The stress-strain curves for the C and CG50 samples are shown in Figure 1. The curves for the remaining composites would lie between the two presented ones and are not shown. The effect of graphite content on σ_M and σ_B of composites is shown in Figure 2.

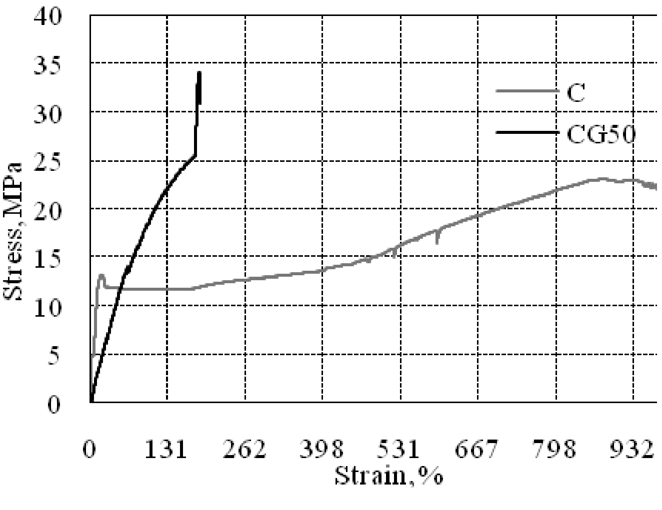

Fig. 1. Stress-strain curve for poly(ε-caprolactone) (C) and composite with 50 wt. % of graphite content (CG50)

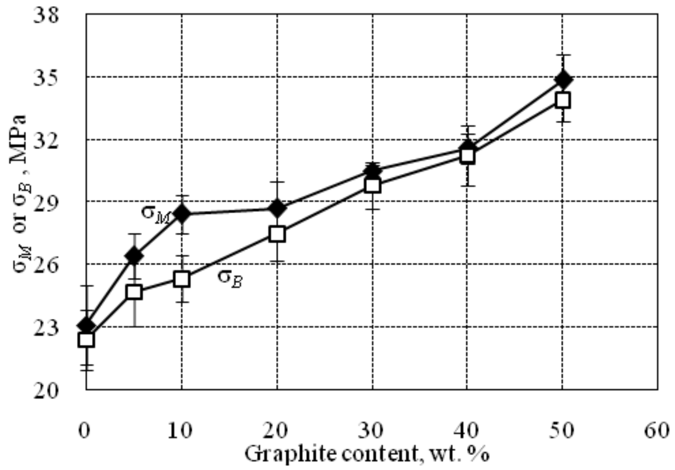

Fig. 2. Tensile strength (σ_M) and tensile stress at break (σ_B) as functions of the graphite content for poly(ε-caprolactone)/graphite composites

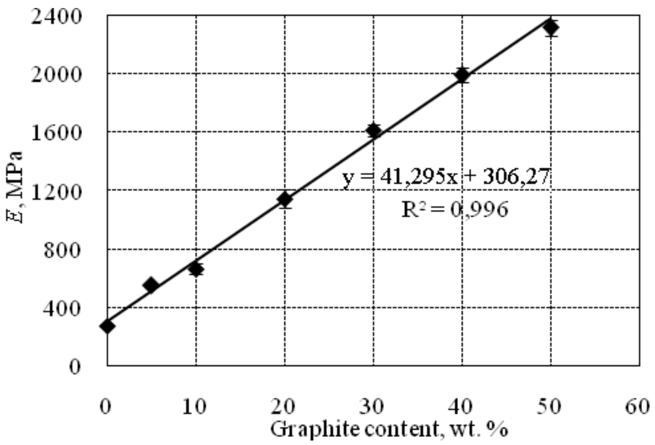

Fig. 4. Longitudinal modulus of elasticity (E) as a function of the graphite content for poly(ε-caprolactone)/graphite composites

The values of σ_M and σ_B increase with the rising content of graphite. When the graphite concentration is 10 wt. % (composite CG10), the difference between σ_M and σ_B is the largest (*ca.* 3.1 MPa). The increase in σ_M of the particular composites is significant and roughly directly proportional to the graphite content. The largest value of σ_M was found for CG50 (34.9 MPa) and it constituted 151 % of the value for sample C (original PCL). This fact demonstrates that distribution of graphite within the polymeric matrix is uniform and that graphite wettability toward plasticized PCL is favorable. As a result, the obtained composites become strengthened, which is proved by the increase in the tensile strength.

Figure 3 presents the effect of graphite content on ε_M and ε_B. The values of ε_M and ε_B significantly decrease with the increasing graphite content while the differences between these quantities for the particular composites are slight. These relations can be approximated with high accuracy (R^2 = 0.9833) by a first-order polynomial. The considerable reduction in the ε_M and ε_B values (that are in sample CG50 more than four times smaller than in sample C) is caused by the graphite particles that diminish mutual slip of the PCL macromolecules. This hinders a possibility for the polymer chains to straighten upon tensile force.

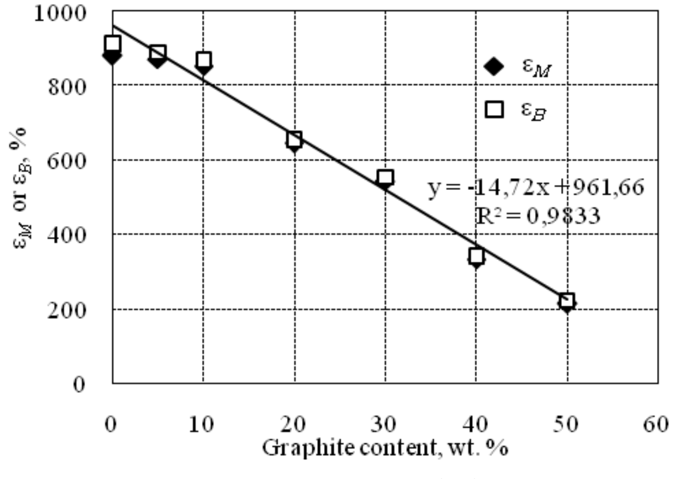

Fig. 3. Tensile strain at tensile strength (ε_M) and tensile strain at break (ε_B) as functions of the graphite content for poly(ε-caprolactone)/graphite composites

As it is shown in Figure 4 the *E* values of the composites linearly increase with the rise of the graphite fraction. The *E* modulus in sample CG50 is more than eight times larger than in sample C. The reason for that is the diminishing of a possibility for the PCL macromolecules to displace with respect to one another, which is caused by the graphite microparticles.

Charpy impact strength

The relationship between u_C and graphite concentration is illustrated in Figure 5. The values of u_C linearly decrease with the rising graphite content. The u_C value for sample CG50 is by *ca.* 57 % smaller than in sample C. This reduction is caused by the graphite particles that hinder

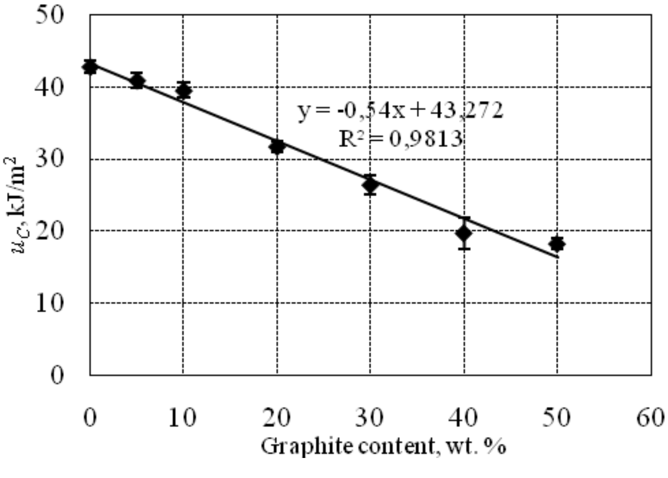

Fig. 5. Charpy impact strength (u_C) as a function of the graphite content for poly(ε-caprolactone)/graphite composites

movements of the PCL macromolecules. Nevertheless, the impact strength of the composites remains relatively high: in the extreme case of CG50, it is 18.8 kJ/m^2, which is significantly higher than that for polylactide.

Melt mass-flow rate

The effect of graphite content on *MFR* is presented in Figure 6. The *MFR* values decrease as the graphite concentration increases. The relations are roughly linear and can be approximated with high accuracy ($R^2 = 0.9846$) by a first-order polynomial. The changes result from a rise in viscosity of plasticized composites caused by graphite. As a consequence, the *MFR* of, *e.g.*, sample CG50 constitutes merely 7 % of *MFR* value of sample C.

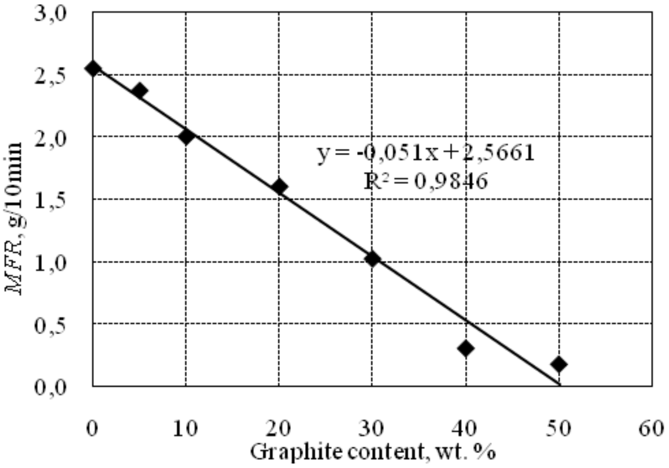

Fig. 6. Melt mass-flow rate (MFR) as a function of the graphite content for poly(ε-caprolactone)/graphite composites

The reduced *MFR* values result in higher flow resistance of plasticized composites in channels of machine equipment used in the processing of plastics and cause an increase in the energy consumption as well as in the cost of wear and tear for processing machines and tools.

CONCLUSIONS

— Graphite microparticles introduced into a poly(ε-caprolactone) matrix cause an essential increase in the tensile strength, large increase in the longitudinal modulus of elasticity (Young's modulus), and decrease in the tensile strain at break. These quantities vary linearly with the increasing graphite content and the relations can be approximated with a high accuracy by a first-order polynomial.

— A reduction in the tensile strain at break does not worsen functional qualities of the studied composites. The composite with the largest graphite content (50 wt. %) exhibits the value of ε_B equal to *ca*. 220 %.

— An increase in the graphite content decreases the impact strength of the composites. Nevertheless, the material containing even 50 % of graphite shows the u_C value relatively large in relation to the values for many other plastics.

— A significant reduction in the melt mass-flow rate with the rising graphite content of the composites limits possibilities of processing of these materials. Therefore, the graphite fraction in the composites should not exceed 20 wt. %.

The above conclusions point out a possibility to utilize graphite microparticles to improve some properties of the poly(ε-caprolactone)/graphite composites. In order to confirm and broaden these conclusions, further research is planned, including studies on the material structure, dielectric properties, and percolation threshold.

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