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THERMOPHYSICAL, RHEOLOGICAL AND MORPHOLOGICAL PROPERTIES OF POLYOXYMETHYLENE POLYMER COMPOSITE FOR ADDITIVE TECHNOLOGIES

S. M. Lebedev, O. S. Gefle, E. T. Amitov, D. V. Zhuravlev, and D. Yu. Berchuk UDC 537.9

The paper presents investigations into thermophysical, rheological, and morphological properties of graphitized carbon nanotube/polyoxymethylene composites containing 30 wt.% graphite and 0.1 wt.% nanotubes. It is shown that thermal conductivity and thermal diffusivity of graphitized carbon nanotube/polyoxymethylene composites increase respectively by 8 and 11 times in comparison with the original polyoxymethylene. And their melt flow index reduces approximately by 3.5 times. In spite of the abrupt decrease in the melt flow index, graphitized carbon nanotube/polyoxymethylene composites can be used in extrusion, jet molding and three-dimensional printing.

Keywords: polyoxymethylene, graphitized carbon nanotube/polyoxymethylene composite, additive technology.

INTRODUCTION

Polyoxymethylene (POM) is a high technology, engineering plastic widely used in various precision devices and such industries as electrical engineering, electronic engineering, motor vehicle, and some others. POM is characterized not only by high mechanical strength, thermal stability, produceability and excellent tribological properties, but also consistent heat resistance owing to its high crystallinity [1–5].

In recent years, a variety of polymer/graphite compositions possessing high thermal conductivity have been created. Thus, Agari *et al*. [6] indicated that thermal conductive polyethylene/graphite composite had 1.53 $W \cdot m^{-1} \cdot K^{-1}$ thermal conductivity at a graphite content of approximately 20 vol.%. In work of Krupa *et al*. [7], it was shown that the highest thermal conductivity of high-density polyethylene/graphite and low-density polyethylene/graphite composites was respectively 2.3 and 2.0 $W \cdot m^{-1} \cdot K^{-1}$ at a graphite content of 37 vol.%. In previous research [8] we showed that the linear low density polyethylene/graphite composite had 6.4 $W \cdot m^{-1} \cdot K^{-1}$ thermal conductivity at a graphite content of 30 vol.%, whereas in [9] we found that thermal conductivity of the polylactide/graphite composite was 3.8 $W \cdot m^{-1} \cdot K^{-1}$ at the same graphite content and 1.0 wt.% of single-walled carbon nanotubes.

In order to increase the working temperature and physical and mechanical properties in modern electronic and electric devices, it is necessary to develop new thermal conductive polymer compositions with higher thermal stability. So there were numerous attempts to improve POM properties allowing to rise the working temperature up to 100–140°C. However, very little published information is available concerning the advanced, thermal conductive POM-based compounds. Thus, Zhao and Ye [10] developed new POM/graphite composites with the additive content of 30 wt.% which increases thermal conductivity up to 1.15 $W \cdot m^{-1} \cdot K^{-1}$ (cf. 0.36 $W \cdot m^{-1} \cdot K^{-1}$ for original POM). In work of He *et al*. [3], a new, POM-based composite material with the addition of copper powder was proposed. It was shown that the copper powder did not affect thermal conductivity at a copper content less than 10 wt.%. At a higher

National Research Tomsk Polytechnic University, Tomsk, Russia, e-mail: lsm70@mail.ru; gefleos@mail.ru; ernar_amitov.91@mail.ru; zhuravlevden1618@gmail.com; berchukdy@gmail.com. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 6, pp. 25–29, June, 2018. Original article submitted October 31, 2017.

concentration of the copper powder in that composition, thermal conductivity reached 0.477 $W·m^{–1}·K^{–1}$ at 25 wt.% Cu as compared to the original POM composite. Recently, Apium Additive Technologies GmbH Company (Karlsruhe, Germany) [11] developed Apium POM-C ESD, a new polymer composite material filled with the antistatic agent applied in additive technologies. There is however no information in the literature about the main properties of this material.

The aim of this work is to study thermophysical, rheological, and morphological properties of graphitized carbon nanotube/polyoxymethylene (CNT/POM) composites.

1. MATERIALS AND METHODS

An engineering plastic KOCETAL® K700 polyoxymethylene manufactured by Kolon Plastics Inc. (Korea) was used in this experiment as a polymer matrix. KOCETAL® K700 is a low viscosity polyacetal polyoxymethylene copolymer grade having a 1.41 g/cm^3 density and 166°C melting temperature. The natural graphite powder with the average grain size of 65 μm and single-walled carbon nanotubes (SWCNTs) Tuball^{TM} from OCSiAl (Novosibirsk, Russia) were used as fillers. All these materials were not additionally processed. The amount of graphite and SWCNTs in polymer compositions was 30 and 0.1 wt.%, respectively.

Polymer compositions were prepared in a Brabender measuring mixer (Germany) of the electrically heated type 50 EHT, with a 55 cm^3 volume of the mixing chamber. Compounding was performed at 190°C during 10 minutes. The rotation velocity of the mixer blades varied from 30 to 90 rpm. Next, graphite powder and SWCNTs were gradually introduced in the polymer melt. Plastic pellets were then produced with a Brabender granulator (Germany) from the composition obtained. Using a hydraulic press, test samples 85×65×6 mm in size were obtained from pellets in a vacuum hot-pressing furnace.

Linseis THB 100 thermal analyzer (Germany) was used to measure thermal conductivity and thermal diffusivity by means of the transient hot bridge method (modified hot wire method) [12]. This analyzer with a strip heater and temperature sensors was placed between two identical plates made of the same composite material.

The melt flow index for the original POM and graphitized CNT/POM composites was measured at 190°C and 2.16 kg load using a CEAST MF20 test machine from Instron (Italy).

Morphology of POM and graphitized CNT/POM composites was studied on Zeiss LEO EVO 50 scanning electron microscope (Germany) at accelerating voltage of 20 kV. Composite samples were fractured in liquid nitrogen. After that silver was deposited on fractured surfaces using a vacuum evaporation method.

Fused deposition modeling was used to produce POM and graphitized CNT/POM composite samples on the Inspire S200 3D printer (Beijing TierTime Technology Co. Ltd, China). This 3D printer is equipped with 0.4 mm nozzle extruder which locates on a computer-controlled platform moving in Cartesian space and a 150×200×200 mm heated chamber with a lower bed. The temperature of the extruding head and the heated chamber achieves 260°C and 100°C, respectively. POM and graphitized CNT/POM filaments with the diameter of 1.75 mm used in conventional process of 3D printing were produced with a Brabender twin screw extruder (Germany).

2. RESULTS AND DISCUSSION

2.1. Thermophysical properties

Thermophysical properties of the original POM and graphitized CNT/POM composites are given in Table 1. According to this table, thermal conductivity λ of the original POM is 0.34 $W·m^{–1}·K^{–1}$, whereas for graphitized CNT/POM composite it achieves 2.785 $W·m^{–1}·K^{–1}$, *i.e.* almost eight times higher than for POM. And thermal diffusivity α increases by more than 11 times.

At a similar content of graphite, thermal conductivity (2.23 $W·m^{–1}·K^{–1}$) and thermal diffusivity ($3.6·10^{–7}$ $m^2·s^{–1}$) [8] are substantially higher for the graphitized CNT/POM compound as compared to the low density polyethylene/graphite composite. This is due to a higher POM crystallinity and the presence of carbon nanotubes.

TABLE 1. Thermophysical Properties

Composites	Thermal conductivity, λ, $W \cdot m^{-1} \cdot K^{-1}$	Thermal diffusivity, $\alpha \cdot 10^6$ $m^2 \cdot s^{-1}$
POM	0.341	0.148
Graphitized CNT/POM	2.785	1.69

TABLE 2. Melt Flow Index Measurements

Composites	POM	Graphitized CNT/POM
Melt flow index, grams per 10 min	27.0	7.6

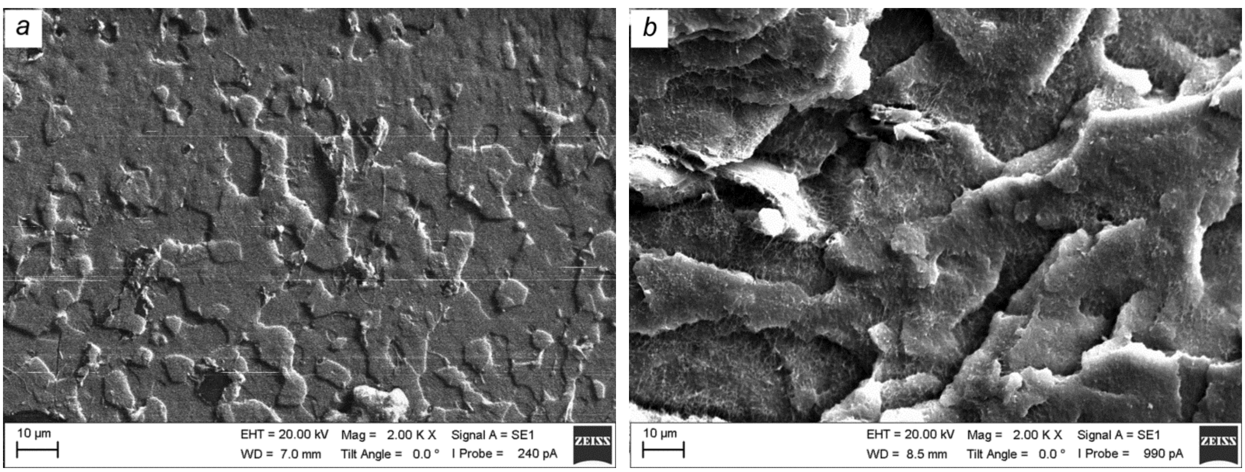

Fig. 1. SEM images of composite morphology: *a* – POM; *b* – CNT/POM; *c* – graphitized CNT/POM.

2.2. Rheological properties

Table 2 contains measurement results of the melt flow index. As can be seen, the introduction of fillers in the POM matrix results in 3.55 times reduction in the melt flow index. This indicates that the graphitized CNT/POM compound becomes more rigid. But even lower values of the melt flow index allow the graphitized CNT/POM compound to be processed not only by such conventional techniques as extrusion and jet molding, but also three-dimensional printing technique.

2.3. Morphology

The morphology of the original POM and graphitized CNT/POM composites was investigated using the scanning electron microscopy (SEM). The content of graphite was 30 wt.% and the content of SWCNTs was 0.1 wt.%. Figure 1 presents SEM images of the original POM and graphitized POM and CNT/POM composites. The particles of graphite and SWCNTs are distributed rather uniformly in the polymer matrix and form a dense, heat conducting network. The introduction of SWCNTs in graphitized POM results in the formation of additional SWCNT bridges which are in a close contact with the surface of graphite particles [9]. It means that both one-dimensional carbon nanotubes and three-dimensional network consisting of graphite particles contribute to the formation of a hybrid network in the POM matrix. A large contact area between the POM matrix and three-dimensional hybrid network increases the number of SWCNT bridges for phonon diffusion and decreases the transient interfacial resistance [13–16].

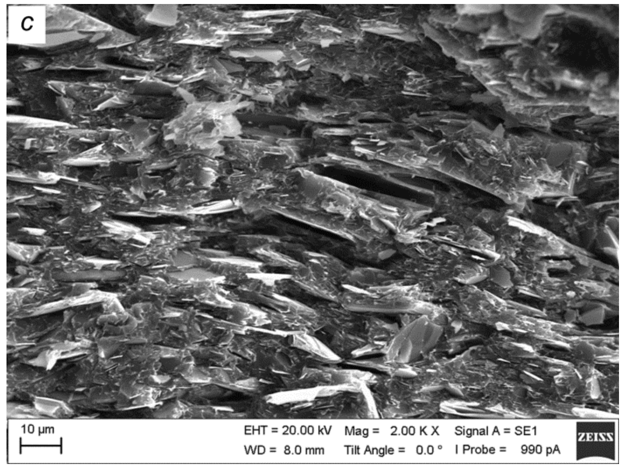

Fig. 1 continued

Fig. 2. POM- and graphitized CNT/POM-based cable clamps fabricated using a 3D printer.

In turn, high values of thermal conductivity and thermal diffusivity are determined by the hybrid three-dimensional network presenting in the bulk of the graphitized CNT/POM compound.

2.4. 3D printing

In order to apprise the potential for the original POM and graphitized CNT/POM compound to be used for 3D printing, small test models of cable clamps are fabricated using a 3D printer (Fig. 2). It is found that these test models possess a high mechanical strength, rigidity and temperature stability. And proposed POM compositions fully comply with requirements for 3D printing technique.

CONCLUSIONS

As a result of this research, we studied thermophysical, rheological, and morphological properties of the original POM and graphitized CNT/POM compound containing 30 wt.% graphite and 0.1 wt.% of carbon nanotubes. It was shown that thermal conductivity and thermal diffusivity of graphitized CNT/POM compound increased respectively by 8 and 11 times in comparison with the original POM.

Rheological measurements showed that the melt flow index of graphitized CNT/POM compound decreased by 3.5 times against the original POM and equaled 7.6 grams per 10 minutes, that is sufficient for its use in extrusion, jet molding and three-dimensional printing.

Graphite particles and SWCNTs were uniformly distributed in the polymer matrix. The extensive, heat conducting network intensively formed within the bulk of the composite material, which was observed during SEM investigations.

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