

# THERMOPHYSICAL AND DIELECTRIC PROPERTIES OF POLYMER COMPOSITES FILLED WITH HEXAGONAL BORON NITRIDE

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*Thermophysical and dielectric properties of polymer composites based on linear low density polyethylene (LLDPE) and polylactide (PLA) filled with hexagonal boron nitride (hBN) have been studied. It is found that all the studied composites possess dielectric properties and increased thermal conductivity compared with initial polymer matrices. Unlike carbon-containing fillers (carbon black, graphite, graphene, carbon nanotubes), hBN is a good insulator and therefore, it is more suitable as a filler for the manufacture of heat-releasing materials with purely white appearance. At the same time, both LLDPE/hBN and PLA/hBN composites with a filler content of 40 wt.% possess comparable thermal conductivity about  $0.7 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , which is almost 95% and 250% higher, than those for the initial LLDPE and PLA, respectively.*

**Keywords:** thermophysical and dielectric properties, polymer composites, hexagonal boron nitride, extrusion.

## INTRODUCTION

Thermally conductive polymer composites open up new opportunities for replacing metal structures in various devices, such as heat exchangers, radiators, “smart” materials (the so-called shape memory polymer composites), electronics, electrical devices, etc., due to the low specific weight, good corrosion resistance, and processability. The smaller the size of such devices, the more difficult it is to remove the generated heat from them. Small electronic devices, such as laptops and mobile phones, cannot be equipped with external cooling systems such as radiators or fans. Therefore, many parts used in these devices must themselves remove heat from these devices [1]. It is well known that carbon-containing fillers such as graphite (G), carbon black (CB), carbon fibers, carbon nanotubes (CNTs), or graphene are often used as fillers for the next generation of thermally conductive materials [2–9].

The thermal conductivity of the polymer/CNT composites can be increased, but the content of CNTs should be more than 5–10 wt.%. However, this is impractical for two reasons. The first of these is economic efficiency. The price of CNTs is very high, \$8.5/g [10], compared to the price of a conventional carbon-containing filler such as graphite or carbon black. The second reason is technology. In [6], we showed that the melt flow index (MFI) for a composite of polylactide/CNT (PLA/CNT) with 3 wt.% of CNT decreases by about 50 times compared to the initial PLA. This indicates that the composites become more rigid, because the presence of a bulk CNT network prevents the movement of polymer chains, making them more brittle.

Despite the fact that the thermal conductivity of composite materials increases with an increase in the CNT content, this effect is monotonic and a sharp insulator–conductor transition, as for electrical conductivity, is not observed. Previously, many authors noted that such a trend is characteristic of all polymer/CNT composites [11–13]. This is due to the high transient thermal resistance at the interfaces between the CNT and polymer matrix, which is known as the Kapitza interfacial resistance [14–19]. Electric current in polymer/CNT composites is transferred by

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electrons moving along the bulk CNT network, while heat in the polymer composites is transferred by phonons, and thermal conductivity is significantly reduced due to phonon scattering at the interfaces between CNTs and polymer matrix [20–22]. For example, Shenogin *et al.* [23, 24] found that the main difference between thermal and electrical phenomena is the ratio of conductivities. For the thermally conductive CNTs,  $K_f/K_m$  is about  $10^4$  (where  $K_f$  and  $K_m$  are the thermal conductivities of the CNTs and polymer matrix, respectively), while for electrically conductive composites, the ratio of electrical conductivities can be on the order of  $10^{12}$ – $10^{16}$ . At such a high ratio of  $K_f/K_m$ , the only way for the electric current is the bulk network of CNTs. For heat flow in the polymer/CNT composites, the predominant paths of thermal energy flow are always associated with the matrix. As a result, electric current is due to numerous chains of CNTs, while the thermal conductivity is controlled by the polymer matrix and the filler–matrix interfaces.

The easiest way to solve this problem is to use graphite or its derivatives as thermally conductive fillers. In our work [5], we showed that the addition of natural graphite powder to a matrix of linear low density polyethylene (LLDPE) up to a filler content of 30 vol.% makes it possible to increase the thermal conductivity by a factor of 17.8 compared to an LLDPE polymer matrix. The thermal conductivity of the developed LLDPE/graphite composites can be increased up to  $6.4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at 30 vol.% of graphite. The LLDPE/graphite composites can be processed by injection molding and extrusion. Dielectric spectroscopy has shown that the LLDPE/graphite composites possess dielectric properties up to 10 vol.% of filler. Adding more than 15 vol.% of graphite to the LLDPE matrix leads to a significant increase in the electrical conductivity by several orders of magnitude.

Xue *et al.* [8] reported that very high thermal conductivity of biopolymer composites polylactide/expandable graphite (PLA/EG) was obtained at a graphite content of 70 wt.%. The thermal conductivity of the PLA/EG composites reached  $26.87 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , which is approximately 100 times higher than that of the initial PLA. However, as reported in [6], the melt flow index for PLA/G composites, even at 30 wt.% of graphite, is below 1.0 g/10 min. That is, these composites cannot be processed by conventional methods such as injection molding or extrusion when the graphite content is about 70 wt.%. Another important limitation associated with the use of expandable graphite is that it is obtained by treating natural or synthetic graphite with acids and is not an environmentally friendly product.

Very often, one of the main requirements for thermally conductive fillers is that they must be non-conductive (insulating) materials, as opposed to carbon-based fillers. One of such fillers is boron nitride (BN). BN is a wide-gap semiconductor and has three crystal forms:

- hexagonal form ( $\alpha$ ) hBN (“white graphite”, has a hexagonal graphite-like crystal structure);
- cubic form ( $\beta$ ) cBN (a type of sphalerite similar to diamond);
- dense hexagonal ( $w$ ) wBN (wurtzite-like, similar to lonsdaleite).

Boron nitride can exist in the form of various amorphous modifications, as well as in the form of hexagonal nanotubes and monolayers.

Hexagonal boron nitride has high thermal and electrical conductivity, low specific gravity, low production cost, and good mechanical properties. The hBN-filled polymer composites can be processed by injection molding and extrusion, unlike the other two forms of BN, which have the highest hardness and are highly abrasive materials. Many authors have studied thermally conductive composites filled with hBN based on epoxy resins [25, 26], polyimide [27], polyethylene [28–30], etc. Unlike graphite, hBN is a good insulator and therefore, it is more applicable as filler for heat-releasing materials that require purely white appearance of final products, such as heat-sinks for LED lighting devices.

In recent years, environmentally friendly biodegradable polymers such as PLA filled with carbon-based fillers have been widely used in various industries due to their excellent properties as a suitable replacement for conventional petroleum-based polymers [6, 31]. However, at present, the results of experimental work on the creation of biodegradable thermally conductive composites filled with hBN are practically absent in the literature [32, 33], which limits the use of “green” environmentally friendly polymer composites.

This work is aimed at the development and manufacture of LLDPE/ hBN and PLA/ hBN composites, as well as a comparative analysis of the thermophysical and dielectric properties of these thermally conductive insulating composites.

## 1. RESEARCH METHODS AND SAMPLES

### 1.1. Materials

Linear low density polyethylene (LLDPE, Hanwha 7635, Korea) with a melt flow index of 20 g/10 min and commercially available biodegradable polylactide (PLA, Ingeo 4043D, NatureWorks LLC, USA) with a melt flow index of 6 g/10 min were used as polymer matrices. Hexagonal boron nitride powder (hBN, Plazmotherm, Russia) sifted through a 325 mesh sieve was used as a filler. The content of the filler in the polymer composites ranged from 0 to 60 wt.% (from 0 to 39 vol.%). All materials were used in the form, in which they were received from the manufacturer, without additional treatment.

### 1.2. Preparation of composites

All the composites were prepared by melt compounding in a 50 EHT measuring mixer (Brabender). The processing temperature was 170–190°C for composites based on LLDPE and 190–210°C for composites based on PLA, mixing time was 10 min. The rotation speed of the mixer blades varied from 30 to 90 rpm. The filler was introduced into the polymer melt gradually to the required fraction, and mixing was carried out until the filler was distributed evenly in the polymer matrix. After manufacture, all composites were granulated using a granulator (Brabender). The large batches of filled composites were produced on a KETSE 20/40D twin-screw extruder (Brabender). The extruder was equipped with two loading hoppers for the polymer matrix material (main loading) and for the filler (side loading).

### 1.3. Preparation of samples

Samples were prepared by hot pressing. The compression molds filled with pellets of the polymer composite were placed in a vacuum oven preheated to 190°C for 3 h. After that, the compression molds were placed in a hydraulic press, where they were pressed at a pressure of 15 MPa for 20 min. Then, the compression molds were slowly cooled at a rate of 4°C·min<sup>-1</sup> to ambient temperature in air. The samples for measurements were in the form of plates 85×65×(1–6) mm in size.

### 1.4. Measurement methods

The real part  $\varepsilon'$  of the complex permittivity  $\varepsilon^*(f) = \varepsilon'(f) - j\varepsilon''(f)$  and the dielectric loss tangent  $\tan\delta = \varepsilon''(f)/\varepsilon'(f)$  (here,  $\varepsilon''(f)$  is the imaginary part of the complex permittivity,  $\delta = (90^\circ - \varphi)$  is the dielectric loss angle,  $\varphi$  is the phase angle between the voltage and current) were measured using the method of dielectric spectroscopy at a voltage of 3 V AC in the frequency range from 1 to 10<sup>5</sup> Hz using the measuring complex “Solartron”. For all samples, five to ten measurements were performed per decade in the entire frequency range studied. For each material, at least three samples were measured.

The thermal conductivity ( $\lambda$ ) of the samples was studied by the Transient Hot Bridge method (THB) (a modified hot wire method [34], DIN EN 993-14, DIN EN 993-15) using a THB-100 analyzer (Linseis). The measuring sensor, including the heater and temperature sensors, was located between two identical 5 mm thick samples made from the same composite material.

The morphology of the composites, the shape and size of the filler powder particles were studied with an optical microscope and using a Leo Evo 50 scanning electron microscope (SEM) at an accelerating voltage of 20 kV. Samples fractured in liquid nitrogen were made for examination with the electron microscope. The fractured surface of the samples was covered with silver before testing.

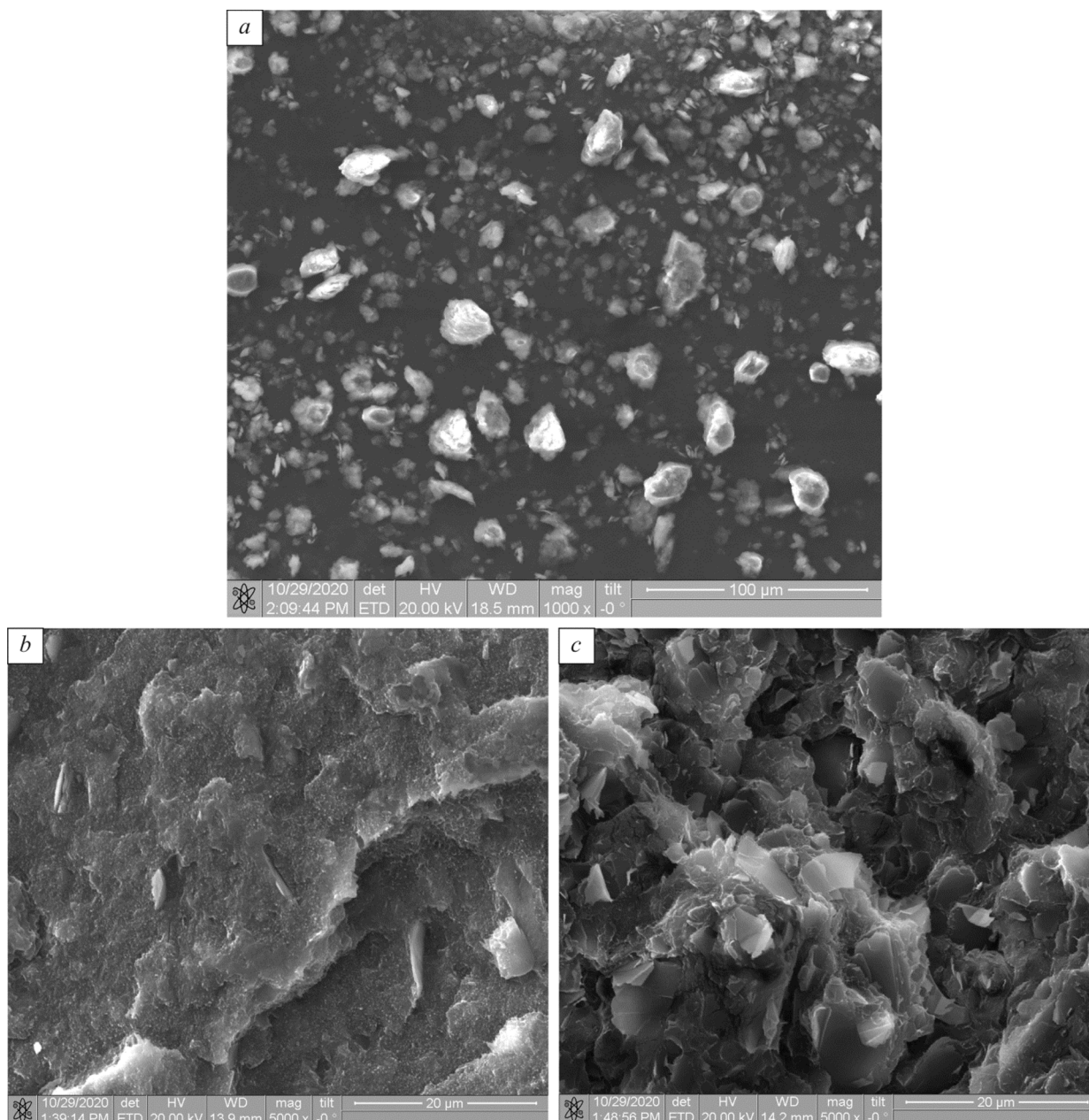


Fig. 1. SEM images of initial hBN powder (a) and composites of LLDPE + 40 wt.% hBN (b) and PLA + 40 wt.% hBN (c).

## 2. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows SEM images of the initial hBN powder and the sub-molecular structure of the LLDPE/hBN and PLA/hBN composites. It was found that the filler particles are uniformly distributed in the volume of the matrix. However, small particles form agglomerates about 10–25 μm in size, which is seen both for the initial hBN powder and for polymer composites. With an increase in the filler content, the filler particles contact each other, forming continuous pathways in the polymer matrix, which leads to an increase in the thermal conductivity of the composites.

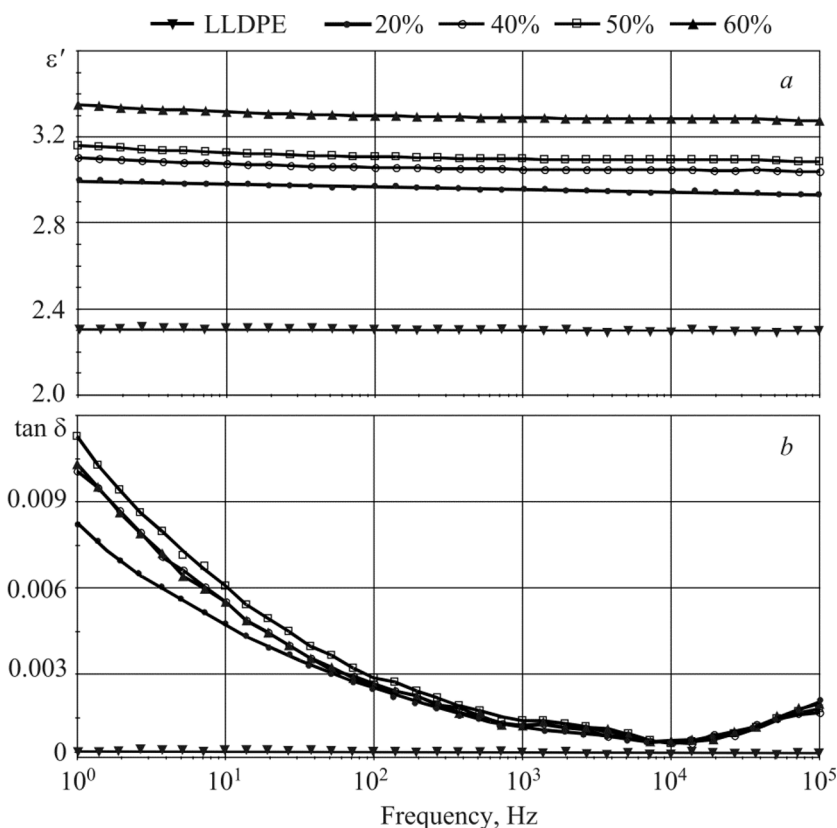


Fig. 2. Frequency dependences of the real part  $\epsilon'$  (a, c) and  $\tan\delta$  (b, d) for composites based on LLDPE (a, b) and PLA (c, d).

The results of dielectric spectroscopy of the initial LLDPE and PLA, as well as composites based on them, are shown in Fig. 2 in the form of the frequency dependences of  $\epsilon'$  and  $\tan\delta$ . It can be seen that upon filling, the real part of the permittivity  $\epsilon'$  for composites based on LLDPE and PLA increases by approximately 35 and 17%, respectively, in the entire studied frequency range, while  $\tan\delta$  does not exceed 0.02 for all composites.

The increase in  $\epsilon'$  is due to the increase in the effective permittivity of the composites due to the higher value of the dielectric permittivity of the filler compared to polymer matrices. For example, the permittivity in the perpendicular direction for a pure hBN monolayer varies from 6.82 to 4.97, while the permittivity in the parallel direction varies from 3.29 to 2.87 at very low and very high frequencies, respectively [35]. In addition, low values of  $\tan\delta$  indicate that all the developed composites have dielectric properties. That is, all LLDPE/hBN and PLA/hBN composites are insulating materials.

Comparison of the dielectric permittivity values of similar PLA/hBN composites is difficult, since the results of studies of such composites are practically absent in the literature. However, Chandar *et al.* [33] showed that the values of the permittivity for PLA/hBN composites with a filler content of 20–30% are 3.2–3.4, which is very close to the values measured by us.

The experimental results of studying the thermal conductivity are shown in Fig. 3. It can be seen that the thermal conductivity of the LLDPE/hBN composites increases from  $0.36 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  for the initial LLDPE to  $0.7 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  for the composite with 40 wt % of hBN, which is about 95% higher than for the initial LLDPE. A further increase in the filler content to 60 wt.% leads to an increase in  $\lambda$  to  $1.26 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ .

For composites based on PLA, the value of  $\lambda$  increases from  $0.193 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  for the initial PLA to  $0.673 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  for PLA with 40 wt.% of hBN, which is approximately 250% higher than for the initial PLA. It can be seen that there is a tendency for a nonlinear increase in the thermal conductivity of both composites with an increase in

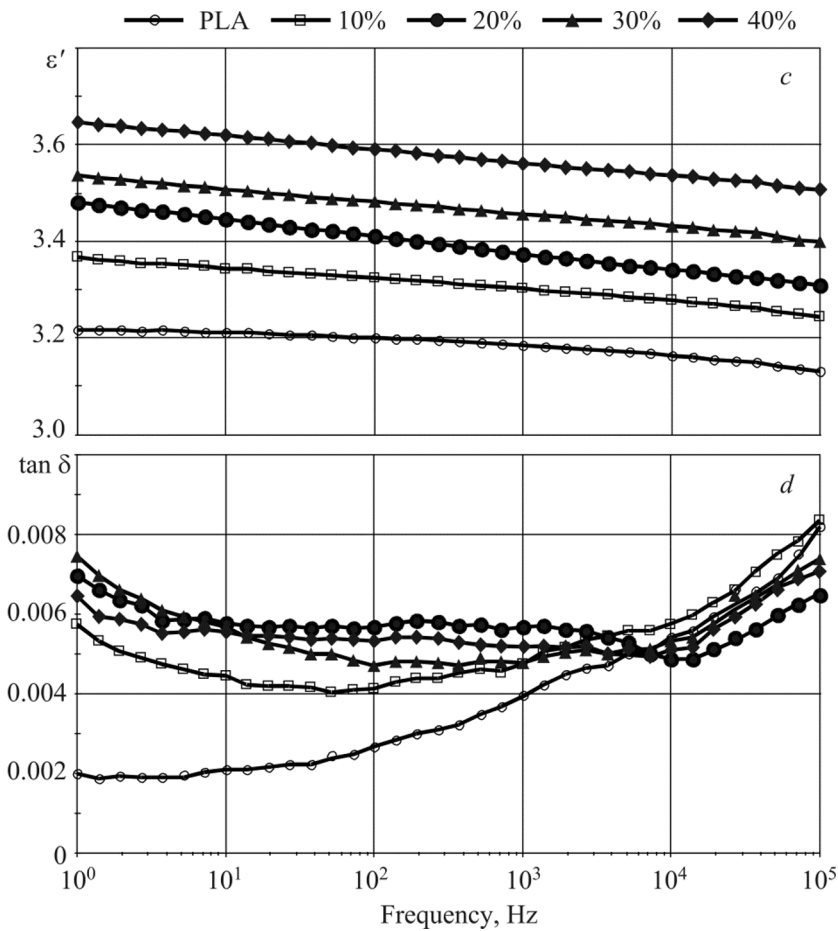


Fig. 2 continued

the filler content, which is due to the formation of a volumetric heat-conducting network of filler particles. The measurement results also showed that the thermal conductivity values for composites based on LLDPE and PLA with the same filler content are practically comparable. However, if we take into account that the time of PLA decomposition in the environment is from 6 months to 2 years, in contrast to 500–1000 years for polyethylene [36], the use of heat-conducting composites based on PLA is more preferable from the point of view of environmental protection, since PLA/hBN composites are biodegradable materials.

## CONCLUSIONS

The thermally conductive insulating composites LLDPE/hBN and PLA/hBN have been developed, manufactured, and studied. It is shown that the real part of the complex permittivity for both LLDPE/hBN and PLA/hBN composites increases by about 35 and 17% at filling from 0 to 40 wt.%. For all composites in the studied frequency range,  $\tan \delta$  does not exceed 0.02, i.e. all composites are insulating materials. The thermal conductivity of composites based on LLDPE and PLA with a filler content of 40 wt. % increases by factors of 1.9 and 3.5, respectively, compared to those for the initial polymer matrices suggesting that all developed composites are thermally conductive materials. A comparative analysis of thermal and dielectric properties of the developed polymer composites showed that biodegradable polymers such as PLA can successfully replace traditionally used petroleum-based polymers for the production of environmentally friendly thermally conductive insulating composites.

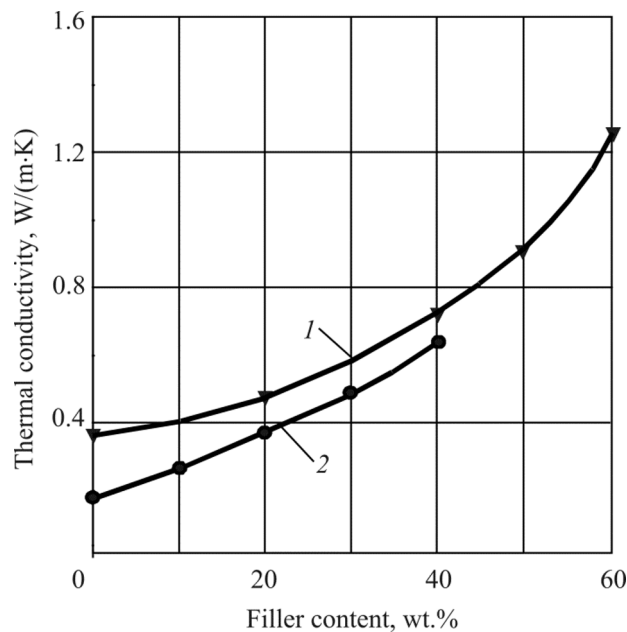


Fig. 3. Dependence of the thermal conductivity coefficient on the filler content for composites based on: LLDPE (1) and PLA (2).

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