Electrically and thermally conductive polyethylene/graphite composites and their mechanical properties

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Abstract

Electrical conductivity, thermal conductivity and ultimate mechanical properties, namely elongation at break and stress at break of low and high density polyethylene/graphite composites were investigated in this paper.

Percolation concentration at about 11 vol.% of the filler for both filled polyethylene's was found. The degree of crystallinity of polyethylene matrix did not have an significant influence neither the percolation concentration nor electrical conductivity of composites.

DSC measurement indicated that filler has no significant influence on the change of degree of crystallinity of polyethylene matrices.

The thermal conductivity of filled HDPE is higher then thermal conductivity of filled LDPE in the whole concentration range due to higher degree of crystallinity of high density polyethylene.

The nonlinear behavior was observed for the dependency stress at break versus filler content. After initial decrease in stress at break, a reinforcing effect was observed. The reinforcing effect was more pronounced for HDPE matrix.
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1. Introduction

Graphite is naturally abundant as well as synthetically prepared inorganic material, which has significant influence on the electrical and thermal conductivity of filled materials, their barrier properties as well as mechanical properties. It is frequently used especially for an improvement of electrical conductivity, antistatic properties as well as thermal conductivity of plastics.

Polymer/graphite composites have long been used in structural, aerospace and sporting goods applications [1–3].

Electroconductive polymeric composites are often used as heating elements, temperature-dependent resistors and sensors, self-limiting electrical heaters and switching devices, antistatic materials for electromagnetic interference shielding of electronic devices, etc. [4].

The importance of thermal conductivity in polymer composites is associated with the need for appreciable levels of thermal conductance in circuit boards, heat exchangers, appliances, and machinery [5]. The of information on thermal conductivity of materials is also necessary for modeling of optimum conditions during processing of materials, as well as for a analysis of transport of heat in materials during practical applications.

The presence of graphite particles has also significant influence on the mechanical behavior of filled polymers [6–8].

Physical behavior of filled LDPE and HDPE, filled with synthetic graphite particles, namely electrical conductivity, thermal conductivity and ultimate properties was investigated in this paper.

2. Experimental

Two grades of polyethylene were used as the matrix, namely low density polyethylene Bralen RA 2–19 (MFI = 1.7 g/10 min, density = 0.916 g/cm^3, particle size <50 μm) from Slovnaft, Slovakia, high density polyethylene Stamylan HD 9089 V (MFI = 8 g/10 min, density = 0.963 g/cm^3) (DSM, The Netherlands), while graphite (EG-10, synthetic graphite, SGL Carbon, UK) was used as the filler. Granulometric parameters of the graphite EG-10 are summarized in Table 1.

The blends were prepared by mixing both components in a 50 ml mixing chamber of Brabender Plasticorder PLE 331 at 170 °C (LDPE matrix) or 200 °C (HDPE matrix) for 10 min at the mixing speed 35 rpm.

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Table 1
Granulometric parameters of particles of graphite EG-10

x_{10} (μm)	x_{16} (μm)	x_{50} (μm)	x_{84} (μm)	x_{90} (μm)	x_{99} (μm)	S_v (m²/g)
10.9	14.0	31.6	59.1	69.2	108.0	0.125

Note: x_i: i% of volume of particles is smaller than dimension x_i; S_v: specific surface of particles.

1 mm thick slabs were prepared by compression moulding of the mixed composite using a laboratory press Fontijne 200 (The Netherlands) at 170 or 200 °C for 3 min. The dog-bone specimens with a working area 35 mm × 3.6 mm × 1 mm were cut from the slabs. The mechanical properties were measured at room temperature using an Instron 4301 universal testing machine (England) at deformation rate 10 mm/min at room temperature.

For the electrical conductivity measurements the prepared composites were compression molded using a laboratory press Fontijne 200 (The Netherlands) at 180 or 200 °C for 2 min under 22.5 kN/cm². The thickness of the compression molded samples was about 0.2 mm. The volume electrical conductivity in polymer composites was measured according to ASTM D 257. Three-electrode electrometer arrangement was used for the dc-measurement of the resistance. The voltage level used varied in the range 0.1–500 V. The electroconductive solution consist of polyethylene glycole (80 g), potassium chloride (1 g), natrium laurylsulphate (0.1 g) and distilled water (25 g), was used to achieve the good electrical contacts between the surface of the sample and the electrode of the conduction tester.

For thermal conductivity measurements the specimens with 50 mm diameter and 10 mm thick have been compres-

sion molded at 170 or 200 °C for 5 min with subsequent cooling under the pressure down to room temperature.

The thermal conductivity was measured using multipurpose apparatus (ISOMET, Applied Precision, Slovakia) for non-steady state measurement of thermal properties. The data are calculated automatically from a time dependence of the thermal flow in the material. Measurements have been made at 25 ± 2 °C with a flat probe.

The crystallinity of the samples was measured using a Perkin-Elmer DSC 2 (England) at heating rate 10 °C/min as a second melting run after normalized crystallization at cooling rate 10 °C/min.

3. Results and discussion

3.1. Electrical conductivity

The dependency of electrical conductivity of composites LDPE/graphite and HDPE/graphite composites on the filler content is shown in Fig. 1. The absolute values of the electrical conductivity are summarized in Table 2.

It is seen that around 11 vol.% of the filler, the sharp increase of electrical conductivity was observed in both cases.
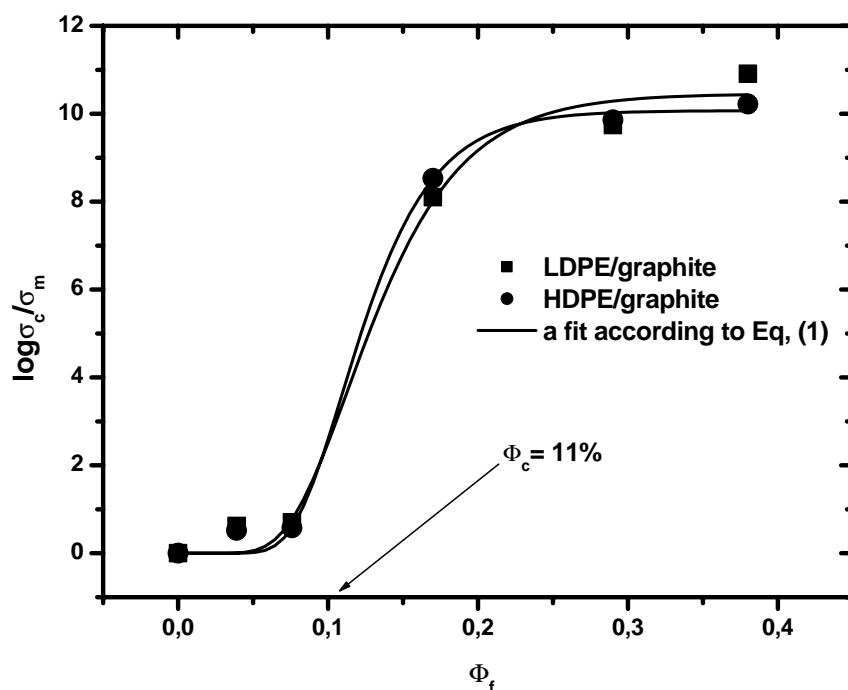

Fig. 1. Electrical conductivity (σ_c/σ_m) of the graphite filled LDPE (squares) and HDPE (circles) as a function of the volume filler content (ϕ_f). Straight line = curve fitting according to Eq. (1).

Table 2
The absolute values of the electrical conductivity of composites

LDPE/graphite, ϕ_f	σ (S/m)	HDPE/graphite, ϕ_f	σ (S/m)
0	4.7×10^{-14}	0	6.3×10^{-14}
0.039	1.9×10^{-13}	0.041	2.9×10^{-13}
0.076	2.3×10^{-13}	0.079	3.7×10^{-13}
0.170	5.9×10^{-6}	0.177	7.1×10^{-4}
0.236	4.9×10^{-5}	0.245	2.2×10^{-5}
0.290	2.6×10^{-4}	0.301	2.4×10^{-4}
0.380	3.8×10^{-3}	0.392	1.2×10^{-3}

Note: ϕ_f: volume portion of the filler; σ: electrical conductivity.

This concentration is generally called percolation concentration. In this case infinite cluster of particles is formed within a polymeric matrix. This cluster penetrates throughout the sample and represents a conductive way for a movement of electrons throughout the sample. From this concentration of the filler the material dramatically changes its electrical conductivity and becomes conductive. Since in a real situation only limited number of experimental points is available, we arbitrary identified a percolation threshold as an inflexion point in an empirical fitting curve. For a fitting of experimental data we suggested Eq. (1) [9]

$$\log\left(\frac{\sigma_c}{\sigma_m}\right) = B(1 - e_f^{-a\phi})^n \tag{1}$$

where B, a, n are adjustable parameters, σ_c is electrical conductivity of composites, σ_m is electrical conductivity of polymeric matrix and ϕ_f is volume portion of filler.

An inflexion point (ϕ_i) of this dependence, which was identified with percolation concentration (ϕ_c) is calculated according to Eq. (2)

$$\phi_i \equiv \phi_c = \frac{\ln(n)}{a} \tag{2}$$

It was found that parameter B can be approximately expressed as

$$B \cong \log\left(\frac{\sigma_{c,max}}{\sigma_m}\right) \tag{3}$$

where $\sigma_{c,max}$ is a value of electrical conductivity of composites at maximum experimentally used concentration of the filler. The parameters B, n, a are listed in Table 3. Eq. (1) represents the good empirical function for fitting of experimental dependence of electrical conductivity versus volume filler content [9–11].

It was found that percolation concentrations are the same and electrical conductivities are very similar for composites

Table 4
Thermal conductivity (λ), density (ρ) and degree of crystallinity (w_c) of polyethylene matrices

Matrix	$w_c{}^a$	$w_c{}^b$	ρ (g/cm^3)	λ (W/(m K))
Amorphous phase	0	0	0.854	0.091[c]
LDPE	0.493	0.381	0.919	0.398
HDPE	0.859	0.749	0.974	0.463
Crystalline phase	1	1	0.997	0.593[c]

[a] The values of w_c were calculated according to Eq. (4).
[b] The values w_c were calculated according to Eq. (5).
[c] The values given by Eiermann [16].

with both PE matrices. Different values of degree of crystallinity had not significant influence on those parameters. On the other hand, a decrease in percolation concentration with an increase in the crystalline content was observed in some cases, especially when carbon black was used as the filler [9,12].

The observation that in our case the degree of crystallinity does not influence the percolation concentration can be caused by the fact that particles of the graphite are much bigger than carbon black particles and they also have higher specific density (1.6 g/cm^3 for carbon black, 2.25 g/cm^3 for graphite).

Dimensions of the particles are of the order of micrometers or tens micrometers [6]. It is possible that the structure, created during mixing in the melt state is more/less the same also in the solid state. It means that the growing crystallites during cooling do not significantly shifts the particles from their initial position to the other place. In the case of carbon black, since the particles are much smaller and lighter, the crystallites created during cooling step can change the initial position of the particles and forms new structure that is dependent on the degree of crystallinity. This hypothesis can be indirectly supported by observations [13], that the cyclic cooling and heating process of the sample has an influence on electrical conductivity of carbon black/polyethylene composites, due to change of degree of crystallinity of polyethylene which results rearrangement of carbon black particles within a polymeric matrix.

3.2. Thermal conductivity

Thermal conductivity as well as the degree of crystallinity (w_c) of the polyethylene matrices is summarized in Table 4. The degree of crystallinity was calculated either from density of polymer (ρ) according to Eq. (4)

Table 3
The values of parameters in Eq. (1): B, a, n, percolation concentration (ϕ_c), calculated according to Eq. (2), maximum experimentaly determined value of electrical conductivity of composites ($\sigma_{c,max}$), electrical conductivity of matrix (σ_m)

Composite	B	a	n	ϕ_c	$\log(\sigma_{c,max}/\sigma_m)$
LDPE/graphite	10.3 (0.5)	21.9 (5.0)	11.9 (7.1)	0.11	10.9
HDPE/graphite	10.1 (0.5)	20.9 (3.8)	11.7 (7.3)	0.11	9.2

Data in brackets are standard deviations.

$$w_c = \frac{1/\rho_a - 1/\rho}{1/\rho_a - 1/\rho_c} \tag{4}$$

where $\rho_a = 0.854\,\text{g/cm}^3$ and $\rho_c = 0.997\,\text{g/cm}^3$ are the published values of density of the amorphous and crystalline phases [14] or from specific enthalpy of melting, determined by DSC, according to Eq. (5)

$$w_c = \frac{\Delta H_m}{\Delta H_m^+} \tag{5}$$

where ΔH_m is specific melting enthalpy of polyethylene and ΔH_m^+ specific melting enthalpy for 100% crystalline polyethylene. The value $\Delta H_m^+ = 293\,\text{J/g}$ [14] has been used for the calculation.

It is generally known that the all amorphous materials have similar values of thermal conductivity [15]. In the case of semicrystalline polymers, an increase of thermal conductivity with an increase in crystalline content was observed as a consequence of a better transport of the heat in a crystalline phase [16]. The simple relation between thermal conductivity of semicrystalline polymers and the weight portion of crystalline phase is expressed in terms of the additive rule [16], given by Eq. (6)

$$\lambda_m = \lambda_c w_c + \lambda_a w_a \tag{6}$$

where λ_m, λ_c, λ_a is thermal conductivity of polymer and its crystalline and amorphous part, respectively and w_c, w_a are weight portion of crystalline and amorphous phase of polymeric matrix.

Experimental data of thermal conductivity of PE summarized in Table 4 also approximately linearly increases with an increase in a weight portion of crystalline phase, according to Eq. (6). The following correlation coefficients obtained from linear fit of experimental data by Eq. (6) were found: $R = 0.967$, for values w_c determined according to Eq. (4) and $R = 0.962$, for values w_c determined according to Eq. (5).

In semicrystalline polymers, the portion of the crystalline phase has an important influence on almost all physical (especially mechanical) properties of polymers. As for composites, it is important to investigate the influence of filler (graphite) on the change of degree of crystallinity of polyethylene.

The specific melting enthalpy of used polyethylene's, as well as the composites filled with 60 wt.% of graphite were determined (Table 5). The value 60% of graphite was chosen, since it is the highest used concentration. From these values can be concluded that the filler has not significant influence on the change of degree of crystallinity of polyethylene.

This change is too small and has no or negligible influence on the thermal conductivity of PE's matrices as well as composites, especially if the average experimental error of thermal conductivity measurements being approximately 3–5%. On the other hand, a small decrease of melting temperatures of composites was observed. The filler probably reduces of lamellar thickness of crystallites and it leads to a decrease of melting temperature [17].

Table 5
The specific melting enthalpy (ΔH_m), melting temperatures (T_m), degree of crystallinity (w_c) and values of the relative change of degree of crystallinity (δw_c) of PE and composites

Material	ΔH_m (J/g^1)	T_m (°C)	w_c[a]	δw_c (%)[b]
LDPE	109.8	107.0	0.38	–
HDPE	215.6	132.2	0.75	–
L60G	109.9	105.9	0.38	0.3
H60G	219.4	130.7	0.76	1.7

[a] Values of w_c are calculated according to Eq. (5), L60G = LDPE + 60 wt.% of graphite.
[b] Values of w_c are calculated according to Eq. (5), H60G = HDPE + 60 wt.% of graphite.

The thermal conductivity of LDPE, HDPE/graphite composites versus graphite content is shown in Fig. 2. It is seen that the thermal conductivity of composites nonlinearly increases with an increase in graphite content. The thermal conductivity of filled HDPE is higher than thermal conductivity of filled LDPE due to higher degree of crystallinity of HDPE matrix.

Generally, the most inorganic fillers have much higher thermal conductivity, then polymers and therefore their incorporation in the material leads to an increase in thermal conductivity of composites. Unfortunately, a prediction of thermal conductivity of filled polymers is very difficult and depends on geometry and orientation of filler particles in the matrix, concentration of the filler, ratio between thermal conductivity of the filler and thermal conductivity of the matrix. On the base of these factors, many different models have been already developed, but none of them has general validity [5], since the most of the model are derived for regular shape of particles, flakes or fibers as well as uniform distribution of their size. In our case, particles of the graphite are irregularly shaped and their size exhibit relatively broad size distribution [6].

3.3. Mechanical properties

3.3.1. Elongation at break
The dependence of elongation at break on the graphite content is shown in the Fig. 3. This dependency is displayed in semilogaritmic scale, due to big differences among values. A steep decrease of elongation at break with an increase in graphite content was observed for both investigated systems. The initial elongation at break of virgin LDPE decreased from the value of 554% to the value of 4%, when 60 wt.% of graphite was used. The same is true for HDPE, where initial elongation at break decreased from 1610 to 2% at the same filler content. The steepest decrease was observed at the lowest used concentration of the filler (1 wt.%). Elongation at break of LDPE filled with 1 wt.% of graphite was found of 70% and elongation at break of HDPE filled with 1 wt.% of the graphite had the value of 27%.

Generally, a decrease of elongation at break with an increase in the filler content is always observed. For description of this behavior, a few models have been
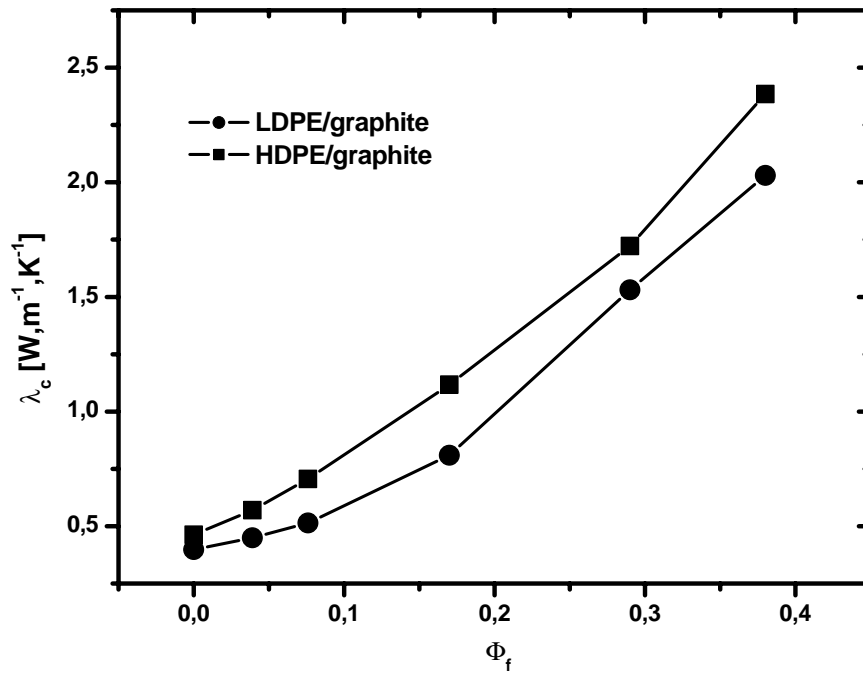
Fig. 2. Thermal conductivity (λ_c) of the graphite filled LDPE (squares) and HDPE (circles) as a function of the volume filler content (ϕ_f).

suggested, Nielsen's model [18] given by Eq. (7) being the most known

$$\frac{\varepsilon_{b,c}}{\varepsilon_{b,m}} = 1 - \phi_f^{1/3} \tag{7}$$

where $\varepsilon_{b,c}$, $\varepsilon_{b,m}$ is elongation at break of composite or matrix, respectively and ϕ_f is a volume portion of the filler.

This model is valid for particles having spherical shape assuming perfect adhesion between phases. Many fillers do not fulfill these conditions. As it can be seen in the Fig. 4, the used graphite has very irregular shape. Particles consist of many sharp edges. Moreover, particles are not uniform. These geometrical factors are expected to contribute significantly to a dramatic decrease of elongation at break. On the
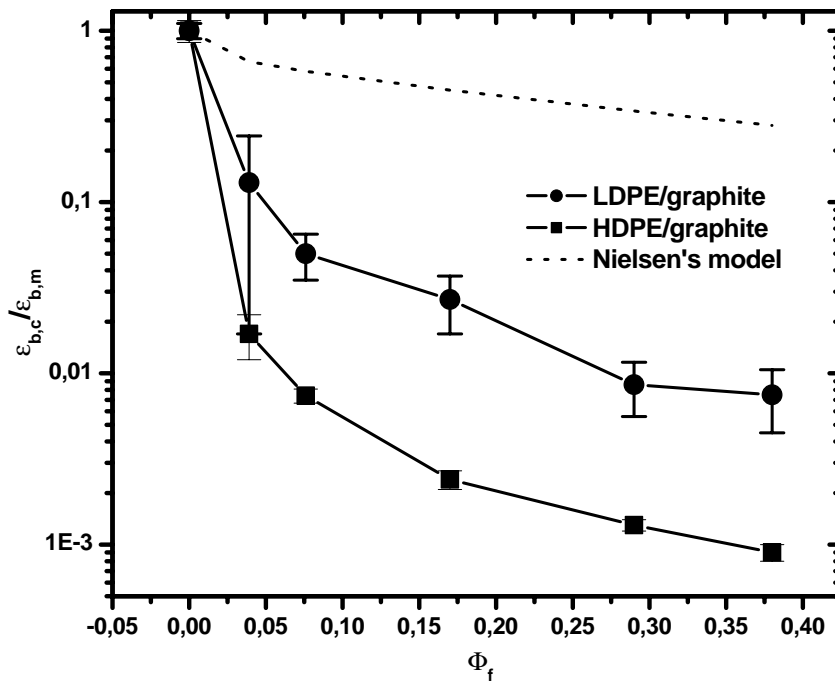

Fig. 3. Elongation at break ($\varepsilon_{b,c}/\varepsilon_{b,m}$) of the graphite filled LDPE (squares) and HDPE (circles) as a function of the volume filler content (ϕ_f). Dotted line = Nielsen's model.
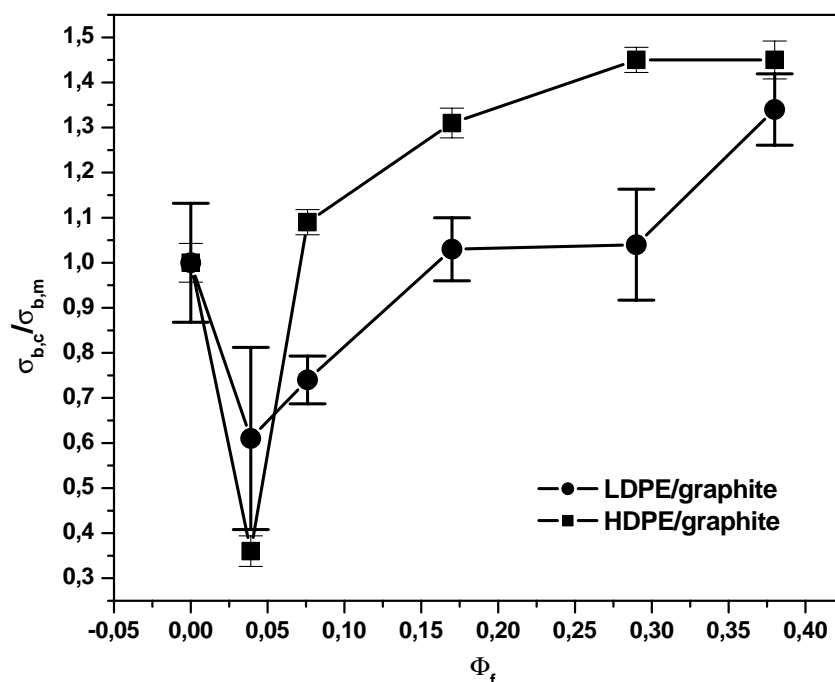
Fig. 4. Stress at break ($\sigma_{b,c}/\sigma_{b,m}$) of the graphite filled LDPE (squares) and HDPE (circles) as a function of the volume filler content (ϕ_f).

other hand, strictly speaking, the use of Nielsen's model is correct only if a deformation is homogeneous. In the case of polyethylene, a neck is created during drawing and therefore stretching is not homogeneous. The presence of defects in front of the neck has a critical influence on the drawability.

3.3.2. Stress at break

Stress at break depends on the filler concentration by a more complex way as seen in Fig. 4. In this case we have to consider the reinforcing effect of the filler leading to an increase of the tensile stress values with increasing filler content on the one hand, and the orientational strengthening occurring for semicrystalline polymers at high deformation on the other hand. The latter effect is indirectly negatively influenced by the filler presence by a steep decrease of the deformation so that orientation of the matrix cannot occur. At low filler contents, the deformation is low enough to prevent the orientation but the reinforcing effect of the filler presence is marginal. Therefore an initial increase of tensile strength has been observed. As seen in Fig. 5, the initial decrease in stress at break is more pronounced for HDPE matrix than for LDPE matrix. The initial stress at break of LDPE (11.4 ± 1.5 MPa) decreased to the value of 6.9 ± 1.3, when filled with 1 wt.% of graphite and the stress at break of neat HDPE decreased from 30.1 ± 1.3 MPa to the value of 7.7 ± 0.8, when filled by 1 wt.% of graphite. This situation can be caused by different values of degree of crystallinity of both polymers. Because crystalline content is higher in HDPE matrix and since the filler can be distributed only in the amorphous phase, the local concentration of the filler in amorphous phase is higher in HDPE than in LDPE, despite

the fact that the total concentration of the filler is the same in both cases. Since the presence of defects in front of the neck has critical influence on the drawability, higher concentration of the defects, caused by higher local concentration of the filler results steeper decrease in stress at break for HDPE matrix. The reinforcing effect is more pronounced with the increase in the filler content while further decrease in deformation has no additional effect on orientation. The reinforcing effect becomes significant at the filler concentration around 30 wt.%. This effect is more pronounced for HDPE matrix, probably due to its higher crystalline content. Since the filler is located only in the amorphous phase, the concentration of the filler related to the amorphous content is higher in HDPE matrix than in LDPE one, the consequence of this fact is that amorphous part of HDPE is more reinforced compared to LDPE due to higher local concentration of the filler in the amorphous phase. For LDPE, the initial stress at break of neat polymer (11.4 ± 1.5 MPa) increased up to 15.3 ± 0.9 MPa when filled by 60 wt.% of the filler. The initial stress at break of virgin HDPE increased from 21.3 ± 0.9 MPa up to 30.1 ± 1.3 MPa when filled by 60 wt.% of the filler.

3.3.3. Young modulus of elasticity

The dependence of Young modulus (E) of composites on the graphite content is shown in the Fig. 5. It is seen that Young modulus monotonously increases with an increase in the graphite content in both cases. The increase is more pronounced for LDPE/graphite composites. On the other hand, the absolute values of Young modulus of composites are higher for HDPE/graphite composites, since Young
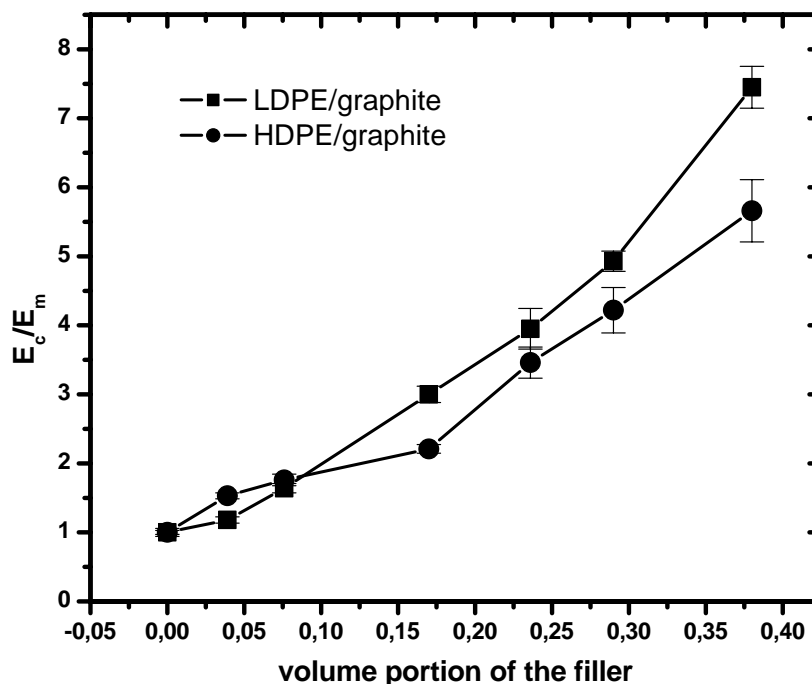
Fig. 5. Young modulus (*E*) of the graphite filled LDPE (squares) and HDPE (circles) as a function of the volume filler content (ϕ_f).

modulus of HDPE matrix is much higher than Young modulus of LDPE matrix ($E = 102 \pm 3$ MPa for LDPE and $E = 569 \pm 33$ MPa for HDPE).

4. Conclusions

The electrical conductivity measurements combined with Eqs. (1) and (2). indicated percolation concentration at about 11 vol.% for both systems. The degree of crystallinity of polyethylene matrix does not significant influence neither the percolation concentration nor electrical conductivity of composites.

DSC measurement indicated that filler has no significant influence on the change of degree of crystallinity of polyethylene matrices.

The thermal conductivity measurements of composites showed their nonlinear increase with the increase in graphite content. The thermal conductivity of filled HDPE is higher then thermal conductivity of filled LDPE due to higher degree of crystallinity

The sharp decrease of elongation at break with an increase in graphite content for both investigated systems were observed. This decrease is much sharper than a decrease, expected according to Nielsen's model. Very irregular shape of particles of our graphite, which consist of many sharp edges (potential stress concentrators) is more probably responsible for this behavior.

The nonlinear behavior was observed for the dependency stress at break versus filler content. The presence of a filler results in both an easier initiation of crack formation via

stress concentration on the filler surface on the one hand and in a decrease of chain mobility due to polymer-filler interactions resulting in lower deformability of the material on the other hand. Therefore, if concentration of the filler is low, the first effect is more significant and the sharp decrease of stress at break is observable. If concentration of the filler increases, reinforcing effect increases and stress at break increases.

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References

[1] T.A. Ezquerra, M. Kulescza, F.J. Balta-Calleja, Synth. Met. 41 (1991) 915.
[2] J. Navarro, A. Roig, P. Noguera, F. Vicente, J. Vilaplana, J. López, J. Mater. Sci. 29 (1994) 4064.
[3] M. Blaszkiewicz, D.S. McLachlan, R.E. Newnham, Polym. Eng. Sci. 32 (1992) 421.
[4] C. Klason, D.H. McQueen, Kubát, Macromol. Symp. 108 (1996) 247.
[5] D.B. Bigg, Adv. Polym. Sci. 119 (1995) 1.
[6] I. Krupa, I. Chodák, Eur. Polym. J. 37 (2001) 2159.
[7] W. Thongruang, R.J. Spontak, M. Balik, Polymer 43 (2002) 2279.
[8] W. Thongruang, R.J. Spontak, M. Balik, Polymer 43 (2002) 3717.
[9] I. Chodák, I. Krupa, J. Mater. Sci. Lett. 18 (1999) 1457.
[10] I. Novák, I. Krupa, I. Chodák, Synth. Met. 131 (2002) 93.

[11] I. Novák, I. Krupa, I. Chodák, Eur. Polym. J. 39 (2003) 585.

[12] F. Lux, J. Mater. Sci. 28 (1993) 285.

[13] M. Omastova, S. Podhradska, J. Prokes, I. Janigova, J. Stejskal, Polym. Degrad. Stab. 82 (2003) 251.

[14] B. Wunderlich, in: Macromolecular Physics II, Academic Press, New York, London, 1973.

[15] D.W. van Krevelen, in: Properties of Polymers, Elsevier, Amsterdam, Oxford, New York, 1976.

[16] K. Eiermann, Kolloid – Z. 201 (1965) 659.

[17] I. Chodák, Prog. Polym. Sci. 23 (1998) 1409.

[18] R. Nielsen, Mechanical Properties of Polymers and Composites, vol. 2, Marcel Dekker, New York, 1974.