THE INFLUENCE OF MOLECULAR STRUCTURE ON THE PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE)/ POLY(BUTYLENE TEREPHTHALATE) BLENDS

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Abstract. It has been confirmed that properties of polymer materials are encoded by the structure at the molecular level. The impact toughness of poly(ethylene terephthalate)/ poly(butylene terephthalate) blends is controlled by macromolecular coils interactions, which are reflected on the structure of their fractal dimension. It has been shown that the interaction parameter defines the fracture type of the indicated blends.

Key words: polymer blends, macromolecular coils, structure, interaction, properties.

Introduction

According to the known Academician Kargin postulate [5], polymer properties are encoded on molecular level and are realized on supramolecular (suprasegmental) one. For poly(ethylene terephthalate)/poly(butylene terephthalate) (PET/PBT) blends, processed by two different methods, the essential distinction of their properties was found [12]. So, the impact toughness of blends PET/PBT, processed by extrusion and subsequent injection molding, is on the average 3.5 times larger of this characteristic for the same blends, processed by injection molding only. The purpose of the present work is the study of this effect on both molecular and supramolecular levels.

Experimental

Commercial engineering grade polymers: PET (9921W-Eastman Chemicals) and PBT (Vestodur X7085-Degusa Huls AG) were used in the research. Two types of blends were prepared: one by injection moulding using Engel machine ES 80/20HLS with the screw length/diameter ratio $L/D = 18$ and $D = 22$ mm and the second mixed at first by extrusion moulding machine Fairex with $L/D = 24$ and $D = 25$ mm and then injected on Engel machine. The processing temperature has been in the range from 498 K to 528 K for injection molding and in the range from 453 K to 513 K for extrusion at pressure of 90 and 30 MPa, respectively. The following PET/PBT were prepared: 100/0; 95/5; 90/10; 80/20; 70/30; 50/50; 25/75; 0/100 wt [12].

Charpy's impact toughness has been measured on impact hammer INSTRON-PWS and Brinell microhardness on the hardness equipment HPK8206 and uniaxial tension tests have been performed on INSTRON-1115 testing machine [12].

Results and Discussion

As it is known [3], the mean-square distance between macromolecule ends $\langle h^2 \rangle$ is given by the following relationship:

$$\langle h^2 \rangle \sim MM^{1+\varepsilon}, \qquad (1)$$

where MM is polymer molecular weight, ε is interaction parameter.

Within the frameworks of fractal analysis the parameter ε is defined with the aid of the equation [8]:

$$D_f = \frac{2}{\varepsilon + 1}, \qquad (2)$$

where D_f is fractal dimension of macromolecular coil, which in case of linear polymers can be estimated as follows [9]:

$$D_f = \frac{2d_f}{3}, \qquad (3)$$

where d_f is a polymer structure fractal dimension, which is determined with the aid of the equation [8]:

$$\frac{H_B}{\sigma_Y} = \left[0.07 + 0.6\ln\left(\frac{3d_f}{3 - d_f}\right) \right], \qquad (4)$$

where H_B is Brinell microhardness, σ_Y is yield stress.

The parameter ε characterizes an interaction type of macromolecular coils in polymer blend: at $\varepsilon = 0$ interaction of attraction and repulsion are balancing ones, at positive ε repulsion interactions are dominant, at negative ε are attraction ones [9].

The impact toughness A_p of polymer specimens without a notch is defined by two factors: the deformation energy release critical rate G_{I_c}, characterizing specimen plasticity, and the length of critical structural defect a_{cr}, initiating fracture process [9]. The value G_{I_c} is determined according to the equation [10]:

$$C_{I_c} = 0.24 + 1.10(d - d_f), \text{ kJ/m}^2, \qquad (5)$$

where d is dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case $d = 3$).

In Fig. 1 the dependence of interaction parameter ε on the concentration of PBT C_{PBT} for the considered blends PET/PBT is adduced. This plot has two features. Firstly, it is a mirror reflection of the dependence of the considered blends impact toughness on their composition, adduced in work [12], and secondly, all values ε are positive, i.e. the repulsion interactions are dominant for all considered blends. The indicated mirror reflection of the parameters A_p and ε supposes A_p growth at ε reduction, i. e. repulsion interaction weakness.
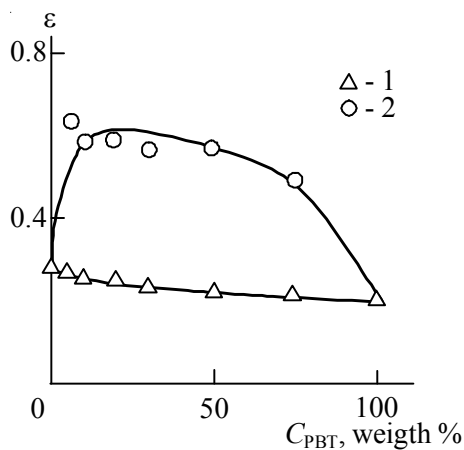

Fig. 1. The dependences of interaction parameter ε on PBT content C_{PBT} for blends PET/PBT, prepared by extrusion and subsequent injection moulding (*1*) and injection moulding only (*2*)

In Fig. 2 the dependence of deformation energy release critical rate G_{I_c}, calculated according to the equation (5), on the parameter ε value is adduced for the considered blends PET/PBT, which demonstrates linear G_{I_c} growth at ε increasing. Such look of the dependence $G_{I_c}(\varepsilon)$ was expected, since repulsion interactions intensification enhances molecular mobility, that always results in polymers plasticity enhancement [6]. The correlation $G_{I_c}(\varepsilon)$ can be described analytically by the following empirical equation:

$$G_{I_c} = 1.56(\varepsilon + 0.33), \text{ kJ/m}^2. \qquad (6)$$

The equation (6) allows to determine limiting values G_{I_c} for the considered blends. At $\varepsilon = -0.33$ (the greatest attraction interaction) minimum value

G_{I_c} is equal to zero and at $\varepsilon = 1.0$ (the greatest repulsion interaction) the maximum value G_{I_c} is equal to 2.07 kJ/m².

The length of critical structural defect a_{cr} can be determined with the aid of the following equation [9]:

$$A_p = \frac{G_{I_c} L}{72 a_{cr}}, \qquad (7)$$

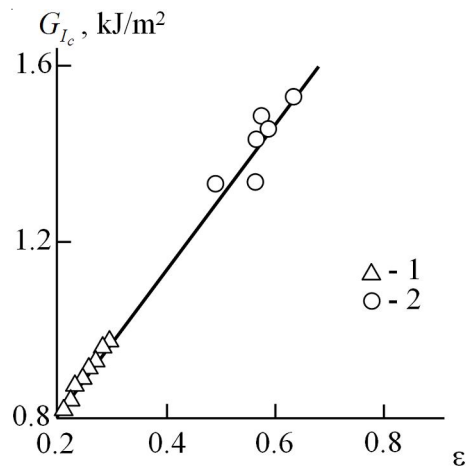where L is distance between impact hammer supports (span).

Fig. 2. The dependence of deformation energy release critical rate G_{I_c} on interaction parameter ε for blends PET/PBT. Designations are the same, that in Fig. 1

In Fig. 3 the dependence of the length of critical structural defect a_{cr} on interaction parameter ε for blends PET/PBT is adduced. The linear a_{cr} growth at ε increasing is observed, that can be described analytically as follows:

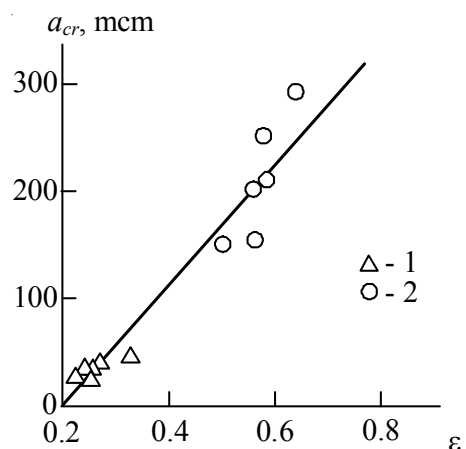$$a_{cr} = 560(\varepsilon - 0.20), \text{ mcm}. \qquad (8)$$

Fig. 3. The dependence of critical structural defect length a_{cr} on interaction parameter ε for blends PET/PBT. Designations are the same, that in Fig. 1

Let us consider the limiting a_{cr} values. At $\varepsilon = 0.20$ the value a_{cr} is equal to zero. The indicated condition $\varepsilon = 0.20$ according to the equation (2) corresponds to $D_f = 1.667$ and according to the equation (3) – $d_f = 2.5$. As it is known [1], the criterion $d_f \geq 2.5$ means the transition from brittle fracture to quasibrittle (quasitough) one, where the main role plays not a_{cr} value, but local (macroscopic) plastic deformation mechanisms. The greatest value a_{cr} at maximum repulsion interaction, i.e. $\varepsilon = 1.0$, is equal to 448 mcm.

The equations (2) and (3) combination allows to obtain the following relationship between basic structural characteristic d_f and molecular parameter ε, which is true for the linear polymers:

$$d_f = \frac{3}{1+\varepsilon}. \qquad (9)$$

Thus, the equations (6)-(9) suppose the correlation between A_p and d_f. This supposition is confirmed by Fig. 4 plot, where the dependence $A_p(d_f)$ for the considered PET/PBT blends is adduced. This dependence shows linear A_p growth at d_f increasing and the equations (6)-(8) combination allows to obtain the following relationship:

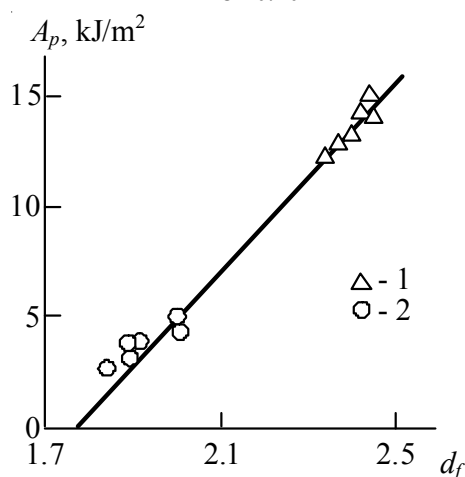$$A_p \sim \frac{\varepsilon + 0.33}{\varepsilon - 0.20}. \qquad (10)$$

Fig. 4. The dependence of impact toughness A_p on structure fractal dimension d_f for blends PET/PBT. Designations are the same, that in Fig. 1

From the relationship (10) it follows, that minimum value $A_p = 0$ is realized at $\varepsilon = -0.33$, i.e. the greatest attraction interaction or at polymer blend zero plasticity, that was to be expected (see

the equation (7)). The greatest value $A_p \rightarrow \infty$ is realized at $\varepsilon = 0.20$ or $d_f = 2.5$. From the practical point of view the condition $A_p \rightarrow \infty$ means the transition from brittle to tough fracture [1].

Conclusions

Thus, the present work results have confirmed the stated above Academician Kargin postulate. The impact toughness A_p of PET/PBT blends is controlled by macromolecular coils interactions, which on molecular level are reflected by structure fractal dimension. It has been shown that interaction parameter ε controls the transition to both absolutely brittle ($A_p = 0$, $\varepsilon = -0.33$) and to tough ($A_p \rightarrow \infty$, $\varepsilon = 0.20$) fracture.

Acknowledgements

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ВЛИЯНИЕ СТРУКТУРЫ НА МОЛЕКУЛЯРНОМ УРОВНЕ НА СВОЙСТВА СМЕСЕЙ ПОЛИ(ЭТИЛЕН ТЕРЕФТАЛАТА)/ПОЛИ(БУТИЛЕН ТЕРЕФТАЛАТА)

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Аннотация. В ходе исследования было подтверждено, что свойства полимерных материалов кодируются структурой на молекулярном уровне. Ударная вязкость смесей поли(этилен терефталата)/поли(бутилен терефталата) регулируется с помощью макромолекулярных взаимодействий, которые отражаются на структуре их фрактальной размерности. Показано, что параметр взаимодействия определяет тип излома указанной смеси.

Ключевые слова: смеси полимеров, высокомолекулярные соединения, структура, взаимодействие, свойства.