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THE COMPOSITE MODELS APPLICATION FOR ELASTIC MODULUS OF POLY(ETHYLENE TEREPHTHALATE)/ POLY(BUTYLENE TEREPHTHALATE) BLENDS DESCRIPTION

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Abstract. The quantitative interpretation of the extreme dependence of elastic modulus on the composition of poly(ethylene terephthalate)/poly(butylene terephthalate) blends has been proposed. At this, the authors apply the basics of the percolation theory and fractal analysis. It has been shown that the extreme increase in elastic modulus is due to the corresponding growth of shear strength of blends components during the autohesional bonding. It is noted that the micromechanical models do not give the adequate description of the indicated effect.

Key words: blend, micromechanical model, percolation, fractal analysis, elastic modulus, interfacial adhesion.

Introduction

The maximum of elastic modulus at equal contents of components in blends is one of the outstanding features of the blends of poly(ethylene terephthalate)/poly(butylene terephthalate) (PET/PBT) [2; 3]. In addition, it is important to note, the elastic moduli of initial PET and PBT are practically equal – the discrepancy between them makes up ~ 1 % by absolute value, that is smaller than their determination experimental error. The authors [2; 3] supposed that variation of elastic modulus of blends PET/PBT at composition change was due to blends components miscibility variation. It is significant that PET and PBT are miscible partly, namely, amorphous phase miscibility (single glass transition temperature) can be realized, but crystalline phases nonmiscibility (two crystallization temperatures) is observed [2]. In the work [6] it has been proposed to consider semicrystalline polymers as composites, in which amorphous phase is played by matrix role and filler role – by crystallites. However, in such treatment the extreme change of crystalline phase characteristics is necessary, whereas regardless of blends PET/PBT production mode these characteristics are changed monotonously and not very significantly [13]. Nevertheless, the blends PET/PBT can be considered as polymer/polymeric composites [11], particularly at the condition, that one polymeric phase is dispersed in another as disperse particles with the size of 0.2-1.5 mcm [10]. With appreciation of the stated above considerations the purpose of the present work is the treatment of blends PET/PBT as polymer/polymeric composites within the frameworks of micromechanical [1] and percolation [5] models for quantitative description of the extreme dependence of their elastic modulus on composition.

Experimental

The industrial production polymers were used: PET PELPET, grade G5801 (intrinsic viscosity [η]=0.8 dL/g), procured from firm Reliance Industries Ltd (India), and PBT LUPOX, grade GP-1000 ([η]=1.0 dL/g), supplied by firm LG Polymers India Pvt Ltd (India). PET and PBT pellets were manually mixed and dried at temperature 393 K for 8 hours in a hot air circulating oven [2].

The blends with PET:PBT ratio of 80 : 20, 70 : 30, 60 : 40, 50 : 50, 40 : 60 and 20 : 80 by weight were prepared by components mixing in melt using twin-screw extruder Haake Rheocord 9 000 of mark TW100 at the screw rate rotation of 40 rpm in the range of temperatures of 423-533 K. Then the extrudate was water cooled and granulated. The extruded pellets were molded into standard mechanical tests specimens by injection molding mode on molding machine Boolani Industries Ltd., production of India, within the range of temperatures 493-553 K [2].

The mechanical tests of blends PET/PBT on three-pointed bending were carried out on universal testing machine LR-50K, Lloyds Instrument according to ASTM 790M-90 at temperature 293 K and cross-head speed of 2.8 mm/min [2].

Results and Discussion

Let us consider the micromechanical models application of the description of blends PET/PBT elastic modulus. In the simplest from the possible cases two models were proposed [1]. For the case of parallel arrangement the uniform strain in both phases is assumed and upper boundary of elastic modulus of blends E_{bl}^{up} is given as follows [1]:

$$E_{bl}^{\text{up}} = E_n\varphi_n + E_m\varphi_m \qquad (1)$$

where E_n and E_m are elastic moduli of filler and matrix, respectively, φ_n and φ_m are volume contents of filler and matrix, accordingly ($\varphi_m = 1 - \varphi_n$).

In case of series arrangement the stress is assumed to be uniform in them and the lower boundary of elastic modulus of blends E_{bl}^{1} is determined according to the equation [1]:

$$E_{bl}^{1} = \frac{E_n E_m}{E_n\varphi_m + E_m\varphi_n}. \qquad (2)$$

At the condition $E_n = E_m$, which is true for the considered blends, the equations (1) and (2) give the trivial result: $E_{bl}^{up} = E_{bl}^{1} = E_n = E_m$, i. e. the indicated equations are not capable of describing the experimentally observed maximum on the dependence of elastic modulus on composition for blends PET/PBT [2; 3]. This is explained by the fact, that all micromechanical models require fulfillment of the condition $E_n > E_m$ for their correct application. One more obvious deficiency of micromechanical models is apriori used in them assumption of perfect adhesion between phases of composite that is far from always being fulfilled for real composites [9].

The percolation model gives the following relationship for E_{bl} determination [5]:

$$\frac{E_{bl}}{E_m} = 1 + 11\left(\varphi_n\right)^{1.7}. \qquad (3)$$

The relationship (3) does not also take into consideration interfacial adhesion level between composite phases and therefore the authors [11] modified it as follows:

$$\frac{E_{bl}}{E_m} = 1 + 11\left(b_\alpha\varphi_n\right)^{1.7} \qquad (4)$$

where b_α is a dimensionless parameter, characterizing the interfacial adhesion level (in case of perfect adhesion $b_\alpha = 1.0$ [11]).

By its physical essence interfacial adhesion between PET and PBT represents the formation of autohesional bonding, shear strength of which τ_c can be determined as follows [15]:

$$\tau_c = 6.28\times10^{-5} N_c^{3.83}\ \text{MPa} \qquad (5)$$

where N_c is the number of intersections (contacts) of macromolecular coils in boundary layer of two polymers (in the considered case – PET and PBT).

Within the frameworks of fractal analysis the value N_c can be determined according to the relationship [14]:

$$N_c \sim R_g^{2D_f - d} \qquad (6)$$

where R_g is gyration radius of macromolecular coil, D_f is its fractal dimension, d is the dimension of Euclidean space, in which a fractal is considered (it is obvious that in our case $d = 3$).

The value D_f is calculated according to the following technique. First Poisson's ratio value ν was estimated with the aid of the formula [8]:

$$\frac{\sigma_Y}{E_{bl}} = \frac{1-2\nu}{6\left(1+\nu\right)} \qquad (7)$$

where σ_Y is blend yield stress.

Then the structure of fractal dimension d_f for blends PET/PBT was determined according to the equation [4]:

$$d_f = \left(d-1\right)\left(1+\nu\right). \qquad (8)$$

And at last for linear polymers the value D_f is determined as follows [7]:

$$D_f = \frac{2d_f}{3}. \qquad (9)$$

In Fig. 1 the relations between parameter b_α, determined with the aid of the equation (4), and shear strength τ_c of autohesional contact PET-PBT is adduced. As it was expected from the most general considerations, between parameters b_α and τ_c the linear correlation is observed, which passes through coordinates origin described by the following empirical equation:

$$b_\alpha = 4.6\tau_c. \qquad (10)$$

The combination of equations (4) and (10) allows to obtain the following relationship for determination of blends PET/PBT elastic modulus:

$$E_{bl} = E_m\left[1 + 11\left(4.6\tau_c\varphi_n\right)^{1.7}\right]. \qquad (11)$$

It is obvious that PBT relative fraction at its content smaller than 50 mass % and PET relative fraction at its very same content is accepted as φ_n. In Fig. 2 the comparison of theoretically calculated according to the equation (11) E_{bl}^{T} and experimentally obtained E_{bl} elastic modulus values for blends PET/PBT is adduced, which show their good correspondence (the average discrepancy between E_{bl}^{T} and E_{bl} makes up less than 5 %).

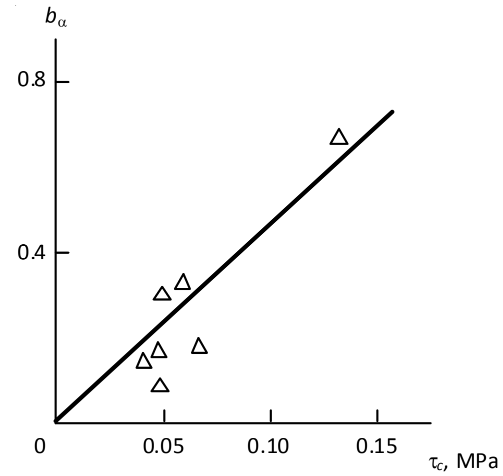

Fig. 1. The relation between parameter b_α, characterizing interfacial adhesion level, and shear strength τ_c of autohesional bonding for blends PET/PBT

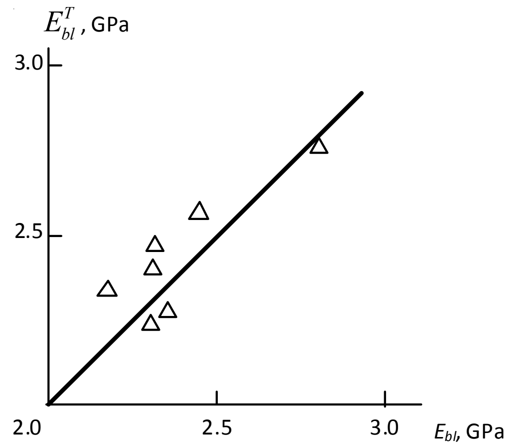

Fig. 2. The comparison of theoretically calculated according to the equation (11) E_{bl}^{T} and experimentally measured E_{bl} values of elastic modulus for PET/PBT blends

Conclusions

Thus, the present work results have demonstrated that micromechanical models cannot describe correctly the dependence of elastic modulus on composition for blends PET/PBT. This is due to non-fulfilment of the conditions, obligatory for the indicated models: essentially larger value of filler elastic modulus in comparison with corresponding characteristic for polymer matrix and assumption of perfect interfacial adhesion (as far as we know, the Sato-Furukawa model [12] is a sole micromechanical model taking into consideration the real level of interfacial adhesion in composites). The considered blends elastic modulus enhancement is due to the growth of contacts number of macromolecular coils of PET and PBT in boundary layer and corresponding enhancement of interfacial adhesion level. The proposed model in which the percolation theory and fractal analysis notions are used, allows precise quantitative description of the experimental data.

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ЗАВИСИМОСТЬ МОДУЛЯ УПРУГОСТИ ОТ СОСТАВА СМЕСИ В КОМПОЗИЦИОННЫХ МОДЕЛЯХ ПОЛИ(ЭТИЛЕН ТЕРЕФТАЛАТА)/ПОЛИ(БУТИЛЕН ТЕРЕФТАЛАТ)

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Аннотация. Была показана прямая зависимость модуля упругости от состава смесей поли(этилен терефталата)/поли(бутилен терефталат), которая может быть использована для перколяции и фрактального анализа. Показано, что модуль упругости показывает экстремальный рост, что обусловлено соответствующим ростом сдвиговой прочности смеси компонентов системы. Микромеханические модели не дают адекватного описания указанного эффекта.

Ключевые слова: смесь, микромеханические модели перколяции, фрактальный анализ, модуль упругости, межфазная адгезия.