ТЕХНИКО-ТЕХНОЛОГИЧЕСКИЕ ИННОВАЦИИ

THE DEFORMABILITY OF POLYCARBONATE/ POLY(ETHYLENE TEREPHTHALATE) BLENDS

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Abstract. It has been shown that the extreme enhancement of strain at break for blends polycarbonate/poly(ethylene terephthalate) blends is due to the corresponding structural changes of the indicated blends, which are characterized by their structure fractal dimension variation. The blends deformability rise can be achieved by enhancement of either Flory-Huggins interaction parameter, or shear strength of their autohesional contact. The transparence threshold of macromolecular coils achievement results in sharp reduction of strain at break, i.e. its decrease practically up to zero.

Key words: polymer blends, deformability, structure, interaction, fractal dimension.

Introduction

Polymer blends represent great practical interest, since they allow to obtain novel polymeric materials, not restoring new polymers synthesis. Polycarbonate (PC) and poly(ethylene terephthalate) are used during many years as engineering materials, having many useful properties. PC/PET blends are of great interest and consequently a large amount of their miscibility structure and properties has been fulfilled [6-8; 16]. It was found out [16], that the blends PC/PET with PC large content had two glass transition temperatures, whereas blends rich in PET exhibited only one. Hence, these blends are only partly miscible. The most interesting feature of these blends mechanical behaviour is their deformability maximum within the range of 60-80 mass. % PET. The authors [16] have pointed out that physical fundamentals of this effect are unclear. Therefore the purpose of the present work is the study of this important from practical point of view effect with fractal analysis notions usage.

Experimental

Polycarbonates were used on the basis of bisphenol A of Lexan 131-111 ($\overline{M}_n$ = 13.300 and $\overline{M}_w$ = 34.200) provided by General Electric Co. and the poly(ethylene terephthalate) was a bottle grade material (intrinsic viscosity = 0.74 dl/g), supplied by Celanese Plastics and Specialties Co., with the commercial designation Petpac 2113 [16].

Pellets of PC and PET were combined in the desired weight ratio and then dried for 12-14 hours in an air oven at 353 K to remove sorbed water. Further the dried pellets were heated to 408 K to promote crystallization of PET and blended in melt with the usage of screw extruder, having screw diameter of 19 mm and screw length/diameter ratio of 20. The extrudate was quenched by passing it through an ice water bath and was chopped into pellets. Then the blends pellets were subjected to injection molding by a ram type machine to form ASTM D-638 dog-bone specimens for mechanical testing. The tension testing was fulfilled on testing machine of Type T5002 of firm Lloyd Instrument Ltd. production at temperature of 293 K and a cross head speed of 50 mm/min [16].

Results and Discussion

As it is known [14], the most general informator about solids structure is its fractal dimension d_f, which can be calculated according to the equation [1]:

$$d_f = (d-1)(1+\nu), \qquad (1)$$

where d is the dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case $d = 3$), ν is Poisson's ratio, which is determined by the mechanical tests results with the aid of the relationship [10]:

$$\frac{\sigma_Y}{E} = \frac{1-2\nu}{6(1+\nu)}, \qquad (2)$$

where σ_Y and E are yield stress and elastic modulus of polymeric materials, respectively.

Within the frameworks of fractal analysis limiting strain at break $\varepsilon_f^{\lim}$ is determined theoretically as follows [11]:

$$\varepsilon_f^{\lim} = C_\infty^{D_{ch}-1} - 1, \qquad (3)$$

where C_∞ is characteristic ratio, which is an indicator of polymer chain statistical flexibility [5], D_{ch} is fractal dimension of a chain part between its fixation point, characterizing molecular mobility level [12].

C_∞ value is connected with dimension d_f by the following relationship [12]:

$$C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3}, \qquad (4)$$

and the simplest method of dimension D_{ch} estimation is the empirical formula [12]:

$$D_{ch} = 2.1d_f - 3.8. \qquad (5)$$

In Fig. 1 the comparison of the obtained experimentally and calculated according to the equation (3) dependences of strain at break ε_f on PET content C_{PET} in blends PC/PET is adduced. As one can see, well enough both qualitative and quantitative (the average discrepancy of theory and experiment makes up ~15 %) correspondence of the indicated dependences is obtained.
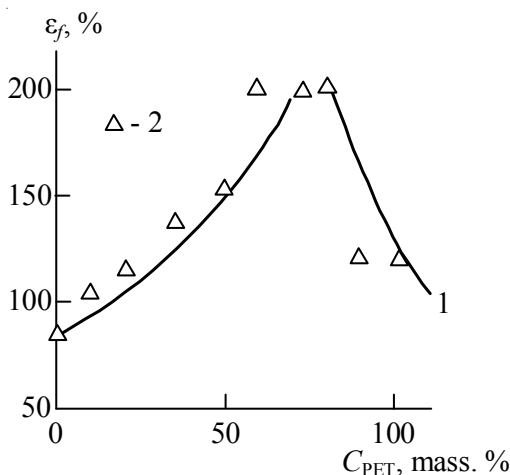

Fig. 1. The calculated according to the equation (*3*) (*1*) and obtained experimentally (*2*) dependences of strain at break ε_f on PET content C_{PET} in blends PC/PET

In Fig. 2 the dependence of ε_f on fractal dimension d_f for blends PC/PET is adduced. As one can see, good enough linear correlation ε_f (d_f) is obtained, which can be approximated by the following empirical equation:
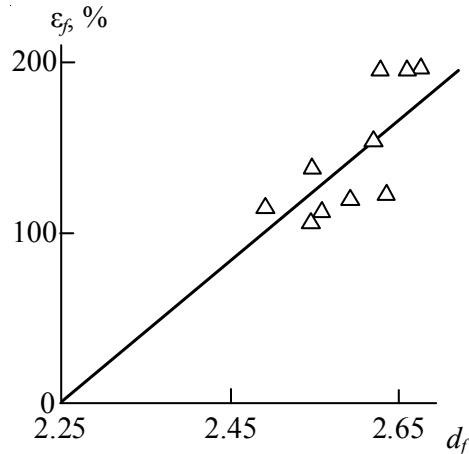
$$\varepsilon_f = 425(d_f - 2.25), \%. \qquad (6)$$

Fig. 2. The dependence of strain at break ε_f on structure fractal dimension d_f for blends PC/PET

The equation (6) allows to estimate limiting maximum ε_f magnitude for the considered blends PC/PET. As it is known [1], the greatest value d_f for real solids is equal to 2.95 and in this case maximum value ε_f is equal to ~298 %. The linear dependence ε_f (d_f) extrapolation to $\varepsilon_f = 0$ at $d_f = 2.25$ is also of interest, the causes of which will be considered below.

There exists a number of specific effects, which should be taken into consideration at their study: components interaction, level of autohesion between them and so on. Interaction between components of the considered blends, i.e. PC and PET, can be described with the aid of Flory-Huggins interaction parameter χ_{AB} [13], which is defined within the framework of fractal analysis with the aid of the equation [9]:

$$D_f = 1.50 + 0.45\chi_{AB}, \qquad (7)$$

where D_f is dimension of macromolecular coil, which is estimated for linear polymers according to the formula [9]:

$$D_f = \frac{2d_f}{3}. \qquad (8)$$

In Fig. 3 the dependence of ε_f on Flory-Huggins interaction parameter χ_{AB} is adduced,

which is approximated well enough by linear correlation and is described analytically by the following empirical equation:

$$\varepsilon_f = 275\chi_{AB}, \%$$ (9)

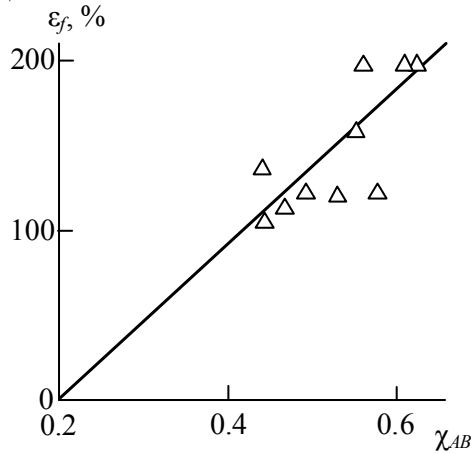Fig. 3. The dependence of strain at break ε_f on Flory-Huggins interaction parameter χ_{AB} for blends PC/PET

At the greatest value $D_f = 1.967$ according to the equation (8) at $d_f = 2.95$ the value $\chi_{AB} = 1.038$ and the greatest value $\varepsilon_f = 285 \%$, that corresponds well enough to the cited above similar value ε_f, which was estimated according to the formula (6).

The level of autohesion between PC/PET blend components can be estimated with the aid of shear strength of autohesional bonding τ_c, which is given within the frameworks of generalized fractal model as follows [15]:

$$\ln \tau_c = (N_c - c) - 4.4,$$ (10)

where N_c is intersections (contacts) of macromolecular coils number in boundary layer of autohesional bonding, c is constant, which is defined according to the equation [15]:

$$c = 16.6(D_f^{av} - 1.50),$$ (11)

where D_f^{av} is average fractal dimension of macromolecular coils.

The value N_c can be calculated (in relative units) according to the following relationship [19]:

$$N_c \sim R_g^{2D_f - d},$$ (12)

where R_g is gyration radius of macromolecular coil, which further at the first approximation is accepted equal to 15 nm.

For the considered PC/PET blends $D_f^{av} = 1.73$ and then the equation (10) can be written as follows:

$$\ln \tau_c = R_g^{2D_f - 3} - 8.218$$ (13)

The obtained according to the equation (13) values τ_c vary within the limits of 0.0051-0.0217 MPa, that corresponds to shear strength of autohesional bonding of other polymer pairs [4]. In Fig. 4 the dependence $\varepsilon_f (\tau_c^{1/2})$ is adduced (such form of the indicated dependence is chosen with the purpose of its linearization) for the considered blends, which has shown ε_f growth at τ_c increasing, that can be expressed analytically as follows:

$$\varepsilon_f = 417\tau_c^{1/2}, \%.$$ (14)

Let us note, that the dependence $\varepsilon_f (\tau_c^{1/2})$ is extrapolated to $\varepsilon_f = 0$, i.e. absolutely brittle solid, at $\tau_c = 0$. This means, that availability of finite nonzero strength of autohesional bonding between blend components is the necessary condition of their nonzero deformability.
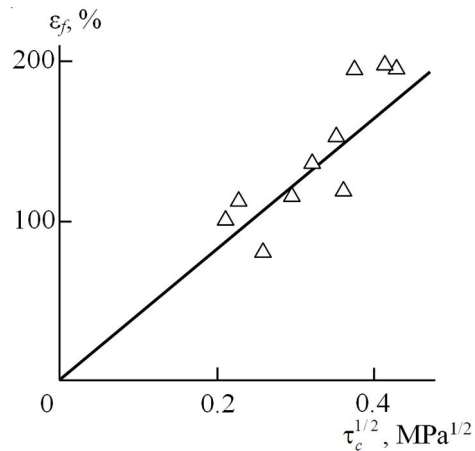

Fig. 4. The dependence of strain at break ε_f on shear strength of components autohesional bonding τ_c for blends PC/PET.

Let us return to the plot of Fig. 2, which gives zero value ε_f at $d_f = 2.25$. As it follows from the equation (8), the indicated value d_f corresponds to the dimension of permeable (transparent) macromolecular coils of $D_f = 1.50$ [2], i.e. such coils, which can pass freely through one another. This effect reflects the relationship (12) – at $D_f \le 1.50$ the exponent at R_g becomes a negative one, that results to N_c sharp reduction and according to the equation (13) – to corresponding reduction of shear strength τ_c of autohesional bonding PC-PET.

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Conclusions

Thus, the present work results have shown that the extreme enhancement of the strain at break for PC/PET blends is due to corresponding structural changes of the indicated blends, which are characterized by their structure fractal dimension variation. The blends deformability rise can be achieved by the enhancement of either Flory-Huggins interaction parameter, or shear strength of their autohesional contact. The transparence threshold of macromolecular coil achievement results in sharp reduction of strain at break, i.e. its decrease practically up to zero value.

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ДЕФОРМИРУЕМОСТЬ МАТЕРИАЛОВ НА ОСНОВЕ СМЕСИ ПОЛИКАРБОНАТ/ПОЛИ(ЭТИЛЕН ТЕРЕФТАЛАТА)

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Аннотация. В статье показано, что наблюдается экстремальное повышение относительного удлинения при разрыве для материала, произведенного на основе смеси поликарбонат/поли(этилен терефтала), которое вызвано соответствующими структурными изменениями указанных смесей, отличающихся своей структурой фрактальной размерности. Повышение деформируемости указанной смеси может быть достигнуто либо путем повышения параметра взаимодействия Флори-Хаггинса, либо прочностью на сдвиг их контактов.

Ключевые слова: полимерные смеси, деформируемость, структура, взаимодействие, фрактальная размерность.