THE DEPENDENCE OF MELT VISCOSITY OF POLYMER NANOCOMPOSITES ON TYPE OF CARBON NANOTUBES FRACTAL STRUCTURES

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Abstract. As it is known, any real fractal object can be simulated as a bulk or surface fractal. In the first case the structure fractality is extended to the entire volume of the object and in the second one – to its surface. For nanocomposites, the matrix of which makes up polymer poly(ethylene terephthalate)/poly(butylene terephthalate) blend, the fractal dimensions of both structure and surface of ring-like formations of nanofiller (multiwalled CNT) were calculated. It has been found out that in case of their notion as bulk fractals, i.e. matrix polymer penetration in ring-like formations internal regions, the strong enhancement of the nanocomposites melt viscosity is observed and in case of surface fractals this parameter is independent on nanofiller contents.

Key words: nanocomposite, blend, carbon nanotubes, melt, viscosity, fractal.

Introduction

Inorganic nanofillers of different types usage for polymer nanocomposites receiving acquires at present wide spreading [9]. However, the indicated nanomaterials melt properties are not studied enough completely. As a rule, when nanofillers application is considered, then the compromise is achieved between improvement of mechanical properties in solid-phase state, enhancement of melt viscosity at processing, nanofillers dispersion problem and process economic characteristics. Proceeding from this, the relation between nanofiller concentration and geometry and nanocomposites melt properties is an important aspect of polymer nanocomposites study.

It has been shown earlier [8], that nanocomposites polypropylene/carbon nanotubes melt viscosity is not changed practically at nanofiller contents variation within the range of 0.25-3.0 mass. %. However, in the work [11] the sharp (in 3.5 times) reduction of melt viscosity of nanocomposites on the basis of blend poly(ethylene terephthalate)-poly(butylene terephthalate), filled with multiwalled carbon nanotubes (PET-PBT/MWCT) was found in comparison with the initial matrix polymer blend at MWCT content of 0.45 mass. % only. Therefore, the present paper purpose is this effect study with the fractal analysis notions use.

Experimental

The polymers industrial sorts were used: PET was supplied by firm GE Plastics and PBT of mark S6110SF NC010, supplied by firm DuPont TM Crastin. As nanofiller MWCT were used with external diameter ranging between 10-30 nm and length of 1.5 mcm of firm Sun Nano production [11].

The PET/PBT blends, having optimal PET content of 20 mass. %, were blended with MWCT at nanofiller contents of 0.15-0.45 % by weight in melt with usage of twin screw extruder (Bersfort FRG Germany) at temperature of 493 K and screw rotation speed of 150 rpm. After receiving, the extrudate was cooled in water and pelletized. The testing samples were prepared from these pellets using injection molding machine (Windsor, India) at temperature range of 523-558 K [11].

The uniaxial tension mechanical tests were performed according to ASTM D628 on testing apparate of model AG Rnisd MC of form Shimadzu Autograph at temperature of 296 K and the cross head speed of 50 mm/min, that corresponds to the strain rate of $1.67 \times 10^{-2}$ s$^{-1}$. Melt flow index (MFI) was measured according to ASTM D1238 [11].

Results and Discussion

As it was noted above, for nanocomposites PET-PBT/MWCT very strong increase of viscosity (MFI reduction) was observed in comparison with matrix polymer blend [11]. This effect was fixed at very small MWCT volume content $\varphi_n$, which can be determined as follows [9]:

$$\varphi_n = \frac{W_n}{\rho_n} \quad (1)$$

where $W_n$ is nanofiller mass content, $\rho_n$ is its density, which for nanoparticles is determined according to the equation [9]:

$$\rho_n = 188(D_{\text{MWCT}})^{1/3}, \text{kg/m}^3, \quad (2)$$
where $D_{MWCT}$ is MWCT diameter, which is given in nm.

According to the continuum conception [10] the relation between composites melt viscosity $\eta$, matrix polymer melt viscosity $\eta_0$ and $\varphi_n$ can be obtained in the form of two simple relationships:

$$\frac{\eta}{\eta_0} = 1 + \varphi_n,$$   \hspace{1cm} (3)

$$\frac{\eta}{\eta_0} = \frac{2.5\varphi}{1-\varphi_n}.$$ \hspace{1cm} (4)

The equations (3) and (4) give the greatest $\eta$ increasing in comparison with $\eta_0$ on 0.8-2.0 %, that does not correspond to experimentally observed $\eta$ growth in 3.5 times.

The authors [8] proposed the fractal model of polymer nanocomposites melt viscosity change, the main equation of which is the following one:

$$\eta \sim \eta_0 l^{2-d_f},$$ \hspace{1cm} (5)

where $l$ is flow characteristic linear scale, $d_f$ is fractal dimension.

Since carbon nanotubes, possessing anisotropy high degree and low transverse stiffness, are formed in polymer matrix ring-like structures with radius $R_{CNT}$ [12; 15], then this dimensional parameter was accepted as $l$, which can be determined with the aid of the equation [2]:

$$\varphi_n = \frac{\pi L_{MWCT} r_{MWCT}^2}{(2 R_{CNT})^3},$$ \hspace{1cm} (6)

where $L_{MWCT}$ and $r_{MWCT}$ are length and radius of carbon nanotubes, respectively.

Since contact polymer matrix-nanofiller is realized through the ring-like structures, then as $d_f$, the authors [8] have accepted these structures surface dimension $d_{surf}$, which is determined according to the following technique. First the specific surface $S_n$ was estimated according to the equation [9]:

$$S_n = \frac{3}{\rho_{CNT} R_{CNT}},$$ \hspace{1cm} (7)

where $\rho_{CNT}$ is the density of MWCT rang-like structures, which is accepted equal to $\rho_n$.

Then the value $d_{surf}$ can be determined with the aid of the following formula [9]:

$$S_n = 410 (R_{CNT})^{d_{surf} - d},$$ \hspace{1cm} (8)

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 MFI on MWCT volume contents $\varphi_n$ is adduced (the curve 1) for the considered nanocomposites, where the value MFI is determined as follows [5]:

$$MFI = \frac{2.33}{\eta}, \text{ g/10 min.}$$ \hspace{1cm} (9)

As it follows from the data of Fig. 1, at the condition $d_f = d_{surf}$ MFI value is practically constant, that does not correspond to the experimental results [11].

As it is known [3], fractals can be divided into two categories: bulk and surface ones. In the first case fractality property is extended to the object volume and in the second one – to its surface only. For the bulk fractals their dimension $d_f$, i.e. dimension of MWCT ring-like structures, is determined with the aid of the relationship [14]:

\hspace{1cm}
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\[ R_{\text{CNT}} \sim \left( \frac{4c_0kT}{3\eta M_0} \right)^{1/d_{\text{CNT}}} t^{1/d_{\text{CNT}}}, \]  

(10)

where \( c_0 \) is nanoparticles initial concentration, which is accepted equal to \( \varphi_n \), \( k \) is Boltzmann constant, \( T \) and \( t \) are temperature and duration of processing, respectively, \( \eta \) is melt viscosity, \( M_0 \) is mass of separate nanoparticle.

Since the parameters \( k, T, t \) and \( M_0 \) are constant, and \( \eta \sim \text{MFI}^{-1} \), then the relationship (10) can be simplified as follows:

\[ R_{\text{CNT}}^{\text{MFI}} \sim \varphi_n \times \text{MFI} \]  

(11)

In Fig. 1 the dependence of MFI(\( \varphi_n \)) for the considered nanocomposites is also added, which is calculated according to the relationship (5) at the condition \( d'_f = d'_f^{\text{CNT}} \), i.e. at simulation of MWCT ring-like structures as bulk fractals. In this case the good correspondence of theory and experiment is obtained.

As it is known [6], for bulk fractals penetration of polymer matrix macromolecules into their internal regions is typical. The number of macromolecules \( n \), penetrating into these regions, is given by the following relationship [6]:

\[ n \sim R_{\text{CNT}}^{\Delta_f}, \]  

(12)

where \( \Delta_f \) is the fractal dimension of polymer melt macromolecular coil, determined as follows [1]:

\[ \Delta_f = (d - 1)(1 + \nu). \]  

(13)

where \( \nu \) is Poisson’s ratio, estimated according to the mechanical tests results with the aid of the equation [4]:

\[ \sigma_f = \frac{1-2\nu}{E} \sigma, \]  

(14)

where \( \sigma_f \) and \( E \) are yield stress and elastic modulus, respectively.

In Fig. 2 the dependence of MFI(\( n \)) for the considered nanocomposites is added. As one can see, MFI reduction (melt viscosity growth) at \( n \) decreasing is observed. At \( n \to 0 \) MFI = 0 and the change of MWCT ring-like structures type from bulk fractal to surface one occurs.

**Conclusions**

Thus, the present work results have shown that the dependence of melt viscosity of nanocomposites polymer/carbon nanotubes on nanofiller contents is defined by fractal structures type, which is formed by the nanofiller. In case of surface fractals very weak dependence of melt viscosity on carbon nanotubes contents is observed and in case of bulk fractals – its essential (in several times) enhancement. The absence of polymer matrix macromolecules penetration in carbon nanotubes ring-like structures internal regions defines the structures transition from bulk fractals to surface ones.

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ЗАВИСИМОСТЬ ВЯЗКОСТИ
РАСПЛАВА ПОЛИМЕРНЫХ НАНОКОМПОЗИТОВ ОТТИПА УГЛЕРОДНЫХ НАНОТРУБОК И ФРАКТАЛЬНЫХ СТРУКТУР

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Аннотация. Как известно, любой реальный фрактальный объект может моделироваться объемной или поверхностной фрактальной размерностью. В первом случае фрактальная структура распространяется на весь объем объекта, а во втором — наблюдается только на ее поверхности. Для нанокомпозитов, матрицей которых является полимерная смесь поли(этилен терефталата)/поли(бутилен терефталата), были рассчитаны фрактальные размерности структуры и поверхности кольцеобразных образований нанотрубок (многостенных углеродных нанотрубок).

Ключевые слова: нанокомпозит, смесь, углеродные нанотрубки, расплав, вязкость, фрактал.