THE BEHAVIOUR FEATURES OF POLYMER NANOCOMPOSITES FILLED WITH CALCIUM CARBONATE

1 Kabardino-Balkarian State University, 173 Chernishevsky str., 360004 Nal’chik, Russian Federation
2 N.M. Emanuel Institute of Biochemical Physics of Russian Academy of Sciences, 4 Kosygin str., 119334 Moscow, Russian Federation

Received: April 14, 2010 / Revised: September 06, 2010 / Accepted: January 21, 2011


Abstract. The most typical behaviour features of polymer nanocomposites filled with dispersed calcium carbonate were considered. The quantitative analysis was carried out within the frameworks of structural model: the cluster model of polymers amorphous state structure and fractal analysis. It has been shown that all changes of the considered nanocomposites properties were defined by polymeric matrix structure variations, which are due to nanofiller introduction.

Keywords: polymer, nanocomposite, elasticity modulus, interfacial adhesion, yield, plasticity, fractal analysis.

1. Introduction

Lately a scientists’ interest to particulate-filled polymer nanocomposites, where the nanofiller is calcium carbonate has been increased. Nanocomposites on the basis of polyethylene [1-8], polypropylene [9, 10], poly(vinyl chloride) [11, 12], butadiene rubber [13] etc. were studied. These studies of nanocomposites polymer/calcium carbonate allow to reveal a number of their specific features, which do not correspond to the known ones at present for polymer composites. Let us note some of them. The elasticity modulus enhancement at calcium carbonate (CaCO₃) introduction in the mentioned matrices is usually small even at using of binding agents [9] and for polypropylene it makes up no more than 50 % at CaCO₃ contents of 40 mas %. Let us remind that similar processing of mineral microfillers allows to increase an elasticity modulus of epoxy polymer by 300–400 % at the same filler content [14]. Secondly, CaCO₃ contents increasing does not practically increase nanocomposites yield stress and sometimes even reduces it [5, 6]. But the most interesting feature of the considered nanocomposites is their plasticity, characterized by either limiting strain at failure εₚ [12], or impact toughness Aᵣ [5, 6, 9, 13], at CaCO₃ contents growth increasing, which often has an extreme character. Let us remind that brittleness of polymers at the introduction of various fillers into them (including nanofillers [11]) is one of the most essential deficiencies of polymer composites in general [14]. And at last, melts of nanocomposites filled with CaCO₃ often discover an anomalous behaviour [15]. A sufficiently large number of works [1-13, 15] which have mainly a qualitative character, taking into consideration characteristics of secondary structures obtained at specimens fracture but giving no interrelation with nanocomposites neat structure were devoted to these features of the mentioned nanocomposites study. Therefore the purpose of the present paper is quantitative analysis of the indicated effects on the example of polymer nanocomposites filled with calcium carbonate.

2. Experimental

Homopolymer of polypropylene (PP) of mark F1 supplied by the Langang Petrochemical Company, China, was used as the polymeric matrix. The dispersed CaCO₃ was purchased from Solvay firm, particles size makes up 70 nm, nanofiller contents vary within the limits of 0–40 mas %. CaCO₃ particles were treated by 1 mas % of coupling agent liquid silane of mark KH550, γ-aminopropyl triethoxy silane, supplied by the firm Hengda, China [9].

Nanocomposites PP/CaCO₃ were prepared in a screw extruder with a length/diameter ratio of 32, and a screw diameter of 25 mm (T55J-25/32, China) at the temperature of 503 K and screw rotation rate of 140 rpm. Then the prepared nanocomposites were palletized and the obtained pellets were molded in Nissei PS40E5ASE casting machine into two types of specimens for
mechanical tests: the samples for the tests on the three-pointed bending have a shape of rectangular bars with the length of 80 mm, the width of 10 mm and the thickness of 4 mm; samples for impact testing have the same shape, analogous width thickness and length of 60 mm. On the last ones V-shaped notch with the length of 2 mm and the tip radius of 0.25 mm was marked.

Flexural tests were made on the apparatus Shimadzu AG-10TA Universal Testing Machine at the temperature of 293 K and the crosshead speed of 2 mm/min. Impact tests were made according to the Izod method at the rate of 3.5 m/s. The reported data were average value of five individual measurements [9].

3. Results and Discussion

As the data of paper [9] have shown, the contents of CaCO$_3$ $W_f$ increasing within the range of 0–40 mas % results to nanocomposites elasticity modulus $E_n$ enhancement from 1387 up to 2086 MPa, i.e. approximately in 1.5 times. The fractal conception of polymer composites elasticity [16] supposes that this parameter increasing is due to modification (“disturbance”) of polymeric matrix structure at the filler introduction. The indicated disturbance degree can be characterized by the excess energy localization regions dimension $D_f$ connected with fractal (Hausdorff) dimension $d_f$ of composites structure according to the Eq. (1) [17]:

$$D_f = 1 + \frac{1}{3-d_f}$$  \hspace{1cm} (1)

In its turn, the value $d_f$ is determined according to the following relationship [17]:

$$d_f = (d - 1)(1 + \nu)$$  \hspace{1cm} (2)

where $d$ is the dimension of the Euclidean space, in which a fractal is considered (obviously, in our case $d = 3$), $\nu$ is the Poisson’s ratio, estimated according to the mechanical tests results with the aid of the formula [18]:

$$\sigma_f = \frac{1 - 2\nu}{E} \frac{1}{6(1+\nu)(1-\nu)}$$  \hspace{1cm} (3)

where $\sigma_f$ is the yield stress, $E$ is the elasticity modulus.

In Fig. 1 the dependences $E'_n(D_f)$ for four nanocomposites are adduced: PP/CaCO$_3$, poly(vinyl chloride)/calcium carbonate (PVC/CaCO$_3$) with CaCO$_3$ particles size of 44 nm, the high density polyethylene/calcium carbonate (HDPE/CaCO$_3$) with particles sizes of 50 and 1200 nm. As it can be seen, all indicated correlations are described by linear dependences with different slope. Obtaining of common correlation for all indicated polymer materials is possible by normalization of the adduced straight lines in Fig. 1 by the means of ratio $E_{pol}/E_{PP}$, where $E_{pol}$ and $E_{PP}$ are elasticity modulus of arbitrary matrix polymer and PP, respectively. Then the adduced elasticity modulus $E_n^{red}$ of the nanocomposite is described by the following generalized formula:

$$E_n^{red} = 0.32 \left( \frac{E_{pol}}{E_{PP}} \right) (D_f - 1)$$  \hspace{1cm} (4)

![Fig. 1. The dependences of elasticity modulus $E_n$ on fractal dimension $D_f$ for nanocomposites on the basis of PP (diameter of CaCO$_3$ nanoparticles $D_p = 70$ nm) (1); HDPE ($D_p = 50$ nm) (2); HDPE ($D_p = 1200$ nm) (3) and PVC ($D_p = 44$ nm) (4)](image)

![Fig. 2. The dependence of reduced elasticity modulus $E_n^{red}$ of nanocomposites, calculated according to the Eq. (4), on fractal dimension $D_f$. Conventional signs are the same that in Fig. 1.](image)
for nanocomposites PVC/CaCO$_3$ value $E_n$ is equal to $\sim 5300$ MPa. Therefore, particulate-filled polymer nanocomposites obey the general laws, obtained earlier for particulate-filled microcomposites.

The authors [19] obtained the following equation, showing the dependence of reinforcement degree $E_n/E_{nm}$ for particulate-filled nanocomposites on their main characteristics:

$$
\frac{E_n}{E_{nm}} = \frac{0.19 W_f l_0}{D_p^{1/2}} \tag{5}
$$

where $E_n$ is the elasticity modulus of matrix polymer, $W_f$ is the nanofiller mass contents, $l_0$ is the length of statistical segment of polymeric matrix, $D_p$ is the nanofiller particles diameter.

The value $l_0$ can be determined according to the formula [20]:

$$
l_0 = C_n l_0 \tag{6}
$$

where $C_n$ is the characteristic ratio, $l_0$ is the length of the main chain skeletal bond. For PP one should accept: $C_n = 6$, $l_0 = 1.54$ Å [21].

In Table 1 the comparison of the obtained experimentally $(E_n/E_{nm})$ and calculated according to the Eq. (5) $(E_n/E_{nm})^f$ values of reinforcement degree for nanocomposites PP/CaCO$_3$ is adduced. As one can see, sufficiently good correspondence of the theory and experiment is obtained (the average discrepancy of $(E_n/E_{nm})$ and $(E_n/E_{nm})^f$ makes up 8.4 %), but for all nanocomposites the condition $(E_n/E_{nm}) < (E_n/E_{nm})^f$ is fulfilled. According to the Eq. (5) such effect can be given by nanoparticles aggregation, i.e. $D_p$ increasing. Using experimental values of reinforcement degree, real sizes of nanofiller particles aggregates $D_p^{agr}$ can be calculated, the dependence of which on the filling mass degree $W_f$ in Fig. 3 is adduced. The data of this figure exhibit rather strong aggregation of nanofiller particles at small $W_f (\leq 10$ mas %) and its small degree at $W_f \geq 20$ mas %. Such unexpected correlation (it is usually considered that the stronger aggregation the higher filler contents [16]) can be explained by nanocomposites melt viscosity $\eta$ change, since in this state only nanofiller particles aggregation is possible.

In Fig. 4 the dependence of melt relative viscosity for nanocomposites PP/CaCO$_3$ $\eta/\eta_0$ ($\eta_0$ is the neat matrix polymer melt viscosity), calculated according to the Einstein’s formula (7) [22] on CaCO$_3$ contents is adduced.

$$
\frac{\eta}{\eta_0} = 1 + \frac{2.5 W_f}{1 - W_f} \tag{7}
$$

As it follows from Fig. 4 plot, at $W_f = 10$ mas % relative viscosity gradient increases essentially (about twice) for large CaCO$_3$ contents. This means that relatively low nanocomposites PP/CaCO$_3$ melt viscosity at small $W_f$ allows rather high nanofiller particles mobility degree in the melt that facilitates their aggregation, since nanoparticles in general have high specific surface, promoting to their strong agglomeration [10, 23]. A melt viscosity enhancement at $W_f > 10$ mas % reduces nanofiller particles mobility in the melt, making their aggregation difficult (compare Figs. 3 and 4). The similar anomalous effect of the melt viscosity change as a function of $W_f$ for nanocomposites PP/CaCO$_3$ was observed in the work [15]. It is significant that, as it has been expected, nanofiller particles aggregation degree influences nanocomposites elasticity modulus $E_n$. In Fig. 5 the dependence $E_n(W_f)$ is adduced, which corresponds completely to Figs. 3 and 4 data. As one can see, in the range of $W_f = 0–10$ mas %, where nanofiller particles aggregation is relatively high (Fig. 3) and the melt relative viscosity is small (Fig. 4), $E_n$ growth at $W_f$ increase occurs much slower than in the range of $W_f > 10$ mas %.

Let us consider further the reasons of the yield stress $\sigma_y$ of relatively small increasing of particulate-filled nanocomposites in comparison with their elasticity modulus $E_n$. So, for nanocomposites PP/CaCO$_3$ at $E_n$ increasing by 50 % $\sigma_y$ enhancement only by 10 % is observed [9] and for nanocomposites HDPE/CaCO$_3$ $W_f$ increasing $W_f$ up to 20 mas % results in $\sigma_y$ reduction in comparison with such nanocomposites with CaCO$_3$ smaller contents [5, 6]. The similar picture is observed for nanocomposites PVC/CaCO$_3$ [12]. Within the frameworks of the cluster model of polymers amorphous state structure yield stress $\sigma_y$ is determined by the following equation [16, 24]:

$$
\sigma_y = \frac{G b p^{1/2}}{2 \pi} \tag{8}
$$

### Table 1

The structural and mechanical characteristics of nanocomposites PP/CaCO$_3$

<table>
<thead>
<tr>
<th>$W_f$, mas %</th>
<th>$E_n/E_{nm}$</th>
<th>$(E_n/E_{nm})^f$</th>
<th>$d_f$</th>
<th>$\varphi_d$</th>
<th>$G$, MPa</th>
<th>$\sigma_{y}$, MPa</th>
<th>$\sigma_{y}^f$, MPa</th>
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<tr>
<td>0</td>
<td>1</td>
<td>1</td>
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<td>2.792</td>
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<td>509</td>
<td>35.4</td>
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</tr>
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<td>1.060</td>
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<td>519</td>
<td>35.6</td>
<td>37.3</td>
</tr>
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<td>1.120</td>
<td>2.796</td>
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<td>35.8</td>
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<td>2.796</td>
<td>0.181</td>
<td>531</td>
<td>36.1</td>
<td>37.3</td>
</tr>
<tr>
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<td>1.200</td>
<td>2.800</td>
<td>0.174</td>
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</tr>
<tr>
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<td>1.400</td>
<td>2.816</td>
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<td>1.600</td>
<td>2.826</td>
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</tr>
<tr>
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<td>1.800</td>
<td>2.840</td>
<td>0.112</td>
<td>735</td>
<td>39.2</td>
<td>39.4</td>
</tr>
</tbody>
</table>
where $G$ is the shearing modulus, $b$ is the Burgers vector, $\rho_d$ is the structure linear defects density (analog of dislocations for crystalline lattices).

Let us consider parameters estimation methods, which are included in the Eq. (8). The value $G$ is determined as follows [17]:

$$G = \frac{E}{d_f}$$  \hspace{1cm} (9)

and the Burgers vector $b$ – according to the empirical equation [16, 24]:

$$b = \left( \frac{62.5}{C_n} \right)^{\frac{1}{2}}, \text{Å}$$  \hspace{1cm} (10)

For polymers as structure linear defects the segments of macromolecules, included in densely-packed regions are accepted, which for nanocomposites with semicrystalline matrix are crystallites, local order regions (clusters) and interphase regions [23]. Relative fraction of the last $\varphi_f$ can be estimated with the aid of the equation [23]:

$$\frac{E_n}{E_m} = 1 + 11(W_f + \varphi_f)^{1.7}$$  \hspace{1cm} (11)

The estimations according to the Eq. (11) have shown practical absence of interphase regions in nanocomposites PP/CaCO$_3$. These estimations are confirmed experimentally by the data of atomic force microscopy on the example of nanocomposites HDPE/CaCO$_3$ [5]. In itself the fact of practical absence of interphase regions in nanocomposites PP/CaCO$_3$ speaks for rather low level of interfacial adhesion nanofiller-
polymeric matrix despite coupling agent usage [23]. The authors [25] show that in case of ideal adhesion between the filler and the polymeric matrix the dependence \( E_d/E_m(W_f) \) was described by the Kerner equation, which can be approximated by the following relationship:

\[
E_d/E_m = 1 + 11.16W_f - 44.4W_f^2 + 96.3W_f^3
\]  

(12)

The other similar relationship (the Guth's equation), used for estimation of composites reinforcement degree in case of ideal adhesion, has the form [26]:

\[
E_d/E_m = 1 + 2.5W_f + 14.1W_f
\]  

(13)

The Eqs (12) and (13) give close values of \( E_d/E_m \) at \( W_f = 40 \text{ mas} \% \) (or \( W_f = 0.4 \)) for nanocomposites PP/CaCO\(_3\): 4.70 and 4.46, that correspond to elasticity modulus \( E_m = 6.52 \) and 6.18 GPa, respectively. Since the experimental \( E_m \) value at the indicated CaCO\(_3\) content is equal to 2.09 GPa [9], then this comparison confirms the conclusion about the low level of the interfacial adhesion for these nanocomposites, which was made above.

Therefore, for the studied nanocomposites one should accept segments, included in crystallites and clusters with relative fractions \( K \) (crystallinity degree) and \( \varphi_{cl} \), respectively, as the structure linear defects. \( K \) value for PP is equal to 0.50 [9] and the value \( \varphi_{cl} \) can be estimated with the aid of the equation [24]:

\[
d_f = 3 - 6 \left( \frac{\varphi_{cl}}{C_S} \right)^{1/2}
\]  

(14)

where \( S \) is the cross-sectional area of macromolecule, which is equal to 34.3 Å\(^2\) for PP [26].

Further the value \( \rho_d \) is calculated according to the following formula [16]:

\[
\rho_d = \frac{K + \varphi_{cl}}{\rho}  
\]  

(15)

In Table 1 the comparison of experimental \( \sigma_t \) and calculated according to the equation (8) \( \sigma_f \) yield stress values for nanocomposites PP/CaCO\(_3\) is adduced and the necessary for such calculation values \( d_f, \varphi_{cl} \) and \( G \) are given as well. As one can see, a good correspondence of the theory and the experiment is obtained (the average discrepancy of \( \sigma_t \) and \( \sigma_f \) makes up 3.6 \%). Let us note the polymeric matrix structure, characterized by the dimension \( d_f \), small change – at \( W_f = 40 \text{ mas} \% \) it makes up by the fractional part of \( d_f \) (which gives the main information about the structure) only 6.7 \%. For comparison, in case of composites polyhydroxyether/graphite at the same filler content \( d_f \) change is equal to 32.8 \%, i.e. approximately in 5 times more [16]. Antibase change of parameters \( G \) and \( \varphi_{cl} \), defining the value \( \sigma_f \) in the Eq. (8) is also significant. Hence, \( \sigma_f \) weak increase at \( W_f \) growth for nanocomposites PP/CaCO\(_3\) is due to a compensating effect of antibase change of parameters \( G \) and \( \varphi_{cl} \) (or \( \rho_d \)).

In conclusion let us consider nanocomposites PP/CaCO\(_3\) plasticity increasing effect at \( W_f \) growth on the example of the impact toughness \( A_p \), which at \( W_f = 40 \text{ mas} \% \) raises in 2.4 times in comparison with neat PP. As Kausch shows [27], the polymer molecular mobility increasing is always accompanied by its plasticity (impact toughness) growth. Within the frameworks of fractal analysis the molecular mobility level can be estimated with the aid of fractal dimension \( D_{ch} \) of the chain part between its fixation points (cross-linking nodes, physical entanglements, clusters, etc.) [28]. The value \( D_{ch} \) can be calculated with the aid of the Eq. (16) [28]:

\[
2 = C_{cl}^{\frac{\varphi_{cl}}{\rho_d}}
\]  

(16)

In Fig. 6 the dependence \( A_p(D_{ch}) \) is adduced, which has an expected form: enhancement of the molecular mobility level, characterized by the dimension \( D_{ch} \), results to the growth of nanocomposites plasticity, characterized by their impact toughness \( A_p \). Let us note, that \( D_{ch} \) and, consequently, \( A_p \) increase is due to the local order level reduction in the amorphous phase of the polymeric matrix, i.e. \( \varphi_{cl} \) decrease at \( W_f \) growth (Table 1), in other words, by polymeric matrix structure “disturbance” at nanofiller introduction.

The fractal analysis application allows to estimate the maximum attainable \( A_p \) value. So, from Fig. 6 plot it follows that for nanocomposites PP/CaCO\(_3\) at maximum \( D_{ch} = 2 \) the limiting magnitude of the impact toughness is equal to 10.4 kJ/m\(^2\).

### 4. Conclusions

Therefore, the quantitative analysis of particulate-filled polymer nanocomposites main features within the frameworks of the fractal analysis and the cluster model of the polymers amorphous state structure performed in the present paper allows to elucidate the following structural causes of the indicated features:

1. The relatively small reinforcement degree of polymer nanocomposites, filled with calcium carbonate, is due to low level of interfacial adhesion polymer-CaCO\(_3\), despite the coupling agent using. Nanofiller particles aggregation plays a definite role in this aspect.

2. The weak increasing of nanocomposites yield stress at CaCO\(_3\) contents growth is due to the compensating effect of the shear modulus change and relative fraction of polymeric matrix local order regions.

3. The melts viscosity anomalous behaviour of nanocomposites, filled with CaCO\(_3\), is due to a strong tendency to aggregation of nanofiller particles in virtue of
their high specific surface at small nanofiller contents and, as a consequence, nanoparticles high mobility. CaCO$_3$ contents increase raises essentially the melt viscosity, reduces the nanofiller particles mobility and decreases their aggregation degree.

4. The plasticity, characterized by the impact toughness, increasing for nanocomposites PP/CaCO$_3$ is due to the polymeric matrix structure “disturbance” at nanofiller introduction and, as a consequence, to the growth of molecular mobility level.

References