

# Plasticity Structural Analysis of Polymer Nanocomposites Filled with Carbon Nanotubes

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**ABSTRACT:** A structural analysis of an increasing plasticity effect for polymer nanocomposites filled with carbon nanotubes was carried out. It was shown that this effect was due to densely packed interfacial layer formation on an atomic scale on the smooth nanotube surfaces, which resulted in changes in the polymer molecular matrix and

structural characteristics. A prediction of the nanocomposite properties as a function of nanotube contents was obtained. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2621–2624, 2009

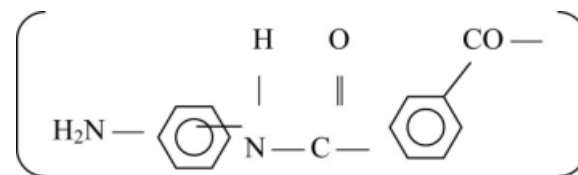
**Key words:** nanocomposites; structure

## INTRODUCTION

For polymer nanocomposites filled with carbon nanotubes (CNTs), the fracture strain ( $\epsilon_f$ ) increases in comparison with the matrix polymer, and nanocomposite plasticity increases have been noted repeatedly. The indicated effect has been noted for epoxy polymer/CNT,<sup>1</sup> phenylone/CNT,<sup>2</sup> and other nanocomposites. In other words, the increasing plasticity effect for the indicated class of nanocomposites has a general enough character. This effect is very important from a practical point of view because the main disadvantage of polymer composites in general is their brittleness, that is,  $\epsilon_f$  decreases with increasing filler contents.<sup>3</sup> Therefore, it is important to provide a theoretical estimation of the increasing polymer/CNT nanocomposite plasticity effect because, in the future, this could provide the possibility of polymer nanocomposite production with an exceptional set of operating characteristics, with simultaneous increases in the rigidity, strength, and plasticity of these polymeric materials. Our purpose in this study was to analyze the structure of the increasing phenylone/CNT nanocomposite plasticity within the framework of the cluster model of polymers with an amorphous state structure<sup>4,5</sup> and also to perform fractal analysis.<sup>6</sup>

## EXPERIMENTAL

A linear heterochain copolymer, phenylone S-2, was used for the polymeric binding of nanocomposites; it had the following chemical composition:



The used CNTs were prepared by gas-phase carbon deposition on a catalyst as a result of the catalytic pyrolysis of carbon-containing gases. The CNTs represented one-dimensional nanosized threadlike formations of polycrystalline graphite with the appearance of a free-flowing black powder. Granules of micrometer sizes had the structure of tangled bundles of multiwalled tubes more than 2  $\mu\text{m}$  long with external and internal diameters of 20–60 and 10–20 nm, accordingly. The nanocomposites were used with CNT contents of 3, 5, and 10 mass %.

The preparation of the composites was realized by a dry-blending method in an apparatus with a rotating electromagnetic field. Samples of phenylone and nanotubes were loaded in a metallic vessel. Ferromagnetic particles (15–17 mm long) in the quantity 0.04–0.06 from an electromagnetic field action volume with a magnetic induction value that was not lower than 0.02 Tl were added to this vessel. The blending duration was 20–30 s. Under the influence of the rotating electromagnetic field, ferromagnetic particles accomplished intensive chaotic motion at the expense mentioned previously. The components were blended evenly; that is, the nanotube aggregation process was suppressed.

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TABLE I  
Molecular, Structural, and Mechanical Characteristics of Phenylone/CNT Nanocomposites

CNT content (mass %)	$d_f$	$C_\infty$	$\varphi_{cl}$	$D_{ch}$	$\varepsilon_f$ (%)	$\varepsilon_f^T$ (%)	$\varphi_{if}^a$	$d_f^T$
0	2.247 ± 0.012	2.33	0.646	1.336	21.8 ± 1.1	21.9	—	2.247
3	2.230 ± 0.012	2.30	0.667	1.318	22.0 ± 1.1	20.2	0.022	2.265
5	2.354 ± 0.018	2.55	0.520	1.439	26.3 ± 1.5	33.8	0.098	2.316
10	2.280 ± 0.014	2.38	0.605	1.376	25.0 ± 1.3	25.8	—	2.247

<sup>a</sup> From eq. (2).

Wear products of the ferromagnetic particles were removed from the prepared mixture by the magnetic separation method.

The tableting process of the powderlike compositions was performed on a PSU-50 hydraulic press. During the intermediate product preparation, which corresponded to the article by shape and size, the sizes during squeezing out from the mold and particularly during drying increased about 1–2% in comparison with mold sizes, in which tableting was realized.

Before the polyamide, phenylone S-2, was shaped, it was necessary to dry it carefully. The processing of nondried phenylone worsens its mechanical characteristics, which results in the formation of surface defects (blisters, bubbles). The drying of the tableted intermediate products was realized in a SPT-200 thermostat over 2–3 h at 473–523 K. Drying was realized in such a way that a tablet from the thermostat was loaded immediately in a mold heated to 523 K.

After loading the intermediate product in a mold it was started to be closed up to the contact of the upper piston with the tablet. Then the material was heated up to 598 K and was sustained without pressure during 10 min, after that the pressure was increased up to 50 MPa. The material was sustained during 5 min at these temperature and pressure. Then the specimen was cooled under pressure and temperature 523 K and then it was removed from the mold.

Mechanical compression testing was done on an FP-100 testing machine at a temperature of 293 K and a strain rate of  $10^{-3} \text{ s}^{-1}$ . The testing specimens had a diameter of  $10 \pm 0.5 \text{ mm}$  and a height of  $15 \pm 0.5 \text{ mm}$ .

## RESULTS AND DISCUSSION

On the basis of this analysis, a basically new conception of the polymer composite structure and properties<sup>7</sup> was taken, which differed in principle from numerous earlier reinforcement theories based on the description of the structure of composites as totally matrix filler.<sup>8</sup> The conception<sup>8</sup> supposes that polymer composite properties are defined by the polymer matrix structure modified by the filler introduction, but actually the filler role modifies and fixes the matrix polymer structure. The distinctive difference in these conceptions<sup>7,8</sup> is the presence in the equations of the last of the filler characteristics [e.g., its elasticity modu-

lus ( $E$ )], whereas they do not account for conceptions<sup>7</sup> such as factors. Therefore, these conceptions<sup>7</sup> can be used for polymer composite property description as theoretical models elaborated for unfilled polymers.

As reported earlier,<sup>9</sup> the introduction of particulates and layered (organoclay) nanofillers does not change the polymer matrix structure, which expresses the condition of the constant  $d_f$ , where  $d_f$  is the fractal (Hausdorff) dimension of the structure. Its value can be determined according to the following equation:<sup>10</sup>

$$d_f = (d - 1)(1 + \nu) \quad (1)$$

where  $d$  is a dimension of Euclidean space in which a fractal is considered (it is obvious that in our case  $d = 3$ ) and  $\nu$  is Poisson's ratio. This is estimated according to the results of mechanical tests with the help of the following relationship:<sup>11</sup>

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

where  $\sigma_Y$  is the yield stress.

As follows from the data shown in Table I, an extreme growth in  $d_f$  was observed for the studied phenylone/CNT nanocomposites. It is also necessary to pay attention to the changing similarity of the nanocomposites' main structural characteristics,  $d_f$  and the experimentally determined  $\varepsilon_f$  (Table I). The determination of the polymer limiting draw ratio ( $\lambda_f$ ) was possible according to the following fractal relationship:<sup>12</sup>

$$\lambda_f = C_\infty^{D_{ch}-1} \quad (3)$$

where  $C_\infty$  is the characteristic ratio serving as an indicator of polymer chain flexibility<sup>13</sup> and  $D_{ch}$  is a fractal dimension of the part of the polymer chain between local order regions (clusters) characterizing the molecular mobility level of the polymer.<sup>5</sup>

Equation (3) parameters can be estimated as follows. The values  $d_f$  and  $C_\infty$  are connected by the following equation:<sup>5</sup>

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

In its turn, the dimension  $D_{ch}$  can be determined with the help of the following equation:<sup>14</sup>

$$\frac{2}{\varphi_{cl}} = C_{\infty}^{D_{ch}} \tag{5}$$

where  $\varphi_{cl}$  is a relative fraction of local order regions (clusters) of the polymer matrix, as determined with the help of the following equation:<sup>6</sup>

$$d_f = 3 - 6 \left( \frac{\varphi_{cl}}{SC_{\infty}} \right)^{1/2} \tag{6}$$

where  $S$  is the cross-sectional area of the macromolecule (which is equal to  $17.6 \text{ \AA}^2$  for phenylone).<sup>15</sup>

Equation (3) allows us to calculate the theoretical value of  $\varepsilon_f$  ( $\varepsilon_f^T$ ) by accounting for two factors. First, the values  $\varepsilon_f$  and  $\lambda_f$  are connected to each other as follows:

$$\varepsilon_f = \lambda_f - 1 \tag{7}$$

Second, the relation of  $\varepsilon_f$  values at tension and compression is about 0.667. The  $\varepsilon_f^T$  values calculated according to the indicated method for the phenylone/CNT nanocomposites are listed in Table I together with the necessary characteristics  $C_{\infty}$ ,  $\varphi_{cl}$ , and  $D_{ch}$ . As follows from the data of this table, a comparison of the experimental  $\varepsilon_f$  values and theoretical  $\varepsilon_f^T$  values of the limiting strain at fracture, which characterized the phenylone/CNT nanocomposite plasticity, showed good correspondence: the average discrepancy was 8.5%, which corresponded to the experimental error of this parameter determination.

Let us consider the physical grounds of the increasing plasticity effect studied for the nanocomposites filled by CNT. The difference of CNT from other nanofillers (disperse particles, organoclays) is their smooth surface<sup>1</sup> on an atomic scale, which results in the stretching of matrix polymer macromolecules on this surface and the formation of a densely packed interfacial layer between the polymer matrix and CNTs.<sup>16</sup> The values of the interfacial region relative fraction ( $\varphi_{if}$ ) for the studied nanocomposites according to the data of ref. <sup>2</sup> are also listed in Table I. The dense packing of these regions supposed that their value of  $d_f$  ( $d_f^{if}$ ) reached the maximum possible magnitude for real solids, namely,  $d_f^{if} = 2.95$ .<sup>10</sup> Furthermore, the calculation of the theoretical value of  $d_f$  ( $d_f^T$ ) could be carried out according to the mixture law:

$$d_f^T = d_f^p (1 - \varphi_{if}) + d_f^{if} \varphi_{if} \tag{8}$$

where  $d_f^p$  is the phenylone structure fractal dimension, which is equal to 2.247 (Table I).

The  $d_f^T$  values calculated according to eq. (8) are also listed in Table I, and their comparison with the  $d_f$  values showed good correspondence (the average discrepancy of  $d_f$  and  $d_f^T$  was 1.5%). On this basis,

the theoretical calculation of  $\varepsilon_f^T$  stated previously was based, as a matter of fact, on the dimension  $d_f$  knowledge; one can conclude that the observed increasing plasticity effect of the polymer/CNT nanocomposite was due to the formation of densely packed interfacial regions on the nanotube surface, and as consequence, the molecular and structural characteristics of polymer matrix ( $C_{\infty}$ ,  $d_f$ ,  $\varphi_{cl}$ , and  $D_{ch}$ ; see Table I) changed. An increase in  $\varepsilon_f$  was accompanied by growth of the dimension  $D_{ch}$  (Table I), that is, by molecular mobility intensification. As Kaush<sup>17</sup> showed, such interrelation is common for polymers.

Let us consider in conclusion the prediction of the properties of the phenylone/CNT nanocomposite containing 30 mass % nonaggregated CNTs. The value  $\varphi_{if}$  in this case can be estimated according to the following equation:<sup>2</sup>

$$\varphi_{if} = 1.86\varphi_f \tag{9}$$

where  $\varphi_f$  is the CNT content.

The nanocomposite elasticity modulus ( $E_{nc}$ ) can be calculated according to the following equation:<sup>9</sup>

$$\frac{E_{nc}}{E_m} = 1 + 11 \left( \varphi_f + \varphi_{if} \right)^{1.7} \tag{10}$$

where  $E_m$  is the phenylone matrix elasticity modulus, which is equal to 1.25 GPa in tension testing.

Then, the value  $E_{nc}$  for the indicated hypothetical phenylone/CNT nanocomposite containing 30 mass % CNTs is 11.85 GPa. The  $d_f^T$  calculation according to eq. (8) gives a value of 2.64 or  $\nu = 0.32$  according to eq. (1). Hence, the  $\sigma_Y$  value for such a nanocomposite according to eq. (2) will be 820 MPa. Finally, calculation according to eqs. (3)–(6) will give a value of  $\varepsilon_f^T$  of 1.2 or 120%. Two technological difficulties prevent the production of such an exceptional total nanocomposite by their mechanical properties, namely, the very high cost of nanotubes, which can be several tens and even hundreds of dollars for one-layered CNT grams, and the technology of the last production, where nanotubes can be obtained in the form of tangled bundles only; at present, the dispersion methods work effectively only up to CNT contents of several percent.<sup>1,2</sup>

### CONCLUSIONS

Hence, the results stated in this article confirm the structural analysis correctness at a limiting strain (plasticity) estimation of phenylone/CNT nanocomposites. The offered model gives good correspondence of theoretical and experimental values. The physical grounds of the increasing plasticity of nanocomposites filled by CNTs is the formation of densely packed interfacial regions on the smooth surface of the nanotubes on an atomic scale. The

offered treatment will allow researchers to predict the nanocomposite properties and to plan methods of their practical realization.

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