

# Influence of Diffusive Processes on the Formation of an Interfacial Layer in Carbon Plastics Based on Phenylone

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Received 13 October 2004; accepted 15 June 2005

DOI 10.1002/app.23118

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The influence of the interfacial layer structure on the intensity of diffusive processes during their formation was shown. An increase in the fractal dimension of this layer structure, which was due to macromolecular coils drawing on the smooth surface of the fiber, was determined by a transition from fast diffusion to slow. This factor

was controlled by both the thickness of the interfacial layer and its strength. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4044–4047, 2006

**Key words:** composites; fibers; interfaces; molecular modeling; strength

## INTRODUCTION

A peculiar feature of polymer composites is the existence of an interfacial layer structure, the properties of which determine to a significant degree their composite properties as engineering materials.<sup>1</sup> This is why so much attention has been paid to the investigation of the given question.<sup>2</sup> Lately, for this purpose, modern physical concepts have been used: scaling, irreversible aggregation models, fractal analysis, and so on.<sup>3,4</sup> Within the terms of these models, the substantial influence of the interfacial layer structure on both the filler surface structure and its formation mechanism has been demonstrated, and it is connected to the degree of participation in the aforementioned layer formation of diffusive processes.<sup>5–7</sup> In general, this interrelation can be formulated as follows: the more diffusive processes there are in the interfacial layer formation, the greater the interpenetration degree is of macromolecular coils and the greater its strength is.<sup>5</sup> Therefore, the purpose of this article is the study of diffusive processes in interfacial layer formation in carbon plastics based on phenylone through fractional derivative theory and fractal analysis.

## EXPERIMENTAL

As the polymer matrix, an aromatic polyamide–phenylone<sup>8</sup> was used, and as the filler, carbon fibers with

a diameter of 7–9  $\mu\text{m}$  and a length of 3 mm were used. The mass content of the carbon fibers was 15%, which corresponded to a nominal volume content ( $\phi_f$ ) of approximately 0.115. The composites were produced by a dry method, including component blending in a rotating electromagnetic field. For this, powdery polymer, carbon fibers, and nonequaxial ferromagnetic particles with a length of 40  $\mu\text{m}$  were placed in a reactor. Then, the reactor was placed in the end window of the generator of the electromagnetic apparatus. Through the action of the rotating electromagnetic field, the ferromagnetic particles began to rotate, colliding with one another, and this resulted in the equipartition (chaotic) distribution of the carbon fibers in the polymer matrix. As a result of the collisions, the particles were worn down, and the products of the wear were mixed. For the removal of the ferromagnetic particles after blending, two methods were used: magnetic and mechanical separation.<sup>9</sup>

The thermal properties were determined with a model UT-S-400 differential scanning calorimeter at a heating rate of 10 K/min.

## RESULTS AND DISCUSSION

At present, the division of diffusive processes into fast and slow<sup>10,11</sup> is commonly accepted. On the basis of this division lies the dependence of the diffusible particle displacement ( $S$ ) on the time ( $t$ ):<sup>11</sup>

$$S \sim t^\beta \quad (1)$$

For the classical case,  $\beta$  is 1/2; for slow diffusion,  $\beta$  is less than 1/2; and for fast diffusion,  $\beta$  is greater than 1/2.

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In terms of fractional derivation theory, it has been shown that the basic parameter (fractional exponent  $\alpha$  is connected to both  $\beta$  and characteristics of the structure), fractal dimension  $d_f$ , by various functional forms depends on the diffusion type. In different terms, structures with the same  $d_f$  value can have very different diffusivity ( $D$ ) values. The interrelation of  $d_f$  (in our case, the fractal dimension of the interfacial layer structure,  $d_f^{if}$ ) and  $\alpha$  can be defined by analogy with ref. 11 as follows. The Herst exponent ( $H$ ) is connected to  $d_f$  as follows:

$$d_f = 3 - H \quad (2)$$

The authors<sup>11</sup> showed that in eq. (1), exponent  $\beta$  is equal to  $(1 - \alpha)/2$  for slow diffusion and  $1/(1 + \alpha)$  for fast diffusion. Equaling  $H$  to the aforementioned expressions for  $\alpha$  according to this technique,<sup>11</sup> we can obtain an interrelation of  $\alpha$  and  $d_f^{if}$  for slow diffusion

$$\alpha = \frac{3 - d_f^{if}}{2} \quad (3)$$

and for fast diffusion

$$\alpha = \frac{1}{d_f^{if} - 1} \quad (4)$$

The value of  $d_f^{if}$  can be calculated with the following equation:<sup>12</sup>

$$d_f^{if} = 3 - 6 \left( \frac{\phi_{if}}{SC_\infty} \right)^{1/2} \quad (5)$$

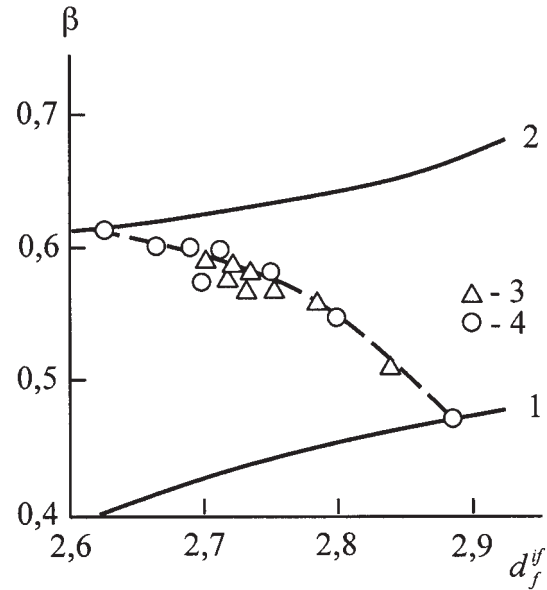
where  $\phi_{if}$  is the relative fraction of the interfacial layers,  $S$  is the cross-sectional area of a macromolecule ( $17.6 \text{ \AA}^2$  for phenylone),<sup>13</sup> and  $C_\infty$  is the characteristic ratio (which is characteristic of the statistical flexibility of a polymer chain<sup>14</sup> and, for drawing on fiber surface macromolecules, is accepted to be equal to  $9^{15}$ ).

In turn,  $\phi_{if}$  can be calculated with the following equation:<sup>16</sup>

$$\phi_{if} = 1 - \frac{\Delta C_p^c}{\Delta C_p^p} \quad (6)$$

where  $\Delta C_p^c$  and  $\Delta C_p^p$  are the values of the specific heat at a constant pressure jump at the glass-transition temperature for the composite and matrix polymer, accordingly.

The second calculation method of exponent  $\alpha$  consists of the direct application of eq. (1) when the thickness of the interfacial layer ( $l_{if}$ ) is equal to  $S$  and the value of  $t$  is accepted to be equal to duration  $t$  of composite production. For  $t = 300$  s,  $l_{if}$  can be calculated as follows:<sup>16</sup>



**Figure 1** Dependence of exponent  $\beta$  on  $d_f^{if}$  for carbon plastics based on phenylone: theoretical calculations for (1) slow and (2) fast diffusion and calculations according to eq. (1) for specimens produced with (3) magnetic and (4) mechanical separation.

$$\left( \frac{l_{if} + r}{r} \right)^3 - 1 = \phi_{if} \frac{\phi_f}{1 - \phi_f} \quad (7)$$

where  $r$  is the fiber radius (4 mcm) and  $\phi_f$  is the volume filling degree (0.115).

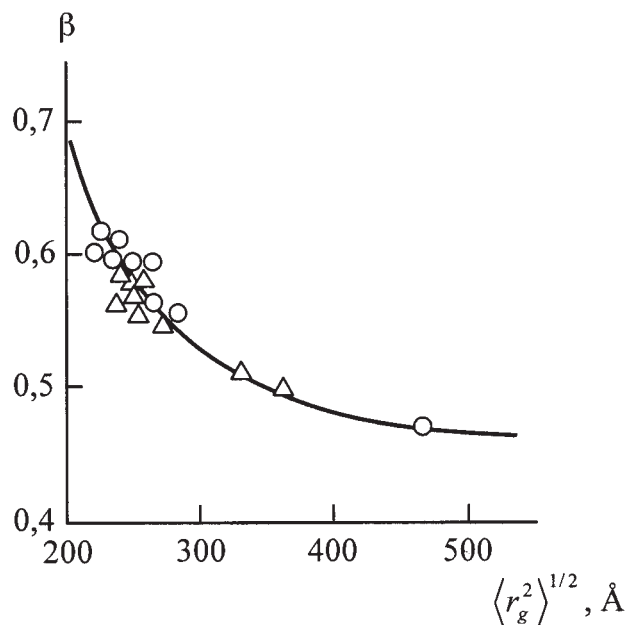
In Figure 1, a comparison of the dependences of  $\beta$  values, theoretically obtained and calculated according to eq. (1), on  $d_f^{if}$  is shown. The values of  $\beta$  calculated according to eq. (1), that is, according to the experimental values of  $l_{if}$  and  $t$ , are intermediate between the theoretical dependences of  $\beta$  on  $d_f^{if}$  for slow and fast diffusion. An increase in  $d_f^{if}$  results in the reduction of  $\beta$  and defines the transition from fast diffusion to slow diffusion. In turn, this reduces  $l_{if}$  from 2.77 to 1.18 mm.

To clear up the physical foundation of this effect, the calculation of the gyration radius ( $\langle r_g^2 \rangle^{1/2}$ ) of macromolecular coils in the interfacial layer was performed. In terms of fractional derivative theory, this parameter can be determined according to the following equation:<sup>11</sup>

$$\langle r_g^2 \rangle^{1/2} = \frac{l_{st}}{(1 - \alpha)\Gamma(\alpha)} N^{1-\alpha} \quad (8)$$

where  $l_{st}$  is the statistical segment length,  $\Gamma(\alpha)$  is the  $\Gamma$  function of Euler, and  $N$  is the polymerization degree.

$l_{st}$  is determined according to the following formula:<sup>17</sup>



**Figure 2** Dependence of exponent  $\beta$  on  $\langle r_g^2 \rangle^{1/2}$  of a macromolecular coil in an interfacial layer for carbon plastics based on phenylene produced with (1) magnetic and (2) mechanical separation.

$$l_{st} = l_0 C_\infty \quad (9)$$

where  $l_0$  is the length of the skeletal link of the main chain (1.25 Å for phenylene).<sup>18</sup>

The interrelation between the structure of the interfacial layer condensed state, characterized by dimension  $d_f^{if}$ , and the fractal dimension of the macromolecular coil ( $D_f$ ) for linear polymers can be defined as follows:<sup>19</sup>

$$d_f^{if} = 1.5D_f \quad (10)$$

The value of fractional exponent  $\alpha$  for such coils is determined as follows:<sup>20</sup>

$$\alpha = D_f - D_f^{tr} \quad (11)$$

where  $D_f^{tr}$  is the fractal dimension of a transparent coil (1.50).<sup>21</sup>

Euler's  $\Gamma$  function for variable  $\alpha$  takes the following form:<sup>22</sup>

$$\Gamma(\alpha) = \left(\frac{\pi}{2}\right)^{1/2} \alpha^\alpha e^{-\alpha} \quad (12)$$

The value of  $N$  in eq. (8) is accepted to be 200.

In Figure 2, the dependence of  $\beta$ , calculated according to eq. (1), on  $\langle r_g^2 \rangle^{1/2}$  of macromolecular coils is shown. As follows from the data of this figure, the increase in  $\langle r_g^2 \rangle^{1/2}$  or the coil drawing degree on the fiber surface results in weakening of the diffusive

processes, as expressed by a reduction of  $\beta$ . In different terms, the more strongly a coil is drawn on a fiber surface, the denser the interfacial layer structure is and the greater its fractal dimension,  $d_f^{if}$ , is, and this results in a weakening of the interpenetration of macromolecular coils, an inhibition of diffusive processes, and a reduction of  $\beta$ , which defines the transition from fast diffusion to slow diffusion.

Let us consider the influence of diffusive processes on the strength of the interfacial layer ( $\sigma_a$ ). This parameter can be estimated as follows:<sup>23</sup>

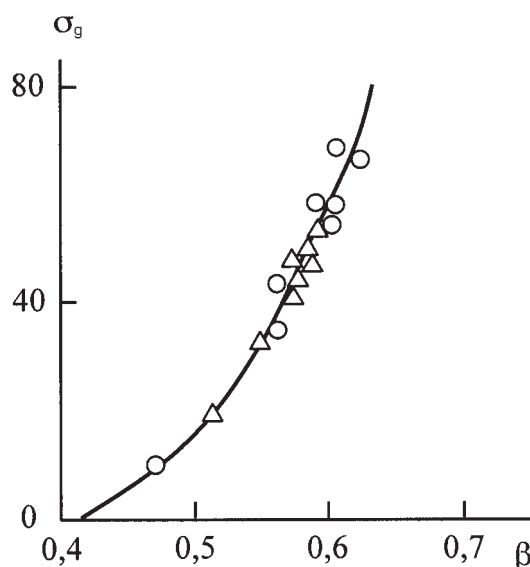
$$\sigma_a = 1.4 \times 10^5 \left( \frac{\phi_{if}}{2N_A S l_0 C_\infty} \right)^{5/6} \text{ (Pa)} \quad (13)$$

where  $N_A$  is Avogadro's number.

In Figure 3, the dependence of  $\sigma_a$  on exponent  $\beta$ , calculated according to eq. (1), is shown, from which follows the fast growth of  $\sigma_a$  with  $\beta$  increasing. Therefore, the amplification of the role of diffusive processes in interfacial layer formation contributes to the increase in the strength. The physical basis of this effect is obvious: diffusion amplification contributes to the interpenetration of macromolecular coils and the formation of denser networks of physical entanglements, and this increases the interfacial layer strength.

## CONCLUSIONS

The results of this study show an influence of the interfacial layer structure on the intensity of diffusive processes during their formation. An increase in the fractal dimension of this layer structure, which is due



**Figure 3** Dependence of  $\sigma_a$  on exponent  $\beta$  for carbon plastics based on phenylene produced with (1) magnetic and (2) mechanical separation.

to macromolecular coils drawing on the smooth surface of the fiber, defines a transition from fast diffusion to slow diffusion. This factor controls both the thickness of the interfacial layer and its strength.

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