Efficiency of Short Fibers in Filling Polymer Composites

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ABSTRACT: The present study showed that in carbon plastics the structure of a short-fiber system (network) can be described by the effective degree of volume filling or by the fractal dimension of the system. Using the effective degree of filling, synergetic behavior was found, and the filler efficiency of the carbon plastics was characterized within the framework of the fractal model of reinforcement.
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INTRODUCTION

At present, the main structural characteristic of a polymer composite generally is considered the degree of volume filling, Φ_f.[1] However, this parameter does not universally provide information on composite structure, especially when the polymer composite is filled by short fibers with their specific strong anisotropy. Microscopic studies of real composite materials have shown convincingly enough the nonequipartitional distribution of the fibers, their aggregation, the disturbance of mutual fiber parallelism, the existence of porosity, and so on.[2] That is why in practice such an idea as that or other properties of a fiber system, including not only the physical properties but also the geometric features of the composition of a material, is often introduced.[2] However, it is obvious that it is more productive to operate not by using such a generalized property but by using the structural characteristics of a fiber system (network) that define any of its properties. Within the framework of fractal analysis of such structural characteristics, the fractal dimension of a particle filler network, D_n, was used, which describes the density of the polymer matrix space filled by the particles or fibers of the filler.[3,4] The phenylone-based carbon plastics investigated in the present study were suitable for studying the influence of fiber system structure on composite properties. This is because with the technology used, production occurred at a constant value of Φ_f but with sufficient variation of other properties; for example, elasticity modulus varied in the range of 2.13–3.36 GPa. Therefore, the purpose of the present study was to formulate and determine the effective degree of volume filling and to describe the influence of this parameter on the properties of the polymeric matrix for the carbon plastics investigated using the fractal analysis and percolation theory methods.

EXPERIMENTAL

An aromatic polyamide–phenylone[4] was used as the polymer matrix and as the carbon fiber (CF) filler, with the fibers having a diameter of 7–9 mm and a length of 3 mm. CF made up 15% of the mass content, corresponding to a nominal degree of volume filling, Φ_f, of approximately 0.115. The composites were produced according to the "dry" method, including component blending in a rotating electromagnetic field. For this purpose, powdery polymer, CF, and nonequiaxial ferromagnetic particles with a length of 40 mm were placed in a reactor. Then the reactor was placed on the end window of the generator of the electromagnetic apparatus. Under the influence of the rotating electromagnetic field, ferromagnetic particles began to rotate, colliding with each other, which resulted in the equipartitional (chaotic) distribution of the CF in the polymer matrix. As a result of the collisions, the particles were worn down, and the products of wear became part of the composition. After blending, two methods were used to remove the ferromagnetic particles: magnetic and mechanical separation.[6]

The specimens used for studying the mechanical properties were prepared by a method of not pressing at a temperature of 603 K and a pressure of 55 MPa. Compression testing was performed on an FP-100 machine at a temperature of 293 K and a strain rate of 10^{-3} s^{-1}.

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

RESULTS AND DISCUSSION

As noted above, the change in the duration of the component blending, t, in the rotating electromagnetic field resulted in substantial variation in the elasticity modulus, E_c (2.13–3.33 GPa), of the carbon plastics studied. Within the framework of the percolation theory, the authors[7] propose the following equation for determining the value of E_c:

$$E_c = E_m(1 + 11\varphi_f^{1.7}), \quad (1)$$

where E_m is the elasticity modulus of the polymer matrix.

It is obvious that in its initial form eq. (1) was not applicable for the description of the E_c behavior of carbon plastics, as the Φ_f is constant, but the value of E_c changes more than 1.5 times. However, this equation can be used for calculating the effective degree of volume filling, Φ_f^{ef}, which expresses the structure of the fiber filler system, determining the macroscopic properties of the composite (given the E_c). In addition, there was great interest in comparing this parameter with the fractal dimension of the particle filler network, D_n, which can be determined according to the equation[4]

$$D_n = 2 + \frac{\varphi_{if} d_{surf}}{1.20}, \quad (2)$$

where Φ_{if} is the relative fraction of the interfacial regions and d_{surf} is the fractal dimension of the filler's fiber surfaces. Because of the technology by which the carbon plastics were produced, the process of fiber aggregation was expressed weakly[8]; then d_{surf} = const = 2.13[9] was adopted. In turn, the value of Φ_{if} was determined according to the equation[10]

$$\varphi_{if} = 1 - \frac{\Delta C_p^c}{\Delta C_p^p}, \quad (3)$$

where $\Delta C_{,p}^c$ and ΔC_p^p are the values of specific heat at a constant pressure jump near the glass-transition temperature for the composite and the polymer matrix, respectively.

The correlation of the structural characteristics of the fiber system (network) in the carbon plastics on the basis of the phenylone Φ_f^{ef} and D_n is shown in Figure 1. As can be seen, linear growth of Φ_f^{ef} was observed as D_n increased. D_n changing within the limits $2.0 \leq D_n < 3.0$[3] made it possible to estimate the variation in the magnitude of Φ_f^{ef} in the interval of 0.060–0.264. Analytically, the correlation between Φ_f^{ef} and D_n is expressed as:

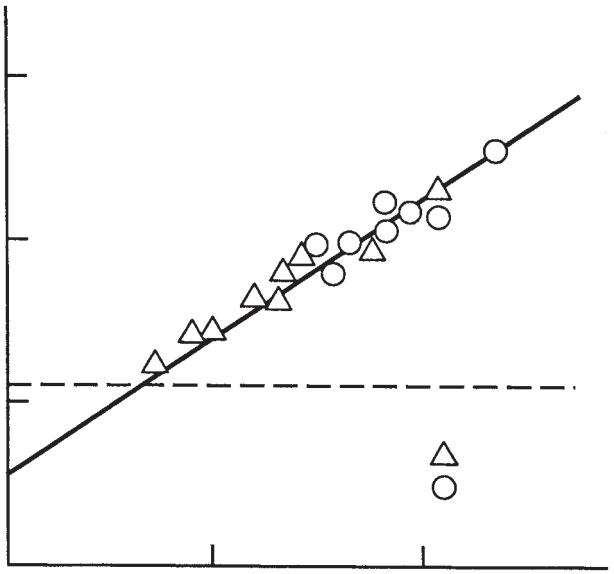

Figure 1 Dependence of degree of effective volume filling, Φ_f^{ef}, on fractal dimension of fiber network, D_n, for carbon plastics on the basis of phenylone produced with the application of (1) magnetic and (2) mechanical separation. Horizontal dotted line is the nominal magnitude, Φ_f.

$$\varphi_f^{ef} = 0.060 + 0.204(D_n - 2). \quad (4)$$

It should be noted that for the carbon plastics considered, the inequality $\Phi_f^{ef} > \Phi_f$ (Fig. 1) occurred, that is, the effective degree of volume filling was always more than the nominal value.

Figure 2 shows the dependence of Φ_f^{ef} on the duration, t, of the blending of the components in the rotating electromagnetic field for the carbon plastics considered. The form of the dependence $\Phi_f^{ef}(t)$ was specific to the synergetic structures: at first, the periodic (ordered) behavior of Φ_f^{ef} was close to sinusoidal with a twofold period; then a transition to chaotic behavior[11] was observed. It should be noted, that the value of Φ_f^{ef} for the carbon plastics produced by mechanical separation was on average 20% greater than that of the specimens produced by magnetic separation. This observation supposes that when mechanical separation was used, the ferromagnetic particle wear products remaining in the composite either directly influenced the structure of the fiber network or (which is more probable) indirectly influenced it by affecting the polymer matrix structure and then, through it, the structure of the network.

As a rule, the efficiency of composite filling is described with the use of the modulus efficiency coefficient, k_e, which is determined according to the equation[12]

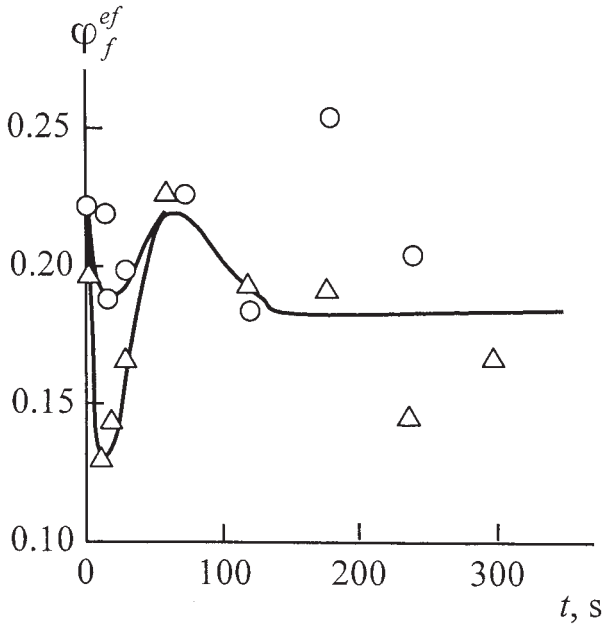

Figure 2 Dependence of degree of effective volume filling, Φ_f^{ef}, on duration, t, of components blending in rotating electromagnetic field. Notation is the same as that in Figure 1

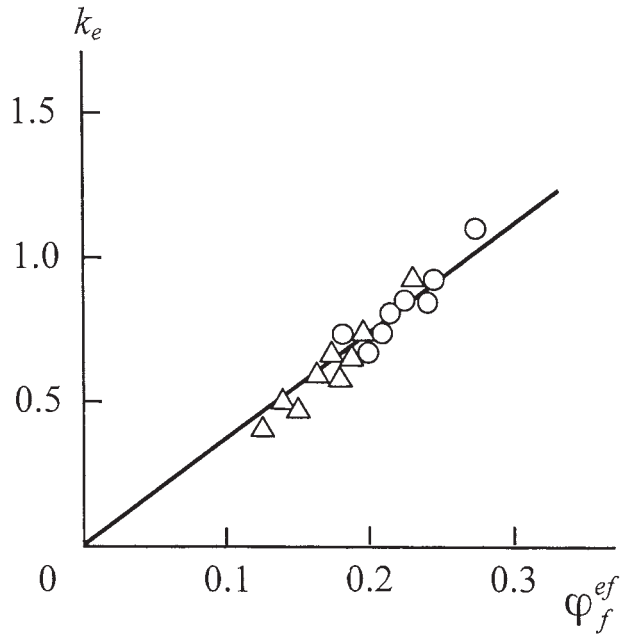

Figure 3 Interrelation of modulus efficiency coefficient, k_e, and degree of effective volume filling, Φ_f^{ef}. Notation is the same as that in Figure 1

$$k_e = \frac{E_c - E_m(1 - \varphi_f)}{E_f \varphi_f}, \quad (5)$$

where E_f is the elasticity modulus of the filler, which was approximately 15 GPa for CF.[8]

Figure 3 shows a comparison of two characteristics of the filling efficiency of the carbon plastics, k_e and Φ_f^{ef}. As can be seen, these parameters are identical and differ only quantitatively; the interrelation between them is given by a simple relationship:

$$k_e = 3.80\varphi_f^{ef}. \quad (6)$$

At the same time, parameters k_e and Φ_f^{ef} have a principal difference between, which expresses the difference between two conceptions of polymer composite reinforcement: the classical conception (mechanics of continua)[13] and the fractal conception.[4] Within the terms of the first conception, the dependence of E_c on E_f is introduced, which is expressed in eq. (5). Fractal conception supposes that the change in E_c is a result of the change (disturbance) in the filling process of the polymer matrix, and so in this conception the E_f is not included. It should be noted the absence of E_f in eq. (1), obtained using the terms of percolation of filled polymer reinforcement, follows the interrelation of the structures of the particle (fiber) filler network and the polymer matrix. The main provider of information on the state of matter is fractal dimension, d_f, which, for the polymer matrix, could be determined according to the equation[14]

$$d_f = (d - 1)(1 + v), \quad (7)$$

where d is the dimension of Euclidean space, in which the fractal is considered (in our case, it obviously was $d = 3$), and ν is Poisson's ratio, the value of which can

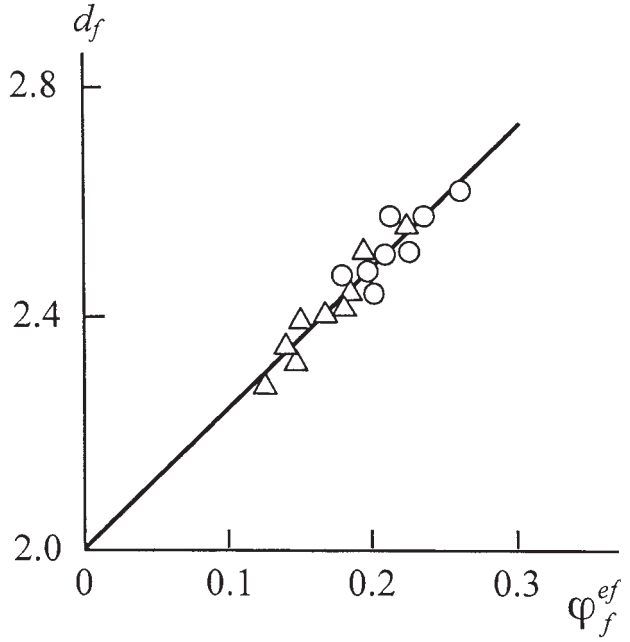

Figure 4 Dependence of structure fractal dimension, d_f, on degree of effective volume filling, Φ_f^{ef}. Notation is the same as that in Figure 1

be calculated with the help of the mechanical testing results using the relationship[15]

$$\frac{\sigma_Y}{E_c} = \frac{1 - 2v}{6(1 + v)}, \quad (8)$$

where σ_Y is the yield stress.

Figure 4 shows the dependence $d_f(\Phi_f^{ef})$, from which an increase in d_f with an increase in Φ_f^{ef} follows, that is, raising the effective degree of volume filling amplified the disturbance of the polymer matrix structure as in particulate-filled polymer composites.[3,4]

CONCLUSIONS

The results of the present study have shown that the structure of a short-fiber system (network) in carbon plastics can be described by the use of the effective degree of volume filling or the fractal dimension of this system. Using the effective degree of filling parameter, synergetic behavior was found, and filler efficiency for carbon plastics was characterized within the framework of the reinforcement fractal model.

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