FRACTAL PARAMETERIZATION OF THE STRUCTURE OF FILLED POLYMERS

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It is suggested to consider the structure of a filled polymer as a set of two or more multifractals. It is shown experimentally that the basic factor determining the fractal dimension of distribution of a disperse filler in the polymer is the size distribution of filler particles.

Introduction

Filled polymers are widely used as structural and functional materials, which inspires increased interest in investigation of their structure and properties. It is widely believed that the properties of these materials depend only on the properties of constituents and their volumetric content [1, 2]. One of the most frequently used approaches is the consideration of filled polymer materials as macroscopically homogeneous systems [3-5]. However, as mentioned by some researchers (see, for example, [6, 7]), numerous models available for describing the properties of particulate-filled polymers have a rather narrow field of application. In this connection, it was necessary to develop an essentially new fundamental approach to this problem. A variant of such an approach is proposed in [8] where the properties of a particulate-filled polymer are assumed to be totally determined by the structure of the polymer belonging to the material (polymer matrix), while the role of the filler is reduced to a modification ("disturbance") of the structure of the polymer, when it fulfills the function of a matrix. This approach is based on the known fact that all the processes governing the properties of filled polymers (fracture, flowability, relaxation, etc.) are realized just in the polymer matrix.

One of the promising and fundamental methods for studying polymer materials is their numerical (computer) simulation. In turn, to create a software for predicting the structure and properties of filled polymers, it is necessary to have a physical insight into the processes taking place in polymers during their production and under various external actions. As such an approach, the principles of synergetics and methods of fractal formalism are being invoked with increasing frequency [9].

There are a lot of various objects with a nonintegral power (fractal) distribution of their sizes [10]. Such a distribution is valid for both micro- [11, 12] and macro-objects [13]. Thus, there are strong grounds to expect a similar size distribution for particles of a disperse filler in filled polymers as well, particularly when aggregation of particles is possible. There is another reason for the assumption of a fractal distribution of filler particles, which, as is known [14], can form a percolation cluster when their content reaches a certain magnitude. Near the threshold of percolation, the cluster, in turn, has a fractal structure [13]. Thus, we may assume that the particles of the disperse filler must form a kind of "skeleton," or a network, of a filled polymer [15], which considerably determines its properties. Such a filled polymer or a polymer composite can be represented as a collection of suspended fractal structures [16] with different weights. So, a fractal can be repre-
sented by the network of filler particles (at least near the threshold of percolation [14]), the polymer matrix [17], the surface of filler particles [18], etc. Therefore, it is necessary to determine the dimensions of the fractals mentioned and their interaction in the total structure of the filled polymer [19], i.e., the polymer can be regarded as a multifractal in the sense that it possesses a statistical self-similarity, which exists within a bounded interval of linear scales.

Within the framework of the multifractal formalism [19, 20], the fractal dimension of the network of filler particles, \( D_n \), is the greatest Hausdorff dimension, i.e., the Renyi dimension \( D_0 \) at \( q = 0 \), where \( q \) is an index [20]. In this case, for the Renyi dimension \( D_q \) (at \( q = 1 \)) must be taken the fractal dimension \( d_p \) of the surface of filler particles [19], which is the dimension of the first subfractal. There exists a certain interrelation between the quantities \( D_n \) (or \( D_0 \)) and \( d_p \) (or \( D_i \)). The quantity \( D_n \) characterizes the size distribution of particles in the polymer matrix and, consequently, represents the index of aggregation of these particles [21]. As is known [22], the fractal dimension of the surface of filler particles, \( d_p \), can vary from 2 to 3. In addition, the quantity \( d_p \) of the filler in the polymer matrix is a power function of the particle aggregation [22]. In other words, we can expect that there is a relation between the parameters \( d_p \) and \( D_n \) and, therefore, a relationship between the basic properties of filled polymers and the fractal dimension of the filler, \( d_p \).

The purpose of the present study is to determine experimentally the fractal parameters of the structure of filled polymers (fractal dimension of the network of filler particles, \( D_n \), of their surface \( d_p \), and of the polymer matrix \( d_m \)), to clarify the physical sense of these parameters and the character of their relationship with the properties of composite materials.

**Experimental**

We investigated polyhydroxyether (PHE) (with the reduced viscosity of a 0.5% solution in chloroform 0.44 dl/g) and graphite powder (G) of trademark GL-1. Filled specimens were prepared from a 17% polymer solution in a blend of two solvents: 1,4-dioxane and \( N,N \)-dimethylacetamide with a weight ratio 1:1 mixed with a necessary amount of graphite powder. The mixture was deposited in water. The obtained powder-filled polymers with graphite content 2, 4, 5, 10, 20, and 40 wt.% was dried in vacuum at ~330 K up to constant weight [23]. Then, the mixture was extruded at a temperature of 470–490 K on a screw extruder and granulated. The specimens for the impact tests with dimensions according to GOST 4647–80 (standard size II) were obtained by injection molding at a temperature of 490 K [24]. Two series of PHE specimens were used in our experiments, namely the specimens filled with nonactivated graphite (PHE–GN) and those filled with the graphite activated by a blend of sulfuric and nitric acids (PHE–GA). The activation of graphite was performed as follows. First, graphite was mixed with the blend of acids and held for 40 min. Then, the blend was heated and boiled for 30 min. The suspension was cooled and flushed out with water until the rinsing water was free from \( \text{SO}_4^{2-} \) ions. The process was completed by drying the graphite powder at 340 K up to constant weight.

The Charpy impact tests were carried out both on specimens without a notch and with a sharp notch (of length \( a = 0.22 \) mm) on a pendulum impact testing machine with a piezoelectric load sensor, the signal from which was transferred to an SV–13 memory oscillograph for obtaining the load—time (\( P — t \)) diagram. This diagram allows us to calculate the elastic modulus \( E [25] \), yield stress \( \sigma_y \), and failure stress \( \sigma_f \) [26]. The notches were made with the edge of a sharpened razor blade. Their length was controlled on the fracture surface of specimens by means of a Zeiss optical microscope (accuracy +0.02 mm). All tests were carried out at a temperature of 293 K.

The structure of graphite-filled PHE specimens was examined by the method of transmission electron microscopy using two–stage replicas of chips which were obtained both at room temperature and the temperature of liquid nitrogen. The replicas were studied in an EMMA–4 transmission electron microscope at magnification 5000×.

The fractal dimension of the network of filler particles (of their distribution), \( D_n \), was measured using the method of [12, 13] based on a known relation

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D_n = \frac{\ln N}{\ln p},
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(1)