

**TECHNOLOGY OF OBTAINING NANOCOMPOSITES ON THE BASIS
OF AN EPOXY BINDER AND A NANO-SIZED FILLER**

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Abstract

Epoxy resin has been modified with nano-SiO₂ particles with diameters from 7 to 50 nm. The experiments show that the Young modulus and strength of nanosilica/epoxy resin-based composite increases up to 25 wt.% and then decreases after SiO₂ content reaches 40 wt.%. A series of experiments has been conducted to study the effect of the size of the filler particles on fracture of composites materials.

Key words: Epoxy resin; Nanosilica; Mechanical properties; Modification.

1. INTRODUCTION

The dynamic development of industrial sectors is impossible without permanent improvement of materials. The use of composite materials (CMs) instead of the traditional ones allows significant reduction of the product weight without deteriorating the strength characteristics, which is particularly important for the aviation and aerospace industry. In addition, CMs may often have unique properties that are not inherent in traditional materials, which make them indispensable for applications in certain areas of engineering.

This paper deals with the research of physical and mechanical characteristics of nano-modified epoxy composite materials, which are widely used in the construction industry as protective impregnations and coatings that increase the carrying capacity, chemical resistance, and durability of building structures. The dependence of the modulus of epoxy resin on the filler size has been studied.

The goal of this work is to develop a method of epoxy resin binder modification by silicon dioxide nanoparticles and a technology of obtaining the corresponding composite materials with improved performance.

2. EXPERIMENTAL PROCEDURE

Polymer materials often do not possess sufficient rigidity and strength to satisfy requirements to various structures made of these materials. Insertion of various reinforcing fillers is a conventional method of improving these properties so that filled polymers could be used as structural materials.

The development of polymer technologies leads to permanent extension of the class of polymers filled by particles, which, in turn, makes the necessity of predicting the mechanical properties of such materials more important.

When viscous thermoplastics are filled by rigid fillers to an extent of more than 20%, a transition from plastic flow to brittle fracture occurs. In this case, significant reduction of the shock viscosity and the fracture work is observed. The elasticity modulus increases with increasing amount of the filler, but

the size and number of cracks arising in the course of loading also increase as the matrix flakes off from disperse particles at the instant when the stress corresponding to the adhesion strength of the system is reached. Theoretical and experimental investigations show that the probability of the emergence of large defects can be appreciably reduced by decreasing the filler particle size and the scatter in the particle diameters.

The strength properties of articles made of polymer composite materials (PCMs) are determined by various factors: mechanical properties of the phases, character of phase interaction, filler geometry, degree of filling, fabrication technology, etc. The PCM strength properties are not constant because of instability of parameters of technological processes of fabrication of PCM articles.

2.1. Materials

In our study, we used hydrophilic nano-sized powders of silicon dioxide called Tarkosil (series T) with specific surface areas of 54, 74, 96, and 150 m²/g, which corresponds to the mean particle sizes of 50, 37, 30, and 18 nm, and Aerosil A-200 (14 nm), A-300 (9 nm), and A-380 (7 nm). The ED-20 epoxy resin was used as a matrix in all experiments. The polyethylene polyamine (PEPA) hardener (1 part of the hardener to 6 parts of epoxy resin) was added for solidification. Samples with a rectangular cross section satisfying the Russian Standard GOST 11262-80 were prepared for experiments (Fig. 1). The body of the chosen resin allowed samples to be made by the casting technology. For this purpose, we prepared moulds from the PentelastTM silicon-based compound with cavities repeating the shape of the samples for mechanical tests. An important factor is the low adhesion of these moulds to epoxy resin. To obtain epoxy resin with lower viscosity, it was heated to 50°C.

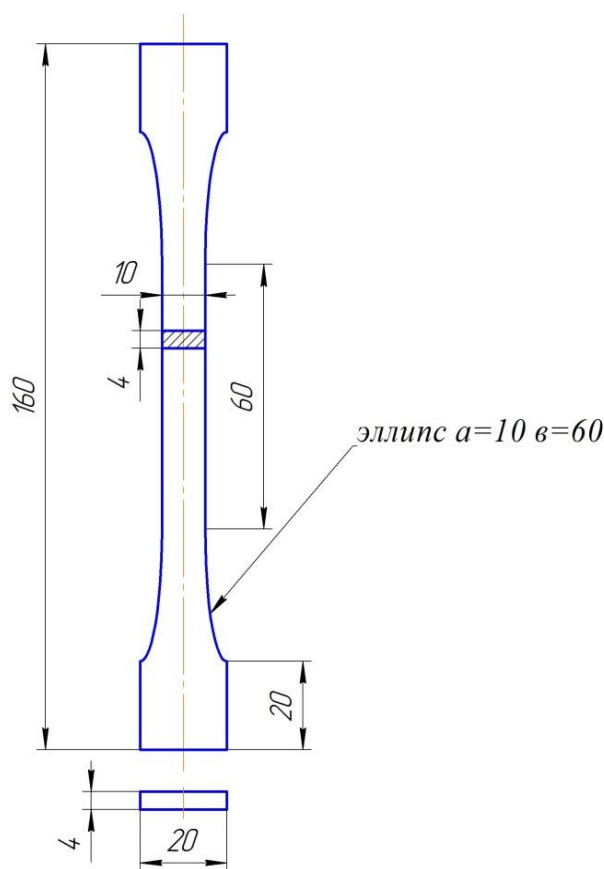


Fig. 1. Shape of the prepared samples

As is known, owing to the high surface energy, the inserted nanoparticles are almost always in the form of agglomerates whose size can reach several micrometers. If the agglomerates are too large, they are dangerous agents serving as stress concentrators in a polymer system (Fig. 2); therefore, such agglomerates should be dispersed or sifted away.

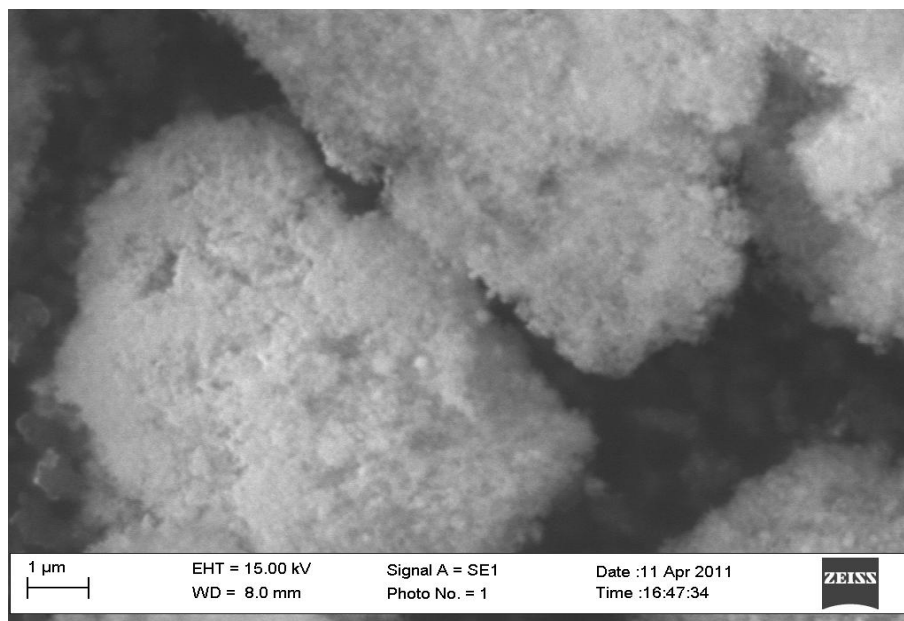


Fig. 2. Photograph of agglomerates of Tarkosil T-20 silicon dioxide particles.

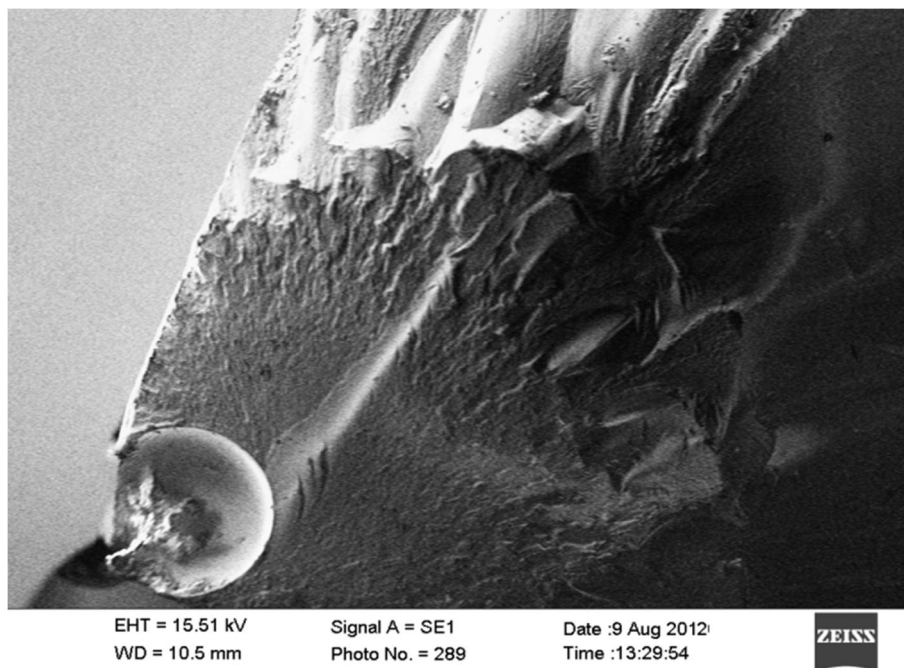


Fig. 3. Photograph of the fracture surface of the solidified epoxy binder modified by nanoparticles.

Moreover, air bubbles are inserted together with the nanopowder, which also serve as stress concentrators (Fig. 3). Air bubbles can be removed from epoxy resin by means vacuum treatment of the resin/powder mixture or ultrasonic dispersion.

Experiments on extension of ED-20 samples with the nanopowder obtained by mechanical mixing and by ultrasonic dispersion (USD) were performed. As is seen from the data presented below (Fig. 4), the samples obtained by means of ultrasonic dispersion have better strength characteristics than the samples obtained by means of mechanical mixing.

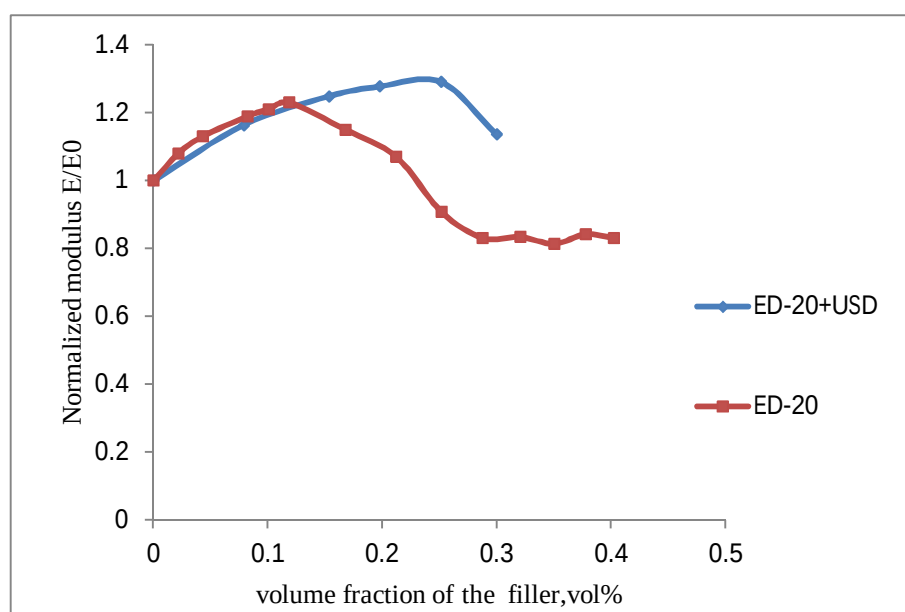


Fig. 4. Normalized modulus of elasticity of the epoxy composite versus the volume fraction of the T-150 filler.

From this figure, we can conclude that ultrasonic dispersion of silicon dioxide nanoparticles in epoxy resin ensures a greater number of adhesive chemical bonds, which increases the material strength. By an example of epoxy resin, it was demonstrated that the quality of the resultant composite is appreciably affected by the uniformity of the nanoparticle distribution.

The analysis of theoretical investigations led to a question about the influence of the level of mixing of the mixture. The powder possesses a large active surface and can adsorb resin or hardener on this surface, thus, changing the stoichiometric ratio in local regions. For our study, we prepared several samples with different sequences of mixing of the species. The following possible variants of dispersion were considered in this work.

1. Epoxy resin
2. The powder was added to epoxy resin containing the hardener, and USD was applied.
3. First, the nanopowder was dispersed in the hardener, which was less viscous, and then epoxy resin was added.
4. The powder was mixed with epoxy resin, and then the hardened was added.

The measured Young modulus and tensile stress are shown in Fig. 5.

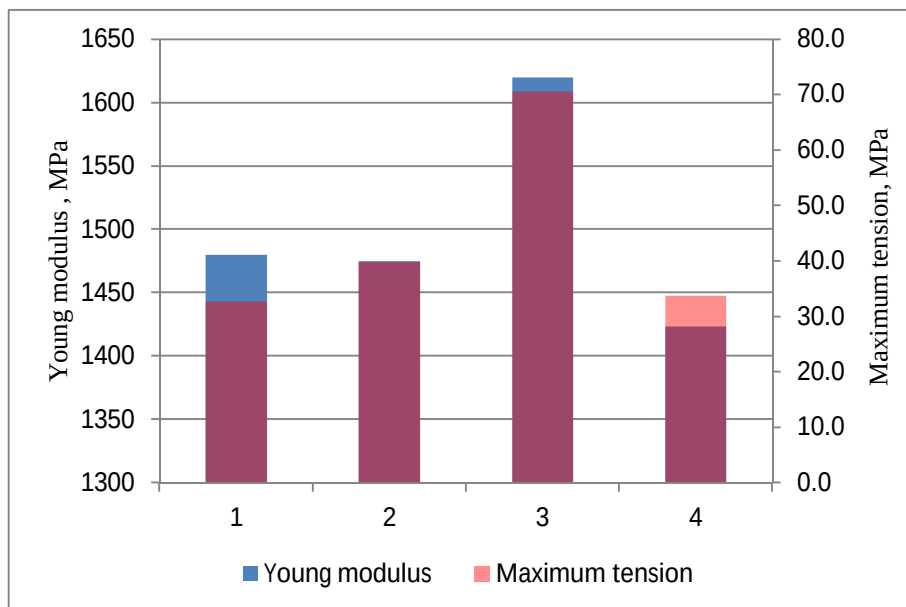


Fig. 5. Young modulus and tensile stress versus the order of addition of the T-150 filler

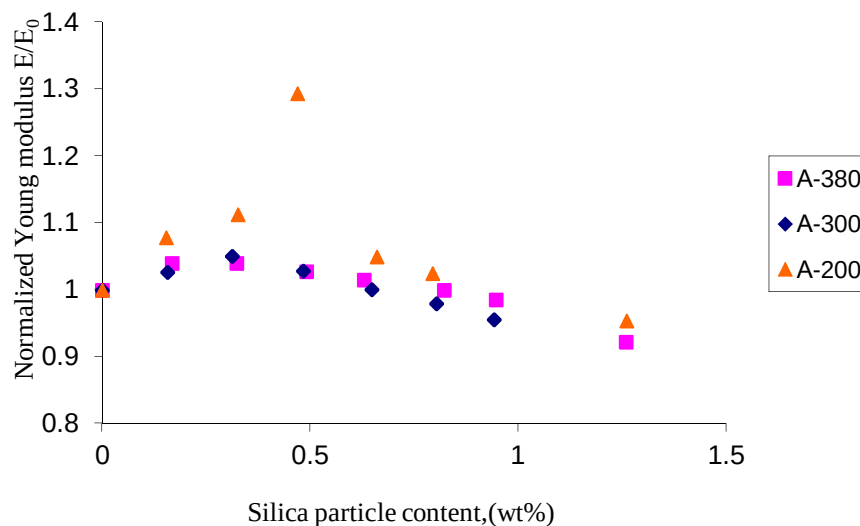


Fig. 6. Normalized Young modulus of ED-20 epoxy resin versus the mass fraction of the Aerosil hydrophilic nanopowder for different particle sizes.

It is seen that the best results are obtained by means of USD of the T-150 nanopowder in the hardened with subsequent addition of epoxy resin.

3.RESULTS AND DISCUSSION

3.1. Experiments on ED-20 tension with the Aerosil nanopowder

For the experiments, we prepared samples from the ED-20 epoxy resin with addition of hydrophilic SiO₂ nanopowders (Aerosil) up to different concentrations. The Young modulus for the samples made of pure epoxy resin obtained under these conditions was $E_0=1.2$ GPa. In what follows, this value is used for normalization of the Young modulus.

In our experiments, we used the A-200 (14 nm), A-300 (9 nm), and A-380 (7 nm) hydrophilic nanopowders. The normalized Young modulus for these nanopowders is shown in Fig. 6. An increase in the Young modulus is observed as the mass fraction increases from 0 to 0.4%, and the maximum value corresponds to 7-15 % at the concentration of 0.3-0.5 wt.% for different fillers. With a further increase in the filler mass fraction, the Young modulus smoothly decreases. This decrease is presumably associated with the increase in the number of filler agglomerates and air bubbles, which still remain in the mixture even after vacuum treatment and USD.

To estimate the particle size effect, we also tested silicon dioxide powders called Tarkosil T-05 (50 nm), T-15 (30 nm), and T-20 (18 nm), and A-200, A-300, and A-380 with a concentration of 0.4 wt.%. The Young modulus was expected to increase with decreasing particle size. Thus, as the particle size of the Tarkosil nanopowder decreases from 50 nm to 18 nm, the Young modulus increased by 30% (Fig. 7)

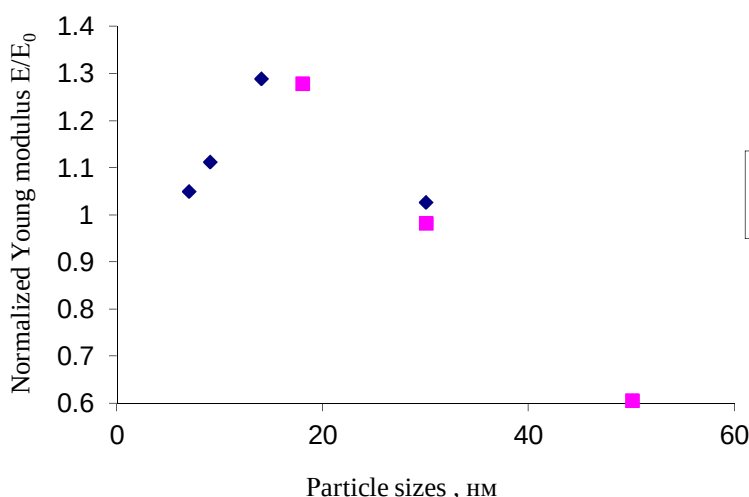


Fig. 7. Comparison of the normalized Young modulus for composites with different particle sizes of the filler

The results for Aerosil nanopowders (A-200) confirm this dependence, but the increase in the Young modulus is not observed with decreasing particle size. In this case, the greatest effect for Aerosil particles is observed for the nanopowder with the particle size of 14 nm (Fig. 7). Reduction of the filler particle size to 9 nm and 7 nm exerts an adverse effect on material strength (3- 5%). Such a dependence suggests that polymer molecules can have a certain characteristic size of the structure, at which the filler particles are arranged between the polymer grid, filling the latter and, thus, reinforcing the substance structure.

The analysis and comparison of the experimental data show that all types of examined nanoparticles affect the crack fracture resistance of the epoxy resin matrix. The influence of particles on the fracture process, however, depends on the particle size distribution. For coarse particles, the main mechanism is the confinement of the crack front by structured polymer regions adjacent to agglomerates. For fine particles, the prevailing mechanism is the resistance to cracking owing to reduction of the number of defects and nonuniformity of the epoxy matrix.

4. CONCLUSIONS

1. A technological process was developed, which allows one to reach the maximum effect of modification of the epoxy matrix by nanoparticles by means of intensification of dispersion of agglomerates by means of ultrasonic dispersion.
2. It was found that the most beneficial way is to insert nanoparticles into the least viscous medium (hardener) because such a medium ensures the minimum obstacles to dispersion of agglomerates and uniform distribution of particles.
3. Optimal levels of filling of the epoxy matrix by nanoparticles were determined: from 0.20 to 0.30 wt.% for binders modified by the Tarkosil and Aerosil particles. If nanoparticles are inserted in optimal proportions, the tensile strength of the epoxy binder increases by 32%
4. The Young modulus was plotted as a function of the nanopowder size. It was shown that the maximum is reached in the interval of the filler particle size from 14 to 18 nm.

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