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Determination of the mechanical characteristics of nanomaterials under tension and compression

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Abstract. In this paper, new method for determining the mechanical characteristics of nanoparticles in a heterogeneous mixture is proposed. The heterogeneous mixture consists of a thermosetting epoxy resin and silicon dioxide powder of different dispersity. The mechanical characteristics of such a material at a constant concentration for nanopowder are experimentally determined. Using existing formulas for obtaining effective characteristics, the Lame coefficients for nanoparticles of various sizes are calculated. The dependence of the elastic characteristics on the particle size is obtained.

1. Introduction

The modern material science assumes the widespread use of composite materials to reduce the weight of structures and to increase the elastic-strength characteristics. The use of filled polymer materials has proved itself in aviation and rocket engineering, automotive industry and others. One of the simplest of these composites is the polymer filled with dispersed particles to change the strength, electrically conductive, heat-conducting properties. Advantages of using dispersed particles in polymers can be called the low cost, high wear resistance of the resulting composites, the possibility of being used together with other reinforcement technologies. Prediction of the properties of heterogeneous materials is a problem whose solution is not possible when taking into account the properties of each particle in the volume. However, it is quite possible to determine the macroscopic characteristics of a heterogeneous material through its physical and mechanical components using models of homogenization. Such approaches have been developed very successfully since the beginning of the 20th century and up to the present, covering an increasing number of features of heterogeneous materials deformation behavior. Using the nanoobjects like nanoparticles or nanotubes in composite materials as filler permits understanding their mechanical properties. The results of prediction by analytical models do not agree with experiments, because they do not take the average size of the filler particles into account [1, 2]. The purpose of this paper is to determine the mechanical properties of nanoparticles for describing the deformation behavior of heterogeneous materials. Experiments to determine the mechanical characteristics were performed on an epoxy resin with the addition of ultra-disperse silicon dioxide powders, namely, the epoxy resin DER-330 (Dow Chemical, USA) actively used in many industries and the Tarkosil silica fume powder (ITAM SB RAS, Novosibirsk, Russia) with different specific surface area (table 1).
Table 1. Roots of transcendental equation (13).

| Filler type  | Specific surface area (m²/g) | Bulk density (kg/m³) | Agglomerates diameter (µm) |
|--------------|-----------------------------|----------------------|---------------------------|
| Tarkosil T-05 | 50                          | 80–100               | 20                        |
| Tarkosil T-15 | 96                          | 70–80                | 10–12                     |
| Tarkosil T-20 | 134                         | 60–70                | 5–7                       |

Figure 1. Agglomerates of Tarkosil T-20 nanopowder.

The powder was manufactured by using a special equipment. This is an industrial electron accelerator with power capacity of 100 kW, a reactor for evaporating matter, a coagulator, a series of cyclones and filters for purification and isolation of nanoparticles [3]. Due to the high electron energy, the evaporated substance is heated at a rate of about 1000°C/sec in the reactor. Then the matter is cooled and moved by air (or other accelerated gas). Passing through the coagulator, a system of filters and cyclones, the vapor condenses into nanoparticles and trapped as a powder. The resulting white powder has a very low bulk density, X-ray amorphous and has a high specific surface area controlled by parameters of equipment. Because of the high surface energy, the particles tend to stick together and form agglomerates of a few microns in size (figure 1).

2. Experimental moduli of epoxy resin with a nanofiller

The preparation and production of heterogeneous materials on the basis on epoxy resin and silica fume powder including the dispersion of particles in the matrix and the preparation of test specimens are described in detail in [4]. The curing agent (IMTHPA) is then added to the epoxy resin mixed with nanopowder in ratio 100 : 2 : 80, respectively. The curing of the mixture was carried out by furnace in step wise mode. Mechanical test parameters were chosen in accordance with ASTM D 790: the loading speed 400 N/min, and the preload 50 ± 10 N. The modulus were determined by the secant method on stress-strain curve in the 1–2% deformation section. The modulus of elasticity of pure epoxy resin was 1450 ± 50 MPa. The test results are graphically shown in figure 2. The obtained data indicate a significant change in the properties...
at low filler concentrations. It is especially worth noting the difference in the elastic properties of heterogeneous materials with a change in the specific surface of the filler. For Tarkosil, the growth of the elastic modulus from 1500 to 1750 MPa is observed with an increase in the surface area. For a larger specific surface more significant, the Tarkosil powders showed less effect on the elastic characteristics of the material.

Despite the same amount of the filler, the elastic properties are higher when the particle size is smaller. Such an experiment may show a change in the elastic properties from a macro object to a nano object. The reasons of this phenomenon are not clearly understandable. This could be the properties of the filler surface and the chemical reactions with epoxy resin or curing agent. The hypothesis advanced by the authors is that when the size decreases, the number of internal defects in filler decreases and the modulus of the nanoparticle becomes closer to the modulus of the crystalline matter.

3. Models of homogenization used to predict the moduli of nanofiller

The elastic properties of heterogeneous materials can be described by different existing models of homogenization using different hypotheses for averaging properties [5, 6]:

\[
\text{Voigt: } K = c_1 K_1 + c_2 K_2; \\
\text{Reuss: } \frac{1}{K} = \frac{c_1}{K_1} + \frac{c_2}{K_2}; \\
\text{Hashin: } K = K_2 + \frac{c_1}{1/(K_1 - K_2) + 3c_2/(3K_2 + 4\mu_2)}; \\
\text{Shtrikman: } K = K_1 + \frac{c_2}{1/(K_2 - K_1) + 3c_1/(3K_1 + 4\mu_1)}; \\
\text{Christensen low volume fraction of filler: } K = K_2 + \frac{(K_1 - K_2)c_1}{1 + (K_1 - K_2)/(K_2 + \frac{3}{2}\mu_2)}; \\
\text{Christensen polydispersity model: } K = K_2 + \frac{(K_1 - K_2)c_1}{1 + [c_2(K_1 - K_2)/(K_2 + \frac{3}{2}\mu_2)]}; \\
\text{Cuento: } \frac{1}{K} = \frac{1 - \sqrt{c_2}}{K_1} + \left(\frac{1 - \sqrt{c_2}}{\sqrt{c_2}K_1 + K_2}\right)^{-1}; \\
\text{Bache–Nepper–Chestenson: } K = K_1^{c_1} \cdot K_2^{c_2};
\]
The combination of Voigt and Reuss models (Takayangi models):

Hirsh–Dugill: \( K = \frac{1}{2} \left( \frac{1}{c_1 K_1 + c_2 K_2} + \frac{c_1}{K_1} + \frac{c_2}{K_2} \right) \)

Popovich: \( K = \frac{1}{2} \left( c_1 K_1 + c_2 K_2 + \frac{1}{c_1/K_1 + c_2/K_2} \right) \)

It should be noted, that the sum of volume concentrations is 1
\( c_1 + c_2 = 1 \).

Relation between \( K, \mu, \) and \( \nu \) is well-known
\[
K = \frac{2\mu(1 + \nu)}{3(1 - 2\nu)}
\]
where \( K \) is bulk modulus, \( \mu \) is shear modulus, \( \nu \) is Poisson ratio, \( c \) is volume concentration.

Elastic constants without an index correspond to a heterogeneous material, index 1 is to a filler, index 2 is to a matrix.

For the above models, the elastic modulus was plotted against the filler concentration. The mechanical properties for the matrix and the filler are
\[
K_1 = 1 \text{ GPa}, \quad K_2 = 100 \text{ GPa}, \quad \nu_1 = 0.3, \quad \nu_2 = 0.3.
\]

The basic principles of constructing such dependencies are

- a monotonous increase in the characteristic from smaller to larger values;
- at a concentration of 0% of one of the components, the composite characteristic is equal to the characteristic of the second component, i.e., \( K = K_2 \) for \( c = 0 \) and \( K = K_1 \) for \( c = 1 \);
- the curves are located inside the Voigt–Reuss fork;
- the compliance with experimental data is attained.

These principles could be ignored like the Berryman model or Christensen low volume fraction, but the main criteria for the prediction of effective modulus of the mixture for different combinations of materials are always required. The application of these models is used to predict the properties of mixtures at a certain concentration, but in our case, when the properties of the filler are not precisely determined, their use is difficult. The approach proposed by the authors is to convert these models to the form \( K_1 = f(K, K_2, c_1, \nu_1, \nu_2) \) and to calculate the modulus of elasticity for the filler nanoparticles. This dependence for the moduli gives only estimates of the contribution of the mechanical properties of the filler in a particular model and their use should be carefully analyzed. In addition, the prediction of the elastic properties of a new material
Figure 3. Dependence of the effective modulus of elasticity on the filler concentration for various models of homogenization.

Figure 4. Estimated modulus of elasticity of the filler in various models of homogenization.

requires the determination of at least two independent elastic constants. In the present paper, it is assumed that Poisson’s ratios of nanoparticles are the same as for the macro material, i.e., only one constant changes. To calculate the modulus of nanoparticles, formulas (1)–(14) used the Poisson coefficients (for nanoparticles $\nu_1 = 0.3$, for resins $\nu_2 = 0.3$). The specific surface area of the particles was recalculated for the radius by the formula $r = 3/(S_{\text{spec}} \cdot \rho)$, where $\rho$ is the density of quartz ($2400 \text{ kg/m}^3$).
The calculation results for the presented models are shown in the figure. The range of the moduli is artificially specified and has limitations: a low level corresponds to the positive modulus of elasticity by definition, and the high level corresponds to the elasticity modulus for the quartz crystal (100 GPa). It should be noted that, for some homogenization models due to the nonlinear dependence, two values can be obtained at once. For models predicting a small increase with increasing concentration, such as the Reuss, Guz, Hirsch, Kulak and others models, the filler modulus values could be very large or negative. For example, for the Reuss model, from \( 1/K = c_1/K_1 + c_2/K_2 \) we can express \( K_1 = f(K, K_2, c_1, \nu_1, \nu_2) \):

\[
K_1 = \frac{c_1 K K_2}{K_2 - (1 - c_1)K}.
\]

The denominator must be greater than zero:

\[
K_{\text{exp}} < \frac{K_2}{1 - c_1}.
\]

This restriction in the Reuss model leads to high estimates of the filler modulus in the case where the inequality is satisfied and to negative values in the case where the experimental values of the modulus of the mixture do not satisfy the inequality. But these models are quite suitable for predicting the properties of fillers if the Young modulus of the filler is smaller than the matrix modulus.

A number of dependencies can predict the properties of the nanofiller in the composition of heterogeneous materials with an increase in their mechanical properties. The models of Voigt, Shtrikman, Popovich, and Cuento give satisfactory results for the entire set of presented experimental data. The Voigt model is applicable for determining the mechanical properties of the components in the experimental region of the experimental data. The applicability of the Voigt model is limited by the condition \( E_{\text{exp}} > E_2 - c_1 E_2 \).

According to the listed models, the elastic modulus increases with decreasing particle size. The averaging models do not take into account the size of the filler particles, but only the volume fraction in the mixture. However, even at this level, it is possible to compare the values of the moduli with the experimental data on nanoindentation or model the properties of particles by the molecular dynamics method [7].

Conclusions
The Young modulus for heterogeneous materials based on epoxy resin with addition of nanosized silicon dioxide powders with different mean particle sizes at constant concentration was obtained. It is shown that as the average size decreases, the modulus of elasticity of the heterogeneous material increases significantly. The method proposed by the authors allows one, using the existing models of homogenization of the elastic properties of a heterogeneous material, to evaluate the characteristics of the filler which cannot be measured by direct experimental methods. Applying the above homogenization models to the obtained set of experimental data, it is shown that the modulus of elasticity of the filler increases with decreasing average particle size.

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