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Investigation of elastic properties of solid polymer materials by indentation method

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The mechanical properties of solid (crystalline) polymer materials are proposed to be investigated simultaneously using two complementary methods based on controlled indentation of a spherical indenter. The first method consists in the direct analysis of the load curve without using the concept of contact stiffness; the second method is based on measurements of the size of prints depending on the magnitude of the static load. The study shows that the reinforcement of a solid polymer with carbon fibers can lead to a significant increase in its elastic-strength properties.

Keywords: polymer composite materials, indentation, Hertz contact theory, spherical stamp, reduced modulus of elasticity, Brinell hardness, ultimate strength.

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The development of new structural materials and the examination of their performance indicators normally involve a comprehensive study of elastic properties. Methods based on continuous or scanning indentation and sclerometry, which are implemented in modern atomic force microscopes and new-generation indentometers are now used widely for this purpose [1–3]. These methods remain efficient in application both to metals (or alloys) and polymer materials [4–7].

The Oliver–Pharr method developed in [8] is the common theoretical basis for instrumental indentation. This method consists in measuring contact stiffness $k = dF/dz$ (where F and z are the elastic force and the vertical indenter coordinate) based on unloading curves with subsequent estimation of the reduced modulus of elasticity. in our view, the method has a significant drawback in that the determination of a derivative of an experimentally measured nonlinear function may result in a considerable error. In addition, the contact region may harden (i.e., the so-called cold-work hardening may occur) in the conditions of plastic deformation, inducing a local enhancement of the Young's modulus. Other drawbacks of the Oliver–Pharr method were examined in [1, pp. 73, 83]. However, instead of measuring the contact stiffness, one may (1) calculate the reduced modulus of elasticity directly by applying the optimization method to the loading curve or (2) estimate the hardness value from the indent radius at a given load. It is evident that the first technique provides the most comprehensive data. The second one is also useful in its own way, since it does not require any unique or costly equipment. In the present study, we apply these two methods in combination to solid (crystalline) polymer materials wherein the viscoelasticity may be neglected. The mechanical properties of such materials are characterized by the Young's modulus.and the yield strength, which is related to the ultimate strength [9].

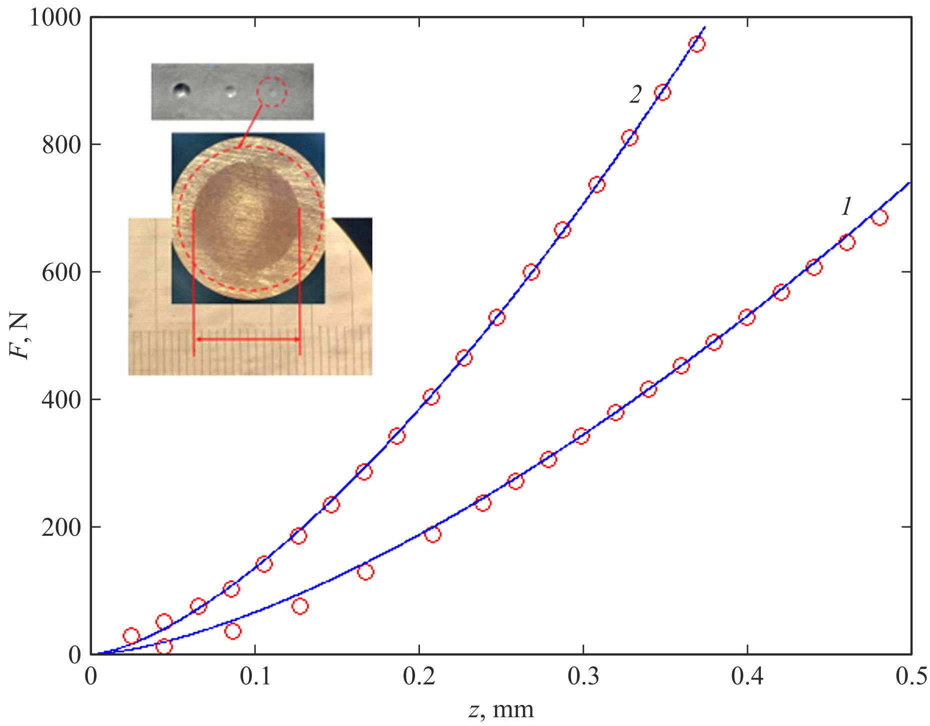
We use the Hertz contact interaction theory for a sphere–elastic half-space system to determine the elastic properties. The key relation of this theory is as follows [10, p. 71]:

$$F = \frac{4}{3}ER^{1/2}z^{3/2},$$

$$\frac{1}{E} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}, \quad (1)$$

where F and z are the load force and the indentation depth, R is the sphere radius, and $E_{1,2}$ and $\nu_{1,2}$ are Young's moduli and Poisson's ratios of contacting bodies. Almost all polymer materials have a significant spread of experimental values of elastic parameters, which is due mostly to composition variations and specifics of the fabrication process. The inherent error of measurement methods is superimposed onto all of this. If we assume that an indenter used in an experiment is ideally hard and neglect the Poisson's ratio of the sample (its square in (1) may fit within the bounds of the experimental error), the measured E value may be regarded as an approximation of the Young's modulus of the sample.

Deformation in real elastic-plastic solid bodies assumes a mixed elastic-plastic nature beyond the yield strength [1, p. 63]. An indent stable in time remains in this case after unloading of the indenter and partial recovery of shape of the contact region. Knowing the size of this indent produced under a given force, one may calculate Brinell



Load curves for polymer materials. *1* — PEEK 450; *2* — PEEK 450 + carbon fiber (10 mass%). Images of Brinell indents are shown in the inset.

hardness

$$\mathrm{HB} = \frac{F}{2\pi R(R - \sqrt{R^2 - a^2})}, \qquad (2)$$

where a is the radius of an indent produced in indentation. We propose to use formulae (1), (2) as the basis for experimental determination of mechanical properties of solid polymer materials.

If the experimental loading curve is linear in logarithmic coordinates, it is fair to assume, in accordance with (1), that measurements are performed in the linear elastic range and that the contribution of plastic deformation is insignificant. The material creep is also zero in this region. Thus, using the linear regression technique, one may derive E directly based on (1) from the experimental data presented in a log-log scale. This makes it unnecessary to measure the unloading curve and determine its slope at the maximum point numerically. Brinell hardness measurements provide an opportunity to estimate the ultimate strength using the following formula [11]: $\sigma_B = k\mathrm{HB}$, where k is a material constant determined experimentally.

The elastic properties of pure polyetheretherketone (PEEK 450) samples and samples reinforced uniformly with carbon fibers (10 mass%) [12] were examined in the present study. Carbon fibers (95–99% carbon) dressed with oligoetheretherketone based on 4,4'-dioxydiphenylpropane and 4,4'-difluorodiphenylketone were used. These polymer materials were chosen for their sufficiently high hardness and resistance to plastic deformation, which are the manifestations of a partially crystalline structure [13]. Fine structural characteristics of PEEK correlate with a high melting temperature (330–360°C) and are attributable to the presence of strong valence bonds.

Indentation experiments were performed using a GT-TCS-2000 test machine. The indent region was monitored visually with a LATIMET-20 optical microscope. Spheres made of structural bearing-grade steel ShKh15 with radii of 1.35 and 2.175 mm were used as indenters. Since the Young's modulus of this steel is 211 GPa, the deformation of spheres in experiments was definitely negligible compared to the deformation of polymer samples.

Spheres were positioned at different points on the surface of the studied samples (see the inset in the figure), and a controlled force was applied vertically to them. The loading rate was 1 mm/min, which is much lower than the rate of mechanical relaxation of polymer samples. The loading mass was increased to 100 kg. At higher values, such nonlinear effects as developed plastic deformation, viscous flow, and polymer expulsion, which was manifested in the form of characteristic buildups of material at the boundaries of indents, were observed for all samples. In general, radius a of indents at different sites on the sample surface varied with load from 0.5 to 1 mm. The following should also be noted here. For formula (2) to be used properly in estimation of the hardness of polymer materials, one needs to measure the size of indents right after indentation. The reason behind this is that indents grow smaller with time due to the process of polymer self-healing. Owing to this effect, the determined hardness values are somewhat higher than the actual ones. The results of experiments at different F and R demonstrate that the hardness of pure samples may reach 420 MPa; the ultimate tensile strength measured for these samples is 70−100 MPa. The hardness and the ultimate tensile strength of samples reinforced with carbon fibers both increase by a factor of 1.3−1.5.

The typical loading curves obtained using spheres of different radii and two PEEK 450 samples (pure and reinforced) are presented in the figure. Circles represent experimental data, and curves are the results of calculation in accordance with formula (1). The reduced modulus of elasticity for curves *1* and *2* is 1.3 and 2.2 GPa. These experiments revealed that the size of spheres has no effect on the end result (within the limits of experimental error): the measured data were almost the same for two spheres of different sizes.

Thus, two methods for analysis of elastic properties of solid polymer materials were implemented in combination in the present study. It was established reliably that, depending on the process parameters, the reinforcement of PEEK 450 polymer with carbon fibers (10 mass%) enhances its elastic-strength properties by a factor up to 2. In our view, further refinement of the technique of production of the composite material combined with application of the efficient diagnostic method discussed above should help achieve an even greater improvement of these properties.

Conflict of interest

The authors declare that they have no conflict of interest.

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