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## MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

# Deformation Behavior of Composites Based on Low-Density Polyethylene and Hollow Glass Spheres

**N. R. Ponomareva[a], G. P. Goncharuk[b], Yu. A. Grigor'ev[b], E. S. Obolonkova[b], and O. A. Serenko[b]**

[a] *Moscow Pedagogical State University, Moscow, Russia*
[b] *Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Moscow, Russia*

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**Abstract**—The mechanical properties of composites of low-density polyethylene with hard particles were examined.

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Two major steps can be distinguished in studies of composites filled with finely dispersed materials. The first step is associated with studies of filled rubbers. Experimental studies showed that the mechanical characteristics (strength and relative elongation at break) of elastic composites with a hard inactive filler are determined by the properties and content of the matrix polymer and monotonically decrease with an increase in its concentration [1]. The second step is associated with studies of composites based on plastic polymers with hard particles. In these materials, transition from plastic strain to brittle fracture (embrittlement) frequently occurs at low degrees of filling [2, 3]. A change in the character of fracture is accompanied by a drastic decrease in the relative elongation at break: from 400–800 to 10–20%. The use of thermoplastics with a high elongation at break and improvement of the quality of polymer mixing with the filler do not allow the embrittlement to be avoided.

According to the assumptions made in [3, 4], embrittlement of composites is associated with necking of the polymer matrix. At a definite degree of filling, the composite fails when a neck is formed. At this kind of fracture, the relative elongation of the material is low. Separate published data indicate that the concentration interval of the plastic behavior of a composite is determined by the capability of the matrix polymer for deformation strengthening, rather than by its elongation at break [3]. In some cases, polymer filling is not accompanied by embrittlement. The material can remain plastic in a wide range of the degrees of filling, despite necking in the matrix polymer [5, 6].

Bazhenov et al. [4, 7] developed a general approach to determination of the deformation behavior of composites based on plastic polymers filled with dispersed materials. Theoretical concepts of possible changes in the deformation behavior of composites were experimentally confirmed in studies of composites based on thermoplastic polymers and elastic particles (rubber-filled plastics) [8, 9]. According to the results of [10, 11], elastic particles deform together with the matrix polymer. This fact may influence the fracture mode of the composites.

The goal of this study was to examine mechanical properties of composites of low-density polyethylene (PE) with hard particles and to assess the applicability of the previously developed approaches to description of the deformation behavior of materials with hard filler particles.

## EXPERIMENTAL

We used low-density polyethylene (LDPE) of grade 15803-020 with the melt flow index of 2 g/10 min at a load of 2.16 kg and temperature of 190°C. As filler we used hollow undressed glass spheres with the particle size from 10 to 90 μm (Vibrotekh-tsentr Limited Liability Company, Moscow, Russia). The absence of dressing on the particle surface was determined by IR spectroscopy.

The polymer was mixed with the filler in a Brabender micromixer at 160°C for 10 min at a rotor rotation rate

of 90 rpm. The concentration of glass spheres was varied from 0.005 to 0.29 vol % (0.1–7 wt %).

The mixtures were processed by hot pressing at 160°C/10 MPa for 10 min. After keeping the material under pressure, the temperature was gradually decreased to 25°C. The thickness of the plates obtained was 1 mm.

From the plates we cut specimens in the form of two-sided blades with the working part dimensions of 28 × 5 mm. Mechanical tests were performed with an Autograph AGS-H dynamometric installation (Shimadzu, Japan). The extension velocity was 50 mm $min^{-1}$. The stresses given in this study are calculated for the initial cross section of the samples.

Microscopic studies were performed with a Hitachi S-520 scanning electron microscope. When studying the behavior of filler particles in the course of extension, the specimen was first extended with a manual mechanical device until a neck formed. Then a part of the material was refixed with a specially designed clamp and examined in the extended state in the electron microscope chamber. We analyzed the elastic zone, the transient zone from the elastic zone to the neck, and the neck.

Figure 1 shows the extension diagrams of LDPE with different content of glass spheres. The initial polymer undergoes strain with the formation of a weakly pronounced neck. After its propagation throughout the working part of the sample, the deformation strengthening step is observed (Fig. 1, curve *1*). A specific feature of the deformation behavior of LDPE is that the strain corresponding to the fluidity peak is 60–70%, in contrast to high-density polyethylene (10–20%). Introduction of a small amount of glass spheres (volume fraction up to 0.09) cases a decrease in the elongation at break but does not affect the shape of the extension diagram (Fig. 1, curve *2*). As the filler volume fraction is increased to 0.18, the specimen fails in the course of neck growth (Fig. 1, curve 3). This behavior is termed unstable neck propagation. It is a truly transition state from plastic to brittle or quasibrittle fracture of the material. As the filler volume fraction is increased further to 0.29, the fluidity peak in the strain curve degenerates, and the curve flattens out. Comparison of the strain in the fluidity peak of the matrix polymer with the fracture strain of the composite LDPE–filler (volume fraction 0.29) suggests that the composite fails at the moment of neck formation, i.e., the fracture is quasibrittle (Fig. 1, curve *4*), although a pronounced fluidity peak in the extension curve is lacking.

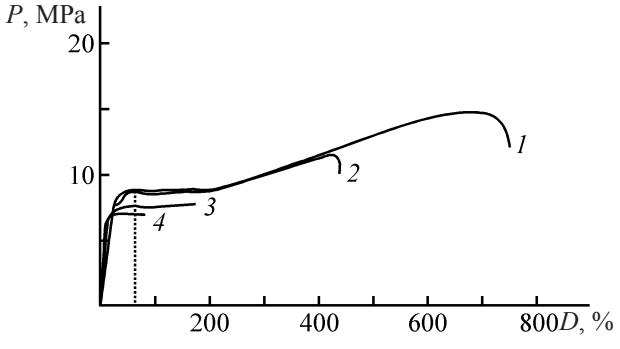


**Fig. 1.** Extension (*D*) curves of LDPE-based composites. Filler volume fraction: (*1*) 0, (*2*) 0.09, (*3*) 0.18, and (*4*) 0.29. (*P*) Stress; the same for Fig. 6. The doted line denotes the strain in the fluiduty peak of the matrix polymer.

The shape of the failed specimens (Fig. 2) confirms this assumption. For example, at a filler volume fraction of 0.22 the specimen fails in the step of neck formation and growth. This is indicated by a characteristic local narrowing in the region of fracture. Furthermore, the strain in the fracture area is higher than the macrostrain (specimen 1). As the filler volume fraction is increased to 0.29, the fracture occurs in the step of neck formation (specimen 2).

Thus, at a definite filler concentration, the neck formed in the composite ceases to propagate throughout the specimen length. The deformation behavior of the material changes from plastic to brittle, or, more precisely, to quasibrittle. A specific feature of the transition from the plastic to quasibrittle fracture in the system LDPE–glass spheres is that the critical concentration of the filler is unusually high: volume fraction 0.22–0.29. Usually the filler volume fraction at plastic–brittle transition in composites with mineral fillers does not exceed 0.12–0.15 [12].

Figure 3 shows how the elongation at break $\varepsilon_c$ of the composites depends on the volume fraction of glass spheres $V_f$. The curve has a steplike shape. At a low filler

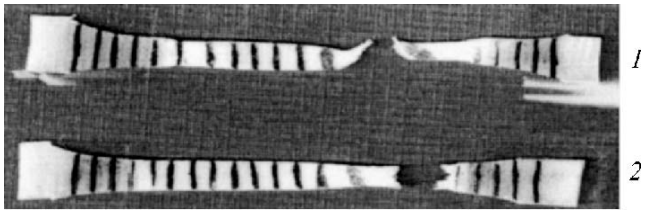


**Fig. 2.** Failed specimens of the composites. Filler volume fraction: (*1*) 0.22 and (*2*) 0.29.

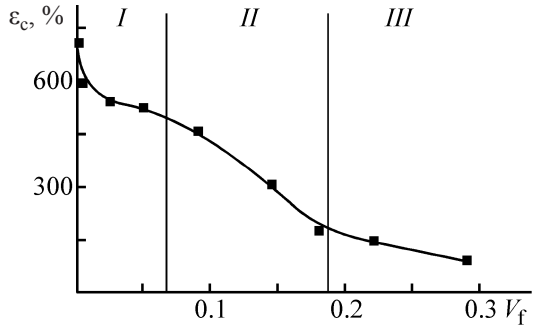


**Fig. 3.** Elongation at break $\varepsilon_c$ of LDPE-based composites as a function of filler volume fraction $V_f$. Zone: (*I*) neck formation and stable growth, (*II*) unstable neck growth, and (*III*) quasibrittle fracture.

content, the composites are characterized by large $\varepsilon_c$ (zone *I*). In this concentration interval, extension leads to the neck formation and propagation. With an increase in $V_f$, the elongation at break decreases (zone *II*). In this interval of filler concentrations, the material fails in the step of neck growth. With a further increase in the content of glass spheres, the composite undergoes brittle fracture on the macrolevel (zone *III*).

Leaning upon the results of [8, 9], we could expect that the LDPE-based composite in which the tensile strength exceeds the upper yield point would preserve plastic properties and exhibit high deformability in a wide range of filler concentrations. An increase in the degree of filling should lead to a plastic–plastic transition, i.e., extension with the neck formation and growth should give way to uniform plastic strain. According to the experimental results, the composite LDPE–glass spheres undergoes embrittlement, which contradicts the theoretical prediction. What are the causes of this fact?

It was noted above that the deformation of composites is determined by the minimal value of one of three parameters of material extension, namely: tensile strength, upper yield point, and necking stress. Let us determine the functional dependences describing the effect of the filler concentration on these quantities.

**Upper yield point.** The dependence of the upper yield point of composites with dispersed fillers on the filler concentration is described by the equation [1, 13]

$$\sigma_y/\sigma_{ym} = (1 - \beta\alpha V_f^{2/3}), \quad (1)$$

where $\sigma_{ym}$ is the upper yield point of the polymeric matrix; $\beta$, shape parameter equal to 1.21 for spherical particles; $\alpha$, fraction of particles detached from the matrix before initiation of the plastic flow; and $V_f$, filler concentration. If particles have a good adhesion to the polymer and are not detached before the onset of the plastic flow, $\alpha = 0$ and $\sigma_y = \sigma_{ym}$. If there is no adhesion between the filler and the matrix, all the particles are detached from the polymer before the onset of plastic flow, and $\alpha = 1$. In this case, Eq. (1) for spherical particles takes the form

$$\sigma_y/\sigma_{ym} = (1 - 1.21V_f^{2/3}), \quad (2)$$

Figure 4a shows the experimental dependence of the relative upper yield point of the composite in coordinates of Eq. (2). The dependence is linear, but the coefficient at $V_f^{2/3}$ is considerably lower than it is implied by Eq. (2). The equation of the experimental straight line is as follows:

$$\sigma_y/\sigma_{ym} = (1 - 0.451V_f^{2/3}). \quad (3)$$

It can be concluded that the upper yield point of the composite LDPE–glass spheres changes with an increase in the filler concentration to a lesser extent than it is implied by Eq. (2).

**Necking stress.** Variation of the lower yield point of a composite material with an increase in the filler concentration is described by the equation [6, 13]

$$\sigma_d/\sigma_{dm} = 1 - \alpha V_f^{2/3}, \quad (4)$$

where $\sigma_{dm}$ is the lower yield point of the polymer and $\alpha$ is the fraction of detached particles in the material neck.

At $\alpha = 0$, the particles are not detached from the matrix, and $\sigma_d = \sigma_{dm}$. At $\alpha = 1$, there is no adhesion interaction of the matrix with the filler, and all the particles are detached.

According to formula (4), the lower yield point of the composite should linearly decrease with increasing filler content. Fig. 4b shows the experimental dependence of the necking stress of the composite on the filler concentration. The experimental results are described by the equation of the straight line

$$\sigma_d/\sigma_{dm} = 1 - 1.37V_f^{2/3}. \quad (5)$$

Thus, the lower yield point also decreases with an increase in the concentration of glass spheres more slowly than it follows from theoretical analysis.

**Ultimate strength.** The influence of the filler concentration on the strength $\sigma_c$ of a composite with spherical particles is described by the "2/3 law" [1]

$$\sigma_c/\sigma_m = 1 - 1.23V_f^{2/3}, \quad (6)$$

where $\sigma_m$ is the matrix strength.

Figure 4c shows the concentration dependence of the relative strength of the system LDPE–glass spheres in coordinates of Eq. (6). The experimental results are fitted by a straight line described by the following equation:

$$\sigma_c/\sigma_m = 1 - 1.42V_f^{2/3}. \quad (7)$$

In this case, the theoretical predictions reasonably agree with the experimental data.

Thus, analysis of the functional dependences of the upper yield point $\sigma_y$, necking stress $\sigma_d$, and strength $\sigma_c$ of the composite LDPE–glass spheres showed that, with an increase in the degree of filling, the strength of the material decreases and the upper and lower yield points vary insignificantly.

The extent of the decrease in $\sigma_y$ and $\sigma_d$ with increasing filler concentration is determined by the extent to which the boundaries between the matrix and glass spheres in the course of extension of the materials remain intact [1, 12–14]. We examined with a microscope a deformed LDPE specimen with a filler volume fraction of 0.05. In the elastic zone, oval pores formed owing to detachment of glass spheres are observed (Figs. 5a, 5b). In the transient zone (Figs. 5c, 5d) and in the neck (Figs. 5e, 5f), the glass spheres are also detached from the matrix polymer. The difference is only in the size of oval pores: it increases in going from the elastic zone to the neck.

The electron micrographs show that the adhesion of glass spheres to the matrix material is low, and in extension of the material the integrity of the boundary between a particle and LDPE is broken in all the three zones of the specimen. This fact indicates that the parameter α in Eq. (1), as well as in Eq. (4), should be close to unity. Hence, the coefficient at $V_f^{2/3}$ in Eq. (1) should be equal to 1.21, and the coefficient at $V_f$ in Eq. (4), to unity. However, the experimental coefficients are lower in both cases. Of course, microscopic analysis of the specimen surface does not furnish information on the state of particles in the bulk of the system. Nevertheless, whereas the less pronounced decrease in the upper yield point of the material can be attributed to the presence of undetached particles in the bulk of the material, in the case of the necking stress it is hardly probable that even a part of particles introduced into the polymers remained undetached from the matrix. The undressed glass spheres that we used are readily detached from the polymer.

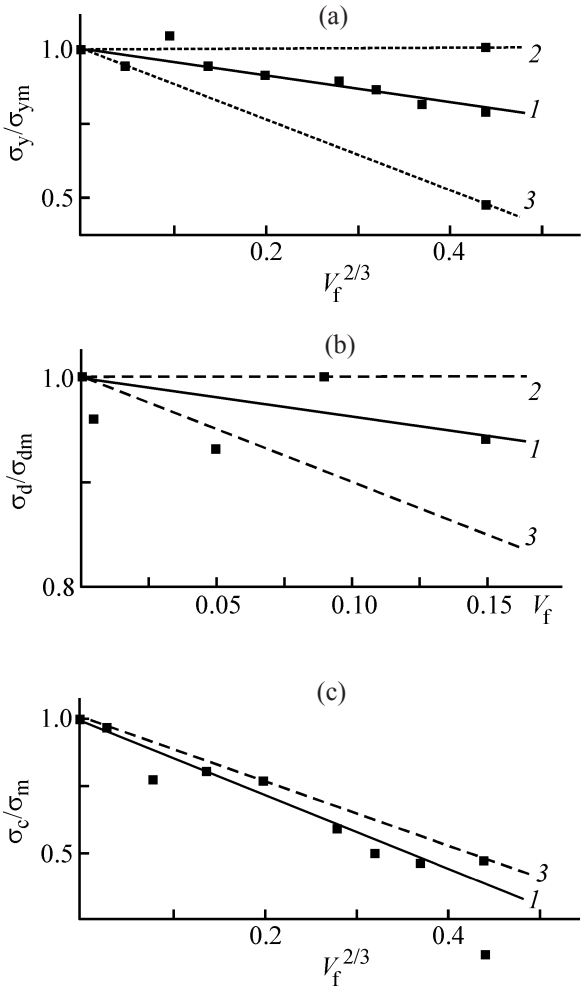


**Fig. 4.** (*1*) Experimental and (*2, 3*) theoretical dependences of the extension parameters of composites on the filler volume fraction $V_f$: (a) upper yield point, (b) necking stress, and (c) strength.

Figure 6 shows the functional dependences describing the experimental values of the strength and of the upper and lower yield points of the composites on the filler volume fraction. For the plastic–plastic transition to occur, it is necessary for the upper yield point of the composite and its necking stress to be equal: $\sigma_y = \sigma_d$. In our system, the concentration dependences of these parameters do not intersect. Hence, because of the weak dependence of $\sigma_y$ and $\sigma_d$ on the filler concentration in the LDPE-based composite, the conditions for the

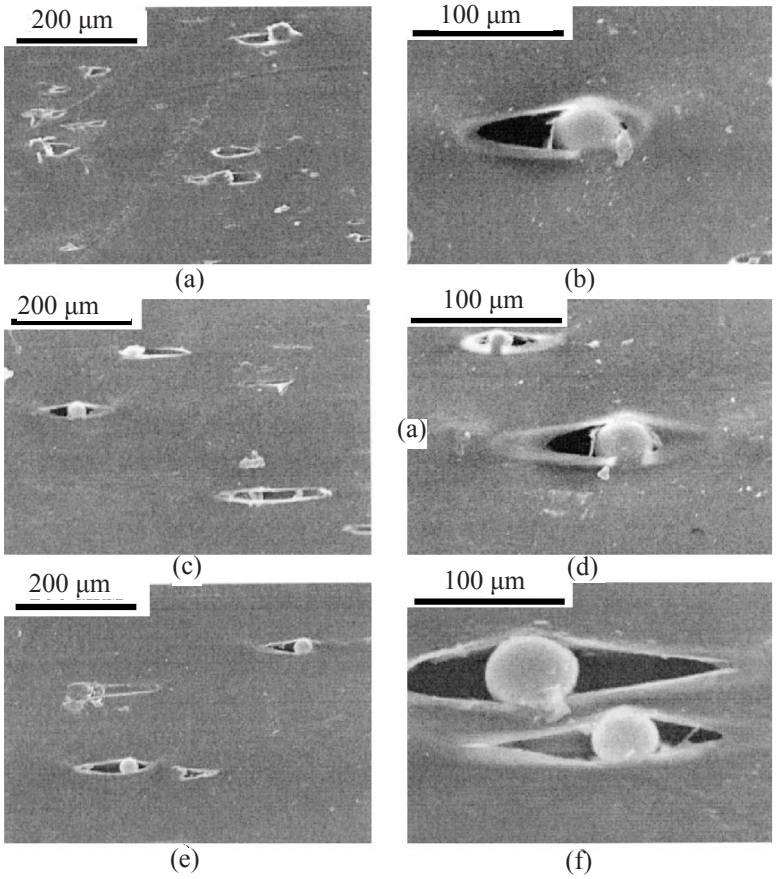


**Fig. 5.** Surface of extended LDPE specimen with the volume fraction of glass spheres of 0.05: (a, b) elastic zone, (c, d) transient zone from elastic zone to neck, and (e, f) neck zone.

occurrence of the plastic–plastic transition are lacking. It should be noted that, up to the filler volume fraction of 0.18, the strength of the material is higher than the neck propagation stress ($\sigma_c > \sigma_y > \sigma_d$), i.e., the minimal parameter is the lower yield point, and the formed neck propagates along the sample. At the filler volume fraction exceeding 0.22, the pattern changes, and $\sigma_c < \sigma_d$. In this case, the material strength becomes the minimal parameter, the neck formed in incapable of propagation, and the composite fails when the neck is formed. The plastic–brittle transition occurs. The intersection point of the dependences $\sigma_c$–$V_f$ and $\sigma_d$–$V_f$ corresponds to the critical filler concentration at plastic–brittle transition, $V_f^*$.

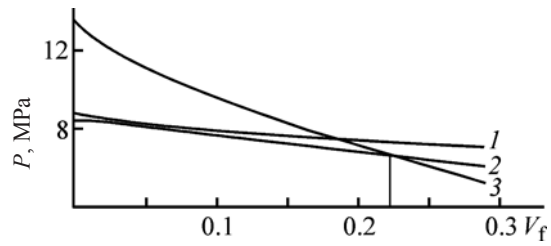


**Fig. 6.** Experimental dependences of the (*1*) upper yield point, (*2*) lower yield point, and (*3*) strength of the composite LDPE–glass spheres on the filler volume fraction $V_f$.

The quantity $V_f^*$ can be calculated using the criterion of this transition: $\sigma_c = \sigma_d$. Using Eq. (6) and taking into account that the lower yield point of the composite varies insignificantly, we can write

$$\sigma_m = (1 - 1.21 V_f^{2/3}) = \sigma_{dm}. \quad (8)$$

Solution of Eq. (8) has the form

$$V_f^* = \left( \frac{\sigma_m - \sigma_{dm}}{1.21\sigma_m} \right)^{3/2}. \quad (9)$$

By substituting the numerical values of $\sigma_m$ and $\sigma_{dm}$, we obtain the volume $V_f^* = 0.23$ (volume fraction). The

calculated and experimental critical filler concentrations at the plastic–brittle transition are in reasonable agreement.

Thus, the cause of embrittlement of the composite LDPE–glass spheres is weak dependence of the upper ($\sigma_y$) and lower ($\sigma_d$) yield points of the material on the filler concentration. At the same time, the strength decreases with an increase in the content of glass spheres, and this decrease is adequately described by the equation derived within the framework of the minimal effective cross section model. At a definite critical concentration of glass spheres, the strength and necking stress become equal. With a further decrease in the degree of filling, the neck becomes incapable to propagate along the specimen, and the material undergoes quasibrittle fracture as the neck is formed.

The cause of the disagreement between the experimental and theoretical results is that the theoretical analysis of the deformation behavior of the composites, performed in [7–9, 15], is based on Eqs. (2), (4), and (6). According to Eq. (2), the upper yield point of the composite decreases more rapidly than the necking stress (4). This fact was responsible for the plastic–plastic transition in the composite PE–vulcanized rubber particles [9]. At a definite filler concentration, the upper yield point and the necking stress of this material became equal. Good agreement between the experimental data and theoretical analysis of the deformation behavior of composites with elastic deformable particles, observed in [8, 9], is due to the fact that introduction into the polymer of soft particles which either are detached or are not detached from the matrix polymer leads to a decrease in the main deformation parameters of the composite in both these cases. With hard particles, the pattern is different. Even detached particles can affect the extent to which the upper and lower yield points decrease and hence can change the deformation behavior of the composite with increasing degree of filling in a different way, compared to the theoretical prediction. Theoretical analysis of the extension of composites with increasing degree of filling does not take into account the role of this factor. Nevertheless, the general approach to description of the deformation behavior of polymeric materials filled with hard dispersed particles remains rightful. The character of their extension is determined by the minimal value of one of the three parameters: upper yield point, necking stress, and tensile strength.

## CONCLUSIONS

(1) A plastic–brittle transition is observed in a composite based on low-density polyethylene and hollow glass spheres with an increase in the filler concentration.

(2) The embrittlement of the composite is caused by weak dependence of the upper yield point and necking stress of the material on the filler concentration. On the other hand, the material strength decreases with an increase in the content of glass spheres. At a definite, critical concentration of glass spheres, the strength and necking stress become equal. With a further increase in the degree of filling, the neck becomes incapable to propagate along the specimen, and it undergoes quasibrittle fracture as the neck is formed.

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