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Abstract

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STUDY OF THE EFFECT OF ADDITIONS OF DISPERSED IRON AS AN ACTIVE FILLER ON THE PHYSICOMECHANICAL PROPERTIES OF POLYMERIC MATERIALS

(Presented by Academician P. A. Rehbinder, June 18, 1960)

In connection with the broad use of polymeric materials in various fields of technology, the problem of increasing their heat resistance and strength is acquiring great importance.

It is known that the mechanical properties of high-molecular compounds can be substantially improved by introducing active fillers into them. In the works of P. A. Rehbinder and his co-workers (1–3), an enhancement of the mechanical properties of polymer systems was found at various degrees of filling with an active filler. The authors of these works showed that, when comparatively small amounts of filler are introduced, the increase in the mechanical properties of the system occurs as a result of reinforcement of the spatial structure formed by the polymer macromolecules. The active filler particles, being located at the nodes of the spatial network, are centers for the development of such a structure. At high degrees of filling—80-90% of the polymer volume (4)—the strengthening effect is associated with the formation of coagulation structures, in which the polymer practically passes into the state of extremely structured films distributed between the filler particles (5).

Of considerable interest is the use of highly dispersed metallic powders as fillers for polymeric materials. It may be assumed that, for some high-molecular compounds, metal will prove to be the most active filler. The presence of a very thin oxide layer on the metallic particles does not noticeably affect the formation of strong adsorption-chemical metal-polymer bonds.

In the present work we studied the effect of additions of iron powder on the strength and heat resistance of several polymeric materials. Both crystalline polymers—polyamide resin-68 and polyethylene (high-pressure)—and an amorphous phenol-formaldehyde resin (resol) were used as the objects of study. Iron

Fig. 1

Figure 1: Fig. 1

powder with a specific surface area $S = 1.2$ m^2/g, obtained by an electrolytic method (in the laboratory of A. T. Vagramyan), was used as the filler. To prepare specimens of a definite composition, the required amount of iron powder was introduced into a polymer solution. The specimens obtained after pressing were tested for strength and heat resistance. The strength of pressed specimens of polyethylene and polyamide resin-68 was evaluated by indentation tests using a cylinder of diameter $d = 1$ mm. The strength of specimens based on phenol-formaldehyde resin was evaluated by uniaxial compression of the specimens. Heat resistance was judged from thermomechanical compression curves (6,7), obtained under a constant load, at a heating rate of 50° per hour.

Figure 1 shows the dependence of the strength of polymers on the concentration of the iron-powder additive. As can be seen from Fig. 1, filler additions in all the cases presented strengthen the polymer system, but the nature of the dependence of strength on the concentration of iron powder is different. Thus, in the case of polyamide resin-68 (curve 1), a crystalline polymer, when iron powder is introduced in an amount of 5%, the system is strengthened by approximately 20%. A further increase in filler no longer affects the strength. In the case of polyethylene (curve 2), in which the amount of crystalline phase does not exceed 50–75%, at first the strength increases only very slightly with increasing filler concentration up to 60%, after which a sharp strengthening of the system is observed, and the maximum strength corresponds to an 85–90% filler content. Here it is necessary to point out that the numerical values we obtained (85–90%) for filling of the polymer system, which cause maximum strengthening, are relative, since the effect of high filling depends substantially on the degree of dispersion of the filler and on the technology of its introduction. Thus, it may be assumed that vibrational action during introduction of the filler will significantly improve the properties of the filled polymer.⁀1

Fig. 1. Mechanical strength of polymer materials as a function of the concentration of iron-powder filler: 1—composition based on polyamide resin-68; 2—polyethylene; 3—phenol-formaldehyde resin (resol)

The strength of specimens based on phenol-formaldehyde resin increases in parallel with the rise in filler concentration. Significant strengthening of the system (by a factor of 2) occurs already with the introduction of 30% filler. At a content of 50% iron powder, the strength increases by a factor of 6. The optimum strengthening, by a factor of 7, corresponds to 75–80% filling. These results show that the mechanism of strengthening of polymer systems when iron powder is introduced into them as a filler is different and depends on the chemical nature of the polymer. The temperature dependence of uniaxial-compression deformations of polymer specimens filled to different degrees with iron powder is presented by the thermomechanical curves in Figs. 2 and 3.

Fig. 2

Figure 2: Fig. 2

Figure 3 graph

Figure 3: Figure 3 graph

Fig. 2. Dependence of deformation on temperature for resol resin at various contents of iron powder in it. 1—0%; 2—10%; 3—50%; 4—80%

Figure 2 gives the curves for specimens based on phenol-formaldehyde resin. The specific load on the specimen was 8 kg/cm^2. As the filler concentration increases, the glass-transition temperature (T_c) of the material rises, which indicates the formation of transverse chemical-

bonds between macromolecules. The deformability of the specimens in this case decreases sharply. Thus, a specimen of pure resol resin, as the temperature is raised, deforms strongly, and at 150° the deformation reaches 40% (curve 1), whereas a specimen filled to 10% (curve 2) deforms at this temperature by 32%, and one filled to 50% by only 8%. At 80% filling, the material deforms by 6% at 300°, and its decomposition begins after 400°. Obviously, in the presence of iron powder the process of formation of the spatial network characteristic of thermosetting resins at elevated temperatures is accelerated. As a result, in the presence of the filler the material becomes considerably more heat-resistant.

Fig. 3. Dependence of deformation on temperature for polyethylene filled with iron powder. 1—0; 2—50; 3—80; 4—90 wt.% iron powder

In Fig. 3 thermomechanical curves are presented for specimens based on polyethylene. The load on the specimen in this case was substantial and amounted to 40 kg/cm^2, which caused flow of the polyethylene without filler already at 40° (curve 1). With an increase in filler in the material, the "flow" temperature* rose somewhat, but the character of the dependence of deformation on temperature, even at 80% filling, remained the same. Only beginning with a concentration of 90% iron-powder content did the course of the curve change sharply. The deformation of the specimen at 150° reached only 8%, after which, with a further increase in temperature up to 400°, it remained constant. This indicates a sharp change in the properties of the material, an increase in its heat resistance. This is also evidenced by the heating curves (8), which give an idea of the phase state of the polymer. In Fig. 4 the solid line shows the heating curve of polyethylene without filler and the dashed line that of polyethylene filled to 90% with iron powder. The specimen had been preliminarily pressed and heated to 220°. On the dashed curve a new effect appeared at 300°, absent on the solid curve. Obviously, it is associated with a phase transformation, the melting of a particularly ordered crystalline phase, which appears in the material when it is filled with iron powder and subsequently pressed.

Figure 4 graph

Figure 4: Figure 4 graph

Fig. 4. 1—thermogram of polyethylene (high pressure); 2—thermogram of polyethylene containing 90 wt.% iron powder

It should be noted that in these experiments the specimen weight remained constant up to 400°. The significant increase in the strength and heat resistance of polyethylene-based specimens, observed only at high filling, indicates that this is associated with a change in the properties of the material, when it is in a film-like, maximally ordered, oriented state. These films are probably fixed on the surface of the solid filler and are bound to it by adsorption-chemical bonds.

* Since in this case the recovery processes after unloading were not studied, the “flow” temperature has a conditional character.

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