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Modification of the Surface Properties of Capron Fibers by Grafting Polystyrene

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Modification of the properties of polymer fibers and films by the method of graft polymerization of vinyl monomers is the subject of numerous studies. In particular, an increase has been noted in the adhesion of rubbers to fibers modified by grafting ([1]).

We studied the effect of grafting polystyrene onto capron fibers on their adhesion to resins widely used in industry—polyester PN-1 and epoxy resin. The graft polymerization was initiated with Co^{60} γ-radiation by the method of preliminary irradiation in vacuum and was carried out from the gas phase. Such a process eliminates the possibility of homopolymer formation ([2]).

In the course of graft polymerization, the concentration of radicals in the fiber sample and the change in the weight of the sample were measured. The amount of grafted polystyrene, ΔP, was expressed as a percentage of the initial weight of the fiber. Experiments were carried out with capron fibers of 20 μ diameter (breaking strength 72 kg/mm^2, elongation 25%). The fibers were washed free of sizing agent successively with benzene, acetone, and ether for 30 min at room temperature.

Styrene was washed free of inhibitor with a 10% aqueous KOH solution, dried over calcium chloride, distilled under vacuum at 38-40°, and thoroughly degassed.

Fiber samples were degassed for 2 hours at 10^{-4} mm Hg and irradiated in a sealed ampoule at room temperature with Co^{60} γ-radiation at an intensity of 150 r/sec. After irradiation, one sample was placed in the resonator of the instrument for recording the EPR spectrum, while another was suspended from the spring of a McBain balance. Styrene was brought into contact with the fiber 18 hours after irradiation, when the intensity of the EPR signal had practically ceased to decrease. The fiber temperature was 26°, and the vapor pressure of styrene was 5 mm Hg.

Sorption of styrene on unirradiated fiber is a reversible process (curve *I*, Fig. 1). On a fiber containing 2.97% grafted polystyrene, significantly less styrene

Figure 1 graph

Figure 1: Figure 1 graph

Figure 2 graph

Figure 2: Figure 2 graph

is sorbed than on the original fiber, and it is likewise sorbed reversibly. The greater part of the styrene sorbed by the irradiated fiber is not desorbed, since graft polymerization of styrene takes place, initiated by free radicals present in the capron. This conclusion is confirmed by experiments measuring the EPR signal, the results of which are presented in Fig. 2. At the moment styrene was introduced, the radical concentration was $2.4 \cdot 10^{18}$ radicals/g and was maintained in vacuum for 24 hours (curve *I*, Fig. 2). In the presence of styrene vapor, the radicals perish (curve *II*, Fig. 2). The shape of the EPR signal does not change during the process of radical decay.

In the first minute of contact of styrene with the irradiated fiber (curve *II*, Fig. 1), the number of radicals in the fiber is practically still unchanged, while the weight of the sample increases by 1%, which is almost two orders of magnitude greater than the weight gain due to sorption by an unirradiated sample (curve *II*, Fig. 1). This

the rapid increase in weight is explained by the growth of polystyrene chains in the surface layer (a polystyrene layer of the order of 10^{-2} mg/cm^2 is formed). Further grafting is slowed by diffusion of the monomer to the growth centers (on average, there is one radical per 30 macromolecules of capron). Therefore, as the amount of grafted polystyrene increases, it is primarily the surface properties of the fiber that change.

Fig. 1. Kinetics of sorption and desorption of styrene on capron fibers. Fiber temperature 26°C, styrene vapor pressure 5 mm Hg. *I*—unirradiated fiber, *II*—irradiated with a dose of 2.7 Mrad, *III*—containing 2.97% grafted polystyrene

In Figs. 3 and 4 are given the results of measuring the wettability of fibers by polyester and epoxy resins before curing, and the adhesion of these cured resins to fibers. All measurements were made at room temperature.

Wetting of capron fibers by liquid resin was determined by a method developed in the laboratory. The magnitude of the adhesion of thermally cured resins directly to the fiber surface was determined by the shear method ([3]).

The wettabilities ($\cos\varphi$) of polystyrene fibers and of untreated capron are identical. However, the grafting of small amounts of polystyrene to capron fibers causes sharp changes in wettability: an increase in $\cos\varphi$ at a content of about 1% grafted polystyrene and a decrease at 2% (Fig. 3). The difference between the wettabilities of fibers with 3% and 12.9% grafted polystyrene is smaller.

Fig. 2. Kinetics of radical decay in capron fibers. The fibers were irradiated with γ-rays from Co^{60}, dose 2.7 Mrad, intensity 150 r/sec, and held for 18 h at room temperature. I—in vacuum, II—in the presence of styrene vapor

Adhesion changes in parallel with wettability. The strength of the adhesive bond of polyester resin to a fiber containing about one percent grafted polystyrene is twice as high as with the original fiber and is 130 kg/cm^2, while at 2% grafted polystyrene it is only 45 kg/cm^2, i.e., three times less than in the case of grafting fractions of a percent of polystyrene, and less than in the case of the original fiber.

The strength of the adhesive bond of epoxy resin to the original capron fiber is 90 kg/cm^2 and also changes in parallel with the change in wettability (curve II, Fig. 4). Adhesion to polystyrene fiber is 72 kg/cm^2.

The experimental data presented indicate a direct relationship between adhesion and the magnitude of wetting. Qualitatively this can be explained as follows. Wettability is determined by the relation

$$\cos\varphi = \frac{\gamma_{\text{v}} - \gamma_{\text{vs}}}{\gamma_{\text{s}}}, \tag{1}$$

where γ_{s} is the surface tension of the resin at the boundary with air, and γ_{v} and γ_{vs} are the surface tensions of the fiber at the boundary with air and with the resin, respectively.

The work of the process of reversible isothermal separation at the phase boundary W_{ad} is expressed by the formula

$$W_{\text{ad}} = \gamma_{\text{s}} + \gamma_{\text{v}} + \gamma_{\text{vs}}.$$

Equation (2) is applicable to the boundaries of liquid phases, but cannot be used for estimating the adhesion of solid bodies to one another because of the various irreversible processes accompanying adhesive separation. However, it may be assumed that, in the reported results of determinations of adhesive strength, the distortions of the adhesion forces are approximately the same in each series of experiments, and the curves in Fig. 4 reflect changes in the work of separation.

Fig. 3. Effect of polystyrene grafting on the wettability of fibers by resins. I—polyester resin, II—epoxy resin.

Fig. 4. Effect of polystyrene grafting on the adhesion of resins to capron fiber. Designations as in Fig. 3.

Obviously, the surface tension of the resin in each of the four series of experiments (curves I and II in Figs. 3 and 4) is constant, and the simultaneous changes in wettability and work of adhesion are associated with a change in the surface tension of the fiber, γ_{v} and γ_{vs}.

The surface free energy depends on the degree of ordering of the structure. Probably, as a result of a change in the structure of the surface layer of the fiber during grafting, the value of the free surface energy passes through a maximum when the content of grafted polystyrene in the fiber is about 1%.

The increase in free surface energy at 2–3% polystyrene is probably associated with loosening of the polystyrene layer that has formed. The subsequent increase in the weight of the fiber is associated with grafting occurring in layers of the fiber removed from the surface; therefore, the surface properties at 3 and 12.9% grafted polystyrene are approximately the same.

Branch of the Physicochemical Institute
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CITED LITERATURE

1. V. V. Korshak, K. K. Mozgova et al., *Vysokomolek. soed.*, **3**, 338 (1963).
2. P. E. M. Allen, J. M. Pogrner et al., *Nature*, **177**, 910 (1956).
3. V. Shchireva, Yu. A. Gorbatkina, G. D. Andreevskaya, *ZhFKh*, **37**, No. 1, 237 (1963).

Note: Figure translations are in progress. See original paper for figures.