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Abstract

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ELECTRON-MICROSCOPIC STUDY OF GRAFTED POLYMERS

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In the electron-microscopic study of grafted synthetic polymers, methodological difficulties arise because the molecules of the homopolymer and of the grafted polymer consist of atoms having almost identical scattering power and, consequently, contrast. Therefore, in electron-microscopic images it is not possible to distinguish the boundary of the grafted layer, or to reveal the distribution of grafted molecules within the polymer.

In the present work we attempted, with the aid of an electron microscope, to determine how the molecules of the grafted polymer are distributed within certain fibers of synthetic polymers. For this purpose, fibers of polyethylene, isotactic polypropylene, and capron were chosen, modified by grafting polyacrylic acid by the method of radiation gas-phase graft polymerization ([1]). These fibers differ in the percentage content of grafted material. For polyethylene the graft amounts to 56.5%, for capron 31%, and for polypropylene 1.8%.*

To increase the contrast of regions of the specimen consisting of grafted molecules, silver atoms, which strongly scatter electrons, were attached to the polyacrylic acid molecules. Contrast enhancement of the specimen was carried out by treating the grafted fibers with a saturated solution of silver sulfate while boiling them for 3 hours. During such treatment, partial replacement of the hydrogen ion of the carboxyl groups of polyacrylic acid by silver ions occurs. Complete replacement of hydrogen ions by silver ions is not achieved, probably because the reaction is reversible and equilibrium is established at a certain stage of replacement of the hydrogen ions. The possibility of formation of anhydride rings of polyacrylic acid is also not excluded. After treatment, the fiber was washed with hot distilled water and dried. With 3-hour treatment, replacement of hydrogen ions by silver ions amounted to 23.6% for polyethylene, 16.6% for capron, and less than 0.5% for polypropylene. For control, the initial homopolymer fibers were subjected to the same treatment.

Preparations for the electron microscope were made by the method of ultrathin sections. A mixture of butyl and methyl methacrylate (1 : 3) was used as the embedding material. In some cases, the sections were washed free of the embedding material in vapors of butyl methacrylate. Sections were obtained with an LKB Productor ultramicrotome. The objects were examined in an IEM-5Y electron microscope.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Electron micrographs were obtained of transverse sections of grafted polyethylene, polypropylene, and capron fibers treated with an Ag_2SO_4 solution, as well as of the corresponding initial fibers before and after treatment with Ag_2SO_4.

* Grafted fibers of polyethylene, polypropylene, and capron were kindly provided by A. V. Vlasov, a staff member of VNIIV, for which we express our gratitude to him.

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Fig. 1. Cross sections of untreated capron fibers: *a* —original fiber, *b* —grafted fiber, 22,000×

Fig. 2. Cross sections of grafted polymer fibers treated with Ag_2SO_4: *a* — polyethylene, *b* —polypropylene, *c* —capron

In Fig. 1a, b (see insert to p. 574) are shown electron micrographs of cross sections of fibers of the original capron and grafted capron without treatment with a silver sulfate solution (the photograph shows a portion of the fiber close to its surface). From these photographs it is evident that, in morphological structure, the homopolymer and the grafted polymer do not differ from one another. Obviously, this is due to insufficient contrast.

Samples of grafted fibers contrasted with a solution of Ag_2SO_4 give a different picture. In this case the scattering power of the section at the edge of the polyethylene and capron fiber increases sharply owing to the presence of silver atoms. In Fig. 2a (see insert to p. 574) is shown an electron micrograph of a cross section of grafted polyethylene after treatment with Ag_2SO_4 solution at a magnification of 30,000×. The width of the region with high contrast is approximately 1-2 μ for capron and 2-3 μ for polyethylene. Grafted polypropylene fibers treated with Ag_2SO_4 have no regions of high contrast. Only at the very surface are silver particles adhering to the fiber observed, which strongly scatter electrons (Fig. 2b). Apparently, such an effect is due to the fact that the grafting of polyacrylic acid molecules to polypropylene is very slight (1.8%), and the substitution of hydrogen ions by silver ions in it amounts to less than 0.5%. It is evident from the micrographs that the scattering power of the edge of the polyethylene fiber is considerably higher than that of capron. The percentage content of grafted polyacrylic acid in polyethylene is also considerably higher than in capron. These results indicate that, for grafted fibers, there is a correlation between the contrast of the micrograph of the section of the object

and the amount of grafted material.

Such agreement is especially clearly noticeable in photographs at higher magnification, where the internal structure of the fiber treated with Ag_2SO_4 solution is distinctly revealed. At high magnifications it is seen that there are silver particles in the fiber, the number of which in polyethylene is considerably greater than in capron. In polypropylene, contrasting particles are not observed inside the fiber at all. In Fig. 2c is presented a micrograph of a cross section of grafted capron after its treatment with Ag_2SO_4 solution at a magnification of 130,000×. In the photographs, contrasting particles of two types are distinguished: some have a size of 50–60 Å, others 150–300 Å. Particles of the first type, as a rule, are arranged in chains of 3–5 particles at equal distances from one another. The distance between particles is 30–40 Å. The chains are located predominantly parallel to the surface of the fiber. The larger particles are scattered at random. The number of both small and large particles decreases with distance from the edge of the fiber.

The high contrast of these particles indicates that they consist of silver atoms. Apparently, it may be considered that the contrasting silver particles correspond to the location of the molecules of grafted polyacrylic acid. This is confirmed by the fact that ungrafted fibers of capron, polyethylene, and polypropylene treated with Ag_2SO_4 under the same conditions do not reveal contrasting particles, but have a picture similar to Fig. 1a. In addition, grafted polypropylene, which has an insignificant percentage of grafted material, has almost no contrasting particles. Consequently, by means of silver atoms it is possible to "label" certain chemical groups of molecules of grafted polyacrylic acid and to reveal their location in synthetic polymer fibers.

Electron-microscopic photographs of sections of grafted fibers of polyethylene, capron, and polypropylene, washed free of embedding material, show a difference in contrast between the edge of the fiber and the middle. However, in this case washing out the methacrylate leads to wrinkling of the sections, which makes their study in the electron microscope difficult.

Thus, electron-microscopic study of cross sections of fibers of capron, polyethylene, and polypropylene modified by grafting polyacrylic acid has shown that it is possible to reveal the regions of grafting

inside the grafted polymer can be achieved only by treating the specimen with a solution of silver sulfate. Without such treatment, no difference is observed in the morphological structure of sections of the original and grafted fiber. From electron-microscopic images of fiber sections contrasted with Ag_2SO_4, it is possible to make a relative assessment of the effectiveness of grafting.

It is evident that the possibility of obtaining a visual representation of the distribution of graft molecules inside the homopolymer makes the method described highly promising for the study of a broad range of grafted polymers. It is quite clear that silver sulfate is not the only contrasting agent. As the field of application of this method is broadened, it may prove necessary to select

other compounds that act selectively on the graft molecules and possess a high scattering power.

It may also be hoped that the method described will make it possible to find a number of interesting physical characteristics of the material. Thus, for example, by estimating from the contrast of the micrographs the number of silver atoms forming a spot, and at the same time the density of distribution of the spots, in our case it is possible to draw conclusions about the geometry of the distribution of the grafted material. The decrease in the number of spots with depth makes it possible in this study to estimate the change in the diffusion coefficient and, consequently, the density of distribution of the grafted material with depth. Further communications will be devoted to these applications of the proposed method.

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