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Abstract

Full Text

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Preparation of Graft Copolymers

Copolymers of Polytetrafluoroethylene with Methyl Methacrylate

Chemistry

Polytetrafluoroethylene (Teflon) is one of the most valuable polymers, widely used in various branches of technology. However, the low adhesive capacity of polytetrafluoroethylene toward other materials in many cases hinders its use. One means of increasing the adhesion of Teflon is the grafting of vinyl monomers onto its surface. According to literature data, this process is carried out after irradiation of Teflon articles. Such a method of activation, however, often entails deterioration of the properties of the original polymer and also has a number of technological drawbacks (^1).

Fig. 1. Diagram of the apparatus for preliminary treatment of polytetrafluoroethylene films by a silent electric discharge

We used a simpler and milder method of activating polytetrafluoroethylene films, which makes it possible to graft vinyl monomers onto the surface of these films. The method consists in activating the films by exposure to a silent electric discharge in air or in a mixture of air with oxygen.

Figure 1 shows a diagram of the apparatus, consisting of a voltage source, two glass tube insulators, and two copper electrodes: one is wound around the outer tube, the other is inserted into the inner one. The diameter of the discharge zone (the difference between the diameters of the tubes) in our experiment was 1.5-2 mm; the discharge was produced by a current of frequency 50 cps and voltage 22-30 kV.

The films were placed in the discharge zone for 10-30 min, after which they were introduced into a vessel with a vinyl monomer, for example methyl methacrylate, and block polymerization of the latter was carried out at a temperature of 85-90° to a conversion of 4-5%. The films were then treated with boiling dichloroethane

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and acetone to remove the homopolymer, dried to constant weight, and changes in their properties relative to the original film were determined. For complete removal of the homopolymer, treatment with solvent was carried out for not less than 10 h. It was found that over the following 50 h the loss in weight of the film was no more than 0.9-1%.

Table 1 gives the results of experiments on grafting methyl methacrylate onto a standard oriented polytetrafluoroethylene film 40 μ thick.

Table 1

No.	Distance between electrodes, mm	Applied voltage, kV	Time, sec	Yield of grafted layer, wt. %
1	1.5	15	60	3.06
2	2	22	10	3.04
3	2	30	30	3.20
4	2	30	30	3.52
5	2	30	30	3.5

It should be noted that in individual experiments higher yields of the grafted layer were achieved—7-8% of the weight of the initial samples.

Table 2 gives the change in the elemental composition of graft copolymers with methyl methacrylate in comparison with the initial polytetrafluoroethylene film.

In Figs. 2 and 3 the IR spectra of polytetrafluoroethylene films, initial and with a grafted layer of polymethyl methacrylate, are compared. The absorption band in the region of 1700 cm^{-1} is characteristic of the stretching vibrations of the CO group. The two other absorption bands found in the spectrum of the graft copolymer,

Table 2

Initial polytetrafluoroethylene	C, % found	C, % calculated	F, % found	F, % calculated	H, % found	H, % calculated
Initial polytetrafluoroethylene	24.9123.98	24.01	73.3973.97	75.99	none	none
Graft copolymer containing 8.42% methyl methacrylate	25.8126.37	26.74	67.6167.03	70.06	0.540.56	0.62
Graft copolymer containing 3.26% methyl methacrylate	25.9125.85	25.00	72.6973.10	73.71	0.290.50	0.26

namely 3000 cm^{-1} and 1450 cm^{-1}, correspond to the stretching and deformation vibrations of the CH_3 group ([2]).

Comparison of the adhesive properties of the initial and graft copolymers showed that, whereas a polytetrafluoroethylene film is not capable of adhering to steel, copolymers with methyl methacrylate have a peel strength, when bonded with one of the heat-resistant adhesives, of from 5 kg/cm^2 to 22–25 kg/cm^2 (depending on the amount of grafted methyl methacrylate).

Fig. 2. IR spectrum of the initial polytetrafluoroethylene film

Regarding the mechanism of activation of the film in our method, the following may be supposed.

Fig. 2. IR spectrum of the initial polytetrafluoroethylene film

Figure 2: Fig. 2. IR spectrum of the initial polytetrafluoroethylene film

Fig. 3. IR absorption spectrum of the graft copolymer with methyl methacrylate

Figure 3: Fig. 3. IR absorption spectrum of the graft copolymer with methyl methacrylate

A silent electric discharge causes ionization of the gases in the discharge zone, which in turn leads to the appearance on the film surface of active radicals that initiate the subsequent grafting reaction. It should be noted, however, that an investigation of the activated film by the EPR method, carried out by us jointly with Ya. S. Lebedev, a coworker of the Institute of Chemical Physics of the Academy of Sciences of the USSR, did not reveal in it any characteristic polymer or peroxide radicals analogous to those formed during the radiochemical treatment of polytetrafluoroethylene ([3]). Apparently, this ex–

is explained by the small number of active particles, which is also confirmed by the relatively low yield of the grafted layer and indicates the mildness of the activation method itself.

As a result of the work carried out, graft copolymers of polytetrafluoroethylene with methyl methacrylate were obtained with preliminary activation of the films by exposure to a silent electric discharge at a frequency of 50 Hz and a voltage of 22–30 kV. The elemental composition, IR spectra, and adhesion to metal of the graft copolymers were investigated.

Fig. 3. IR absorption spectrum of the graft copolymer with methyl methacrylate

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