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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Graft Polymerization of Acrylic Acid onto Powdered Polyethylene

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Abstract—Radiation-induced graft polymerization of acrylic acid onto powdered polyethylene samples of various granulometric compositions was studied. The resulting graft polymer can be used as a cation-exchange sorbent. The ion adsorption properties of the synthesized cation exchanger were characterized.

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Radiation-induced graft copolymerization is a widely used method for purposeful modification of materials (primarily polymers). Several processes based on radiation grafting, implemented on the semicommercial and even commercial scales, have been described [1, 2]. Among them are radiation procedure for textile finishing, synthesis of ion-exchange membranes, and preparation of polyethylene films with grafted polyacrylic acid. Graft copolymerization shows much promise in production of biocompatible materials and enzyme immobilization [3, 4]. Radiation-induced graft polymerization is widely used for preparing various sorbents, e.g., by introducing ionogenic groups [5].

The advantages of radiation-induced graft polymerization are versatility (it is possible to modify polymeric materials of any nature, size, and shape, e.g., films, fibers, or powders), possibility of modification to any preset depth by varying the ionization energy, and modification in a wide temperature range, including low temperatures at which substance initiators do not operate.

This study concerns modification of powdered polyethylene (PE) with polyacrylic acid (PAA) by graft polymerization and determination of the ion-adsorption characteristics of the resulting cation exchangers.

EXPERIMENTAL

We used HDPE powder of grade 273-00. The PE powder was fractionated by sieving.

To create centers of graft polymerization initiation, PE powder samples were exposed to ^{60}Co γ-ray radiation at room temperature at a dose rate of up to 0.7 Gy s^{-1} to absorbed doses of 50, 100, and 150 kGy. The gel fraction content *g* (%) in the irradiated PE samples was determined by exhaustive extraction with toluene in a Soxhlet apparatus. The concentration of peroxides in the irradiated PE powder was determined by iodometric titration [6] in benzene (total content of peroxy groups in PE) and alcohol (content of peroxy groups on the PE surface).

Graft polymerization of acrylic acid (AA), which was not specially purified, was performed in a glass vessel in an inert gas (nitrogen) atmosphere in the presence of Fe(II) ions at 85 ± 1°C. The degree of grafting was determined gravimetrically as the weight ratio of the grafted PAA to the initial PEE (%). The concentration of Fe ions in the solution was determined spectrophotometrically using complexation with sulfosalicylic acid [7].

Sorption of metal ions was studied in the static mode by the limited volume method [8]. The adsorbate ion concentration in the solution was determined spectrophotometrically [Cu(II) and Mn(II) ions] and by titration (sodium and ammonium ions). The optical density of solutions was measured with a KFK-3-01 concentration photoelectrocolorimeter in 1.0-cm-thick quartz cells.

Effect of γ-irradiation on characteristics of PE powder. The effect of ionizing radiation on PE mainly

consists in cross-linking of polymer macromolecules and oxidation of chains in the presence of atmospheric oxygen [1]. The three-dimensional structures formed can significantly affect the mechanical properties and morphology of the polymer and thus will determine the accessibility of carboxy groups to ion exchange.

Studies of the extraction kinetics of PE powder with a particle size of 0.25–0.5 mm, γ-irradiated to a dose of 150 kGy, showed that the minimum required extraction time was 24 h. In the subsequent experiments, the gel fraction content was determined by extraction for 24 h.

Examination of the influence of the γ-irradiation dose on the cross-linking yield showed that, for the PE powder fraction with a particle size of 0.25–0.5 mm, the gel fraction yield increases from 50 to 65% with an increase in the γ-irradiation dose by a factor of 3 (from 50 to 150 kGy) (Fig. 1). Variation of the granulometric composition of PE powder in the interval 0.05–2 mm does not affect the cross-linking yield (see table).

We examined how the particle size of PE powder affects the concentration of peroxides (hydroperoxides and dialkyl peroxides) on the surface and in the bulk of the polymer upon γ-irradiation. We found that the total content of peroxides decreased with increasing particle size, but their content on the surface increased (Fig. 2). Such distribution of peroxides in the bulk of PE particles upon γ-irradiation is determined by diffusion of oxygen into the polymer. Namely, with an increase in the PE particle size the oxygen diffusion controls the formation of peroxides in the bulk of PE particles to a greater extent, and peroxides are predominantly formed on the surface.

Influence of the PE particle size on the gel fraction yield. γ-Irradiation dose 150 kGy, extraction time 24 h, solvent toluene

Diameter, mm	*g*, %
<0.05	65 ± 3
0.05–0.1	64 ± 3
0.25–0.5	69 ± 3
0.5–1	68 ± 3
1–2	69 ± 3

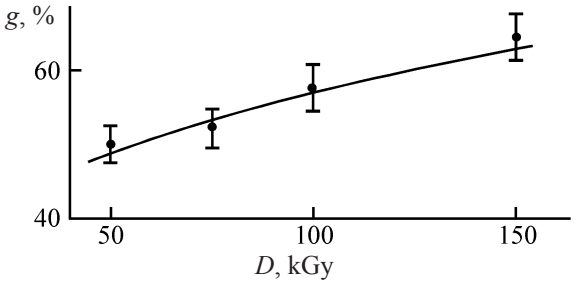

Fig. 1. Influence of the γ-irradiation dose *D* on the gel fraction yield *g*. Particle size 0.25–0.5 mm, extraction time 24 h, solvent toluene.

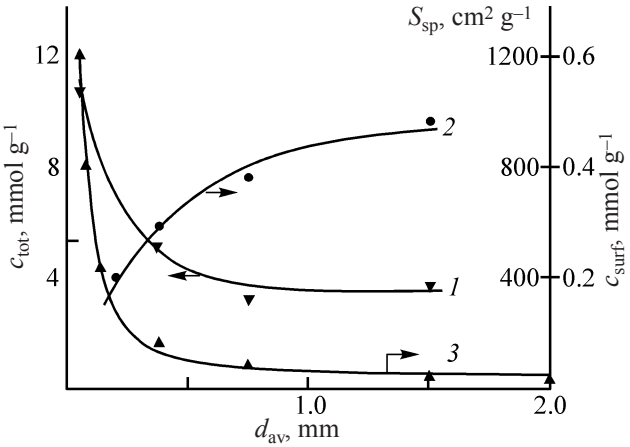

Fig. 2. Influence of the PE particle size d_{av} on the (*1*) total concentration c_{tot} of the peroxides formed, (*2*) concentration of peroxides on the surface c_{surf}, and (*3*) specific surface area of particles S_{sp}. γ-Irradiation dose 150 kGy; the same for Figs. 3 and 4.

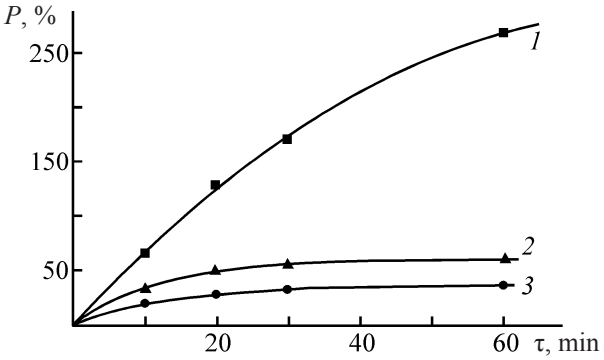

Fig. 3. Kinetic curves of graft polymerization of AA from its (*1*) alcoholic, (*2*) aqueous-alcoholic, and (*3*) aqueous solutions onto PE powder. (*P*) Yield and (τ) time.

Graft polymerization of acrylic acid onto PE powder. We studied the kinetics of graft polymerization of AA onto PE powder from alcoholic (methanol), aqueous-alcoholic, and aqueous solutions of the monomer.

Graft polymerization of AA occurs at the highest rate in an alcoholic solution, and within the process time the degree of grafting (weight of grafted PAA) does not reach the limiting value. In aqueous-alcoholic and aqueous solutions, the limiting degree of grafting is attained in 30 min (Fig. 3). Similar results were obtained in experiments on graft polymerization of AA onto film materials [6]. The trends we observed can be accounted for by the fact that graft polymerization of AA onto PE is diffusion-controlled. Therefore, a decrease in the polarity and quality of the solvent in which the polymerization is performed leads to an increase in the rate and limiting degree of grafting. This is due, on the one hand, to improvement of the wettability of the PE powder and, on the other hand, to a decrease in the degree of swelling of grafted PAA chains in the grafting solution. These factors make the initiation centers (peroxides) and propagating radicals more accessible to Fe(II) ions and monomer molecules, compared to graft polymerization in a polar (water) solvent.

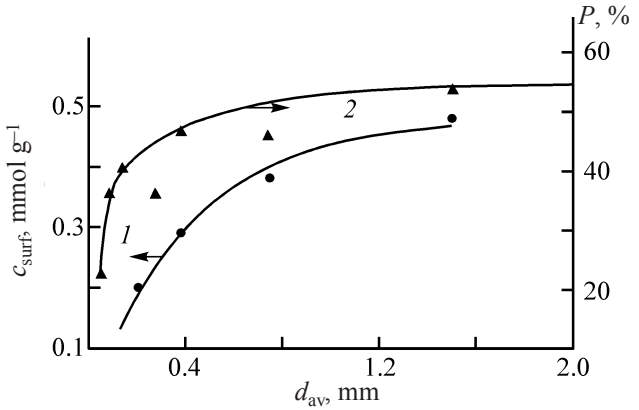

Fig. 4. Influence of the particle size of PE powder d_{av} on the (*1*) surface concentration of peroxides c_{surf} and (*2*) limiting degree of grafting *P*.

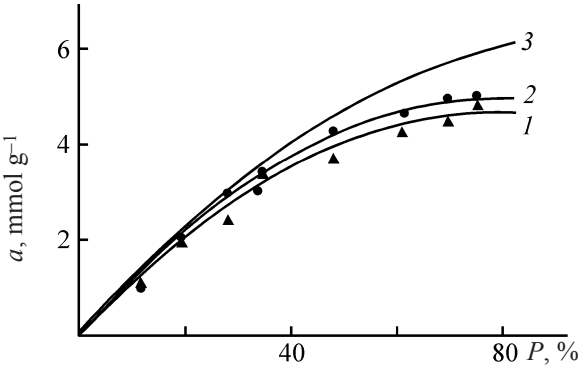

Fig. 5. Adsorption a of (*1*) sodium and (*2*) ammonium ions as a function of PAA content *P*. (*3*) Maximum possible adsorption.

We examined how the grafting solution composition affects the adsorption properties and degree of swelling of graft polymers. Comparison of the adsorption values of sodium ions by graft polymers prepared from alcoholic, aqueous-alcoholic, and aqueous solutions of AA showed that in none of the cases the adsorption of sodium ions reached the maximum possible value. Furthermore, the adsorption value is virtually equal for all the graft polymers prepared from alcoholic, aqueous-alcoholic, and aqueous solutions of the monomer, which suggests similar conformational structure of the copolymers prepared.

The swellability of the graft polymer with 270% degree of grafting in distilled water reaches almost 150%. In the process, the initial granulated structure of the polymer changes essentially. Therefore, in further experiments graft polymerization was performed from an aqueous solution of the monomer for 1 h.

The influence of the PE particle size on the limiting degree of grafting is shown in Fig. 4. As can be seen, the limiting degree of grafting increases with an increase in the particle size of the PE powder and reaches 25% for particles with the diameter smaller than 0.05 mm and 55% for particles with the diameter exceeding 1 mm, i.e., the modification process is not determined by the surface area of the PE powder. Comparison of the influence exerted by the particle size of the PE powder on the surface concentration of peroxides (Fig. 4, curve *1*) and on the limiting degree of grafting (Fig. 4, curve 2) suggests that the limiting degree of grafting is determined by the content of peroxides on the polymer surface, i.e., the graft polymerization under these conditions is predominantly a surface process.

Sorption characteristics of the cation exchanger. As a result of modification with PAA, the PE powder acquires ion-exchange properties. The scheme of the cation-exchange sorbent based on the PE powder with grafted chains of an ionogenic monomer (PAA) is similar to that described in [9].

The capability of the ion exchanger for ion adsorption was quantitatively evaluated by the adsorption value a (mmol g^{-1}) defined as the amount of ions adsorbed by 1 g of the ion exchanger.

The maximal, or theoretical, adsorption value of ions a_{max} (mmol g^{-1}) was determined from the degree of grafting and calculated by the formula

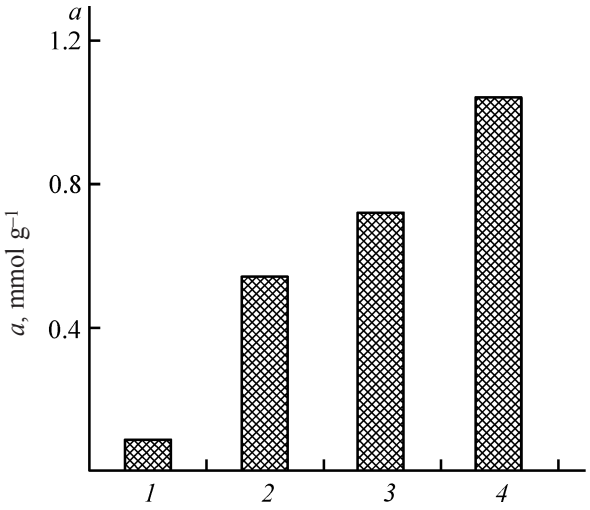

Fig. 6. Influence of the ionic form of the ion exchanger on the adsorption of Cu(II) ions *a*: (*1*) H form, (*2*) Na form, (*3*) NH_4 form, and (*4*) maximal adsorption.

$$a_{max} = \frac{P \times 1000}{(P + 100) \times 72},$$

where *P* is the degree of grafting of PAA (%) and 72 g mol^{-1} is the molecular weight of acrylic acid.

We studied the adsorption of sodium, ammonium, copper(II), and manganese(II) ions on the ion exchanger in relation to the PAA content in the copolymer (degree of grafting). We found that, with an increase in the PAA content, the ion adsorption increases. However, it does not reach the maximum possible value (Fig. 5). The adsorption values for sodium and ammonium ions are virtually equal. Thus, not all the carboxy groups are accessible to ion adsorption, which is associated with steric inaccessibility of these groups. The fraction of groups inaccessible to ion exchange increases with an increase in the PAA content in the ion exchanger.

Sorption of transition metals. When the cation exchanger contains carboxy groups, adsorption of transition metal ions is due to simultaneous formation of an ionic bond and a coordination bond by the donor–acceptor mechanism. The higher the polarity of the oxygen–metal bond, the stronger the polymeric complex.

We studied adsorption of Cu(II) and Mn(II) ions. The limiting adsorption of Cu(II) decreases in the order NH_4 form > Na form > H form, amounting to 0.72, 0.55, and 0.09 mmol g^{-1}, respectively (Fig. 6).

A study of the adsorption of Cu(II) ions in relation to the PAA content in the ion exchanger showed that, with an increase in the PAA content, the ion adsorption increases and its value depends on the form in which the ion exchanger was taken. For example, at a PAA content of about 70%, the ion adsorption reaches 1 and 1.3 mmol g^{-1} for the ion exchanger in the Na and NH_4 forms, respectively (Fig. 7).

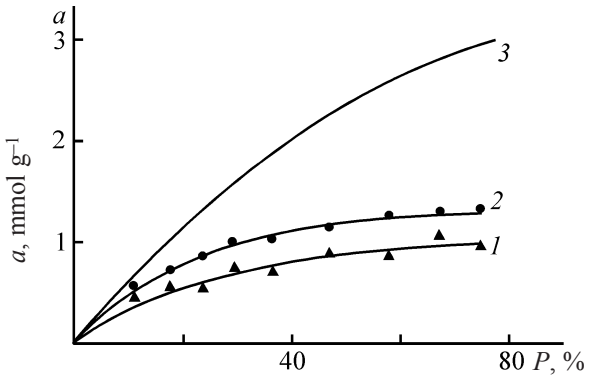

Fig. 7. Adsorption of Cu(II) ions *a* on the ion exchangers in the (*1*) NH_4 and (*2*) Na forms as a function of the PAA content *P*. (*3*) Maximum possible adsorption.

Experiments on adsorption of Mn(II) ions showed that the ion adsorption monotonically increases, reaching the limiting value of 1.5 mmol g^{-1} for the ion exchanger in the Na form.

CONCLUSIONS

(1) The cation-exchange sorbent prepared contains carboxy groups capable of firmly retaining transition metal ions by their binding in a polymeric complex.

(2) The sorbent can be used for recovering and concentrating transition metal ions from aqueous solutions.

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