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BRIEF COMMUNICATIONS

Composites of Acrylate Copolymers and Fullerene

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Abstract—Preparation conditions of composites of vinylmethyltetrazole–acrylate copolymers with fullerene were studied. The sorption properties of the composites were studied in relation to the C_{60} content.

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Fullerene-containing polymers and composites are promising materials for medicine, biology, building, and optics [1–3]. Materials with required particular properties can be prepared by modification of the initial polymer matrix with fillers. Introduction of fullerenes (F) into atactic PMMA affects the thermal oxidative degradation of the polymer matrix [4].

Previously we showed that introduction of fullerene into acrylate formulations slightly decreases the tensile strength of the films but substantially increases their relative elongation (ε ~1100%). Data on the preparation and properties of composites of vinylmethyltetrazole–acrylate copolymers with fullerene are scarce. The aim of this study was to prepare fullerene-containing acrylate composites and to examine their sorption properties.

EXPERIMENTAL

Films of composites of vinylmethyltetrazole–acrylate copolymers with fullerene were prepared by radical polymerization in aqueous solutions at 10–60°C in the presence of the ammonium persulfate (APS)–tetramethylethylenediamine initiating system. *N*,*N*'-Methylenebisacrylamide (MBAA) was used as the cross-linking agent. The degree of neutralization of acrylic acid α ranged from 0.1 to 0.9. The polymerization was performed at the initial monomer concentration of 10–57%, the concentration of 2-methyl-5-vinyltetrazole (MVT) of 0–65 wt % of the weight of acrylic acid (AA), and the concentration of the cross-linking agent of 0–0.9 wt % of the total monomer weight. The properties and purification procedures of other chemicals and the procedures for preparing composites and studying their sorption properties were reported previously [6]. The composites were prepared in aqueous solutions in 8–15 h.

Solid fullerene (C_{60}) was introduced with stirring in the first polymerization step. Since the composite is heterogeneous, the fraction of the unchanged modifier was determined gravimetrically after swelling of the composite in distilled water for 5–7 days.

The preparation conditions and some properties of composites of new vinylmethyltetrazole–acrylate copolymer with fullerene are presented in the table. It is seen that the copolymer yield decreases and the gelation onset time increases with increasing the fullerene concentration in the reaction mixture. This fact suggests that fullerene inhibits the initiation of the free-radical copolymerization [7]. It should be noted that the copolymer yield increases with increasing the AA concentration in the initial monomer mixture.

The kinetic curves of swelling of composites of vinylmethyltetrazole–acrylate copolymers with fullerene, prepared at different concentration of the cross-linking agent, are shown in Fig. 1a. The equilibrium swelling of these composites with different fullerene content is attained within 5–10 h, which is significantly faster than the time required for equilibrium swelling of vinylmethyltetrazole–acrylate hydrogels without the modifier.

As seen from Fig. 1a, the equilibrium swelling of the absorbing composites decreases with increasing the concentration of the cross-linking agent. This is due to shortening of the polymer segment between the cross-links of the polymeric network.

The kinetic curves of swelling of the fullerene-containing acrylate composites with different modifier content are shown in Fig. 1b. As seen from Fig. 1b,

Preparation conditions and properties of the composites of acrylate copolymers (solvent water)

Sample no.	Copolymerization conditions							Gelation onset time, h	Copolymer yield, %
	AA : MVT weight ratio	α	bath ratio	[MMBA]	[APS]	[F]	*T*, °C		
				wt %					
1	100 : 0	0.4	57	0.2	0.6	0.1	60	0.5	70
2	100 : 0	0.4	50	0.2	1	0.0	50	1	85
3	100 : 0	0.4	50	0.2	0.6	0.0	50	1.2	80
4	100 : 0	0.4	50	0.1	0.6	0.1	50	1.5	80
5	100 : 0	0.4	50	0.15	0.6	0.1	50	1.4	82
6	100 : 0	0.3	35	0.15	1	0.0	30	2	64
7	100 : 0	0.3	35	0.15	1	0.1	30	2.5	65
8	100 : 0	0.3	35	0.15	1	0.0	30	2.5	72
9	100 : 0	0.3	30	0.15	1	–	30	1	93
10	100 : 0	0.6	30	0.1	1	0.0	30	1.5	76
11	50 : 50	0.6	50	0.2	0.6	0.1	50	0.25	67
12	35 : 65	0.9	50	0.2	0.6	0.1	50	0.5	60
13	65 : 35	0.5	50	0.2	0.6	0.1	50	1	73
14	100 : 0	0.4	57	0.2	0.6	–	50	1	92
15	100 : 0	0.1	50	0.1	0.6	2.3	11	10	56
16	35 : 65	0.9	50	0.1	0.6	0.1	50	5	76
17	35 : 65	0.3	50	0.1	0.6	0.7	11	12	48

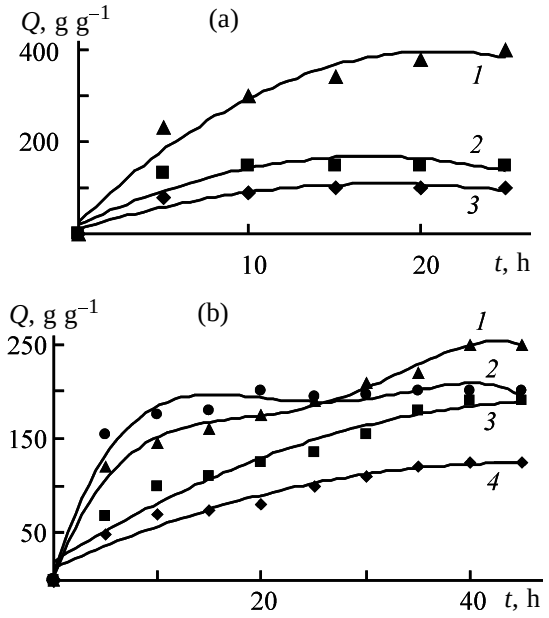

Fig. 1. Equilibrium degree of swelling *Q* of (a) vinylmethyltetrazole–acrylate copolymer and (b) fullerene-containing polymer composites in distilled water at 15°C as a function of time *t*. (a) Concentrations of fullerene and APS 0.1 and 0.6 wt %, respectively; α = 0.4. MBAA concentration, wt %: (*1*) 0.1, (*2*) 0.15, and (*3*) 0.2. (b) Concentrations of APS and MMBA 1 and 0.15 wt %, respectively; α = 0.3. Fullerene concentration, wt %: (*1*) 0.03, (*2*) 0.1, (*3*) 0.01, and (*4*) 0.

the initial swelling is accelerated as the fullerene content in the composite increases. The dependence of the equilibrium swelling passes through a maximum at the fullerene C_{60} concentration of 0.03 wt %. Ginzburg et al. showed [4] that aggregation of C_{60} molecules at their definite concentrations decreases the effect of the fullerene on the properties of PMMA films.

Fullerene C_{60} is insoluble in water but is a component of partially water-soluble material. The fullerene can be removed from the condensed phase during dissolution of the polymer. This is the case in prolonged swelling of the composites with the fullerene content higher than 0.7 wt %.

It should also be noted that the equilibrium degree of swelling of the vinylmethyltetrazole–acrylate copolymer prepared under the similar conditions but without the modifier is smaller that that of the copolymer modified with C_{60}. This can be due to fullerene–copolymer intermolecular interactions affecting the absorption properties of the acrylate composites. Stabilization of monomolecular layers of C_{60} by aqua aggregation was demonstrated in [8].

The fact that swollen fullerene-containing composite holds its shape allows preparation of articles with required geometrical parameters.

CONCLUSIONS

(1) Absorbing composites of vinylmethyltetrazole–acrylate copolymer with fullerene were prepared.

(2) The influence of the modifier on the absorption properties of the composites was demonstrated. The dependence of the equilibrium degree of swelling of the composites on the fullerene content passes through a maximum. These dependences allow prediction of the properties of composites with different modifier content.

(3) The rate of the swelling of the composites in distilled water depends on the fullerene content in the sample.

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