

V.N. KISLENKO, E.I. KURIATNIKOV

GRAFT COPOLYMERS OF UNSATURATED MONOMERS WITH STARCH

Abstract

The influence of reagent concentration on monomer conversion and grafting efficiency was investigated for the graft initiated by ammonium peroxodisulfate polymerization of methyl acrylate and natural oil onto starch.

The monomer conversion and grafting efficiency increased when the initiator concentration increased. An increase of the monomer concentration led to increase in the monomer conversion and a decrease in the grafting efficiency. The grafting efficiency of oils decreased in the order olive oil, linseed oil, sunflower seed oil. The conversion of natural oil decreased with increase in the oil concentration in the reaction mixture.

The influence of reagent concentration on elongation at break, breaking strength, swelling capacity and water vapor permeability of films obtained from graft copolymer dispersions was investigated. The breaking strength was independent of the concentration of monomers and starch, but decreased when initiator concentration increased. The elongation increased with the increase in the methyl acrylate concentration. The water swelling capacity of films decreased with increase in the concentration of initiator and decrease in the starch concentration. It was independent of the oil concentration.

Introduction

The polymer solutions and dispersions can be used for obtaining glues, lacquers, paints in industry. Dispersions of acrylic polymers, solutions of poly(vinyl alcohol) [1-3], cellulose ethers [4] are used as film forming compounds. However, these polymers cannot be used in some cases, for example, in food or pharmaceutical industry, because dispersions of industrial polymers contain monomers, emulifiers and other additives. Therefore, further novel polymer dispersions based on natural substances are very interesting.

In this paper the results of the investigation of film forming dispersions based on the natural substances and physico-mechanical properties of film obtained from them are presented.

Materials and methods

Industrial potato starch, linseed oil, olive oil and sunflower seed oil, purified from solid particles, distilled methyl acrylate and recrystallized ammonium peroxodisulfate were used. The solution of starch was obtained by heating of starch dispersion in distilled water at 97–98°C about 0,5 h. Graft copolymer was prepared of methyl acrylate and natural oil with starch obtained at 70°C by addition of ammonium peroxodisulfate as the initiator followed by addition of monomers, methyl acrylate and natural oil, into the starch solution. The reaction mixture was heated for 2 h at 70°C. The reaction mixture became milk in 5–10 min after blending reagents.

Oil conversion, S_o , was determined by centrifugation of dispersion at 8000 min^{-1} for 30 min. Oil separated from water dispersion. Oil conversion was calculated according to equation:

$$S_o = (m_o - m_k)100/m_o$$

Where m_o is the oil mass admixed into the reaction mixture, m_k is the oil mass separated after centrifugation.

It was found that under this condition the whole oil mass was separated from the solution. The experimental error was below 5%.

The methyl acrylate conversion, S_m , in dispersion was determined by the bromide – bromate method [5].

Grafting efficiency, GE, was determined by 80 h acetone extraction of methyl acrylate copolymer with oil from the film. The film contained the mixture of this copolymer with graft copolymer of these monomers to starch. The grafting efficiency was calculated according to equation:

$$GE = (m_g - m_c)100/m_g$$

Where m_g is the mass of polymer film without the mass of starch in it and m_c is the mass of copolymer of methyl acrylate and oil extracted from the film.

The swelling capacity, δ , of the film in water was determined in the sample immersed for 24 h in distilled water at 20°C [6]. It was calculated with equation:

$$\delta = m_s 100/m_o$$

where m_s is the mass of swelling film, and m_o is the mass of dry film.

The water vapor permeability, P , of the film was determined as the relation of the mass of water evaporated from the pot covered with film to the mass of water, evaporated from the free water surface of this pot [7].

The breaking strength, δ , and the elongation at break, ϵ , of films was determined using "TIRA test 2200" instrument.

Results and discussion

Polymerization of natural oils, initiated by ammonium peroxodisulfate in starch solution practically does not occur. Oil conversion was below 5%. Conversion of natural oil was increased when methyl acrylate has been used as comonomer. Graft copolymer of methyl acrylate and natural oil starch was available in this process. A decrease in the reaction rate and monomer conversion was observed when reaction temperature decreased to 55–60°C. At temperature increased to 80–85°C, acrylate evaporated (boiling temperature 80.5°C), and the grafting efficiency significantly decreased. Therefore, the polymerization has been carried out at 70°C.

Dependence of conversion of natural oil, methyl acrylate and grafting efficiency on the reagent concentration in the mixture is given in Table 1. Increase in the linseed oil concentration from 0.7 to 4.2% led to decrease in the oil conversion. That can be rationalized in terms of the mechanism of the process. The equilibrium concentration of methyl acrylate in the water phase and oil droplets was established as a result of its diffusion from oil drops. Initiation of the polymerization proceeded in the water phase. Initiating radicals interacted with the methyl acrylate molecules and starch in the water solution. Then starch macroradicals, adding methyl acrylate molecules, initiated the graft polymerization. In the first stage, the oligomer radicals of methyl acrylate were formed in the water phase. These oligoradicals had surface-active properties and adsorbed on the surface of oil drops, where they initiated copolymerization of methyl acrylate to natural oil [8]. Therefore, the copolymerization of methyl acrylate with natural oil occurred at high concentration of methyl acrylate in oil. At its low concentration in droplets, the polymerization rate was very slow and in consequence the oil conversion was low. The polymerization of methyl acrylate proceeded in the water phase. It was suggested by increase in the monomer conversion when the concentration of methyl acrylate increased at the constant methyl acrylate-to-natural oil ratio. In this case, one could observe a decrease in the grafting efficiency of monomers onto starch. Evidently, copolymer of methyl acrylate with natural oil formed by the reaction of chain transfer from graft copolymer onto monomer molecules in the oil drops.

An increase in the starch concentration did not influence the natural oil conversion. However, that led to an increase in the methyl acrylate conversion. At the same time, conversion of methyl acrylate and natural oil increased, when the initiator concentration increased from 0.35 to 1.4% (Table 1). Evidently, the high viscosity of

starch solution led to an increase in the radical concentration in it, as a result of the gel-effect. In this case the grafting efficiency also increased.

Investigation of the influence of the oil nature on the grafting process showed (Table 2) that the oil conversion increased when the olive oil was used and decreased for sunflower seed oil. Evidently, it was associated with the number of the double bonds and the length of carbon chains in corresponding molecules. The methyl acrylate conversion and grafting efficiency were independent of the oil variety.

Table 1

Physico-chemical characteristics of graft copolymers of methyl acrylate and linseed oil with starch.

[MA], %	[St], %	[LO], %	[I], %	[S _o], %	[S _m], %	[GE], %
7,0	7,0	0,70	0,70	80	96	76
7,0	7,0	2,10	0,70	55	97	79
7,0	7,0	4,10	0,70	15	94	96
3,5	7,0	1,05	0,70	35	97	82
7,0	7,0	2,10	0,70	55	97	79
10,5	7,0	3,15	0,70	60	96	47
14,0	7,0	4,20	0,70	65	98	44
7,0	5,0	2,10	0,70	65	94	55
7,0	7,0	2,10	0,70	55	97	79
7,0	10,0	2,10	0,70	70	95	86
7,0	7,0	2,10	0,35	35	92	70
7,0	7,0	2,10	0,70	55	97	79
7,0	7,0	2,10	1,05	70	98	85
7,0	7,0	2,10	1,40	85	98	90

Table 2

Influence of the origin of oil on physico-chemical characteristics of graft copolymers at the concentration of methyl acrylate 7.0%, starch 7.0%, oil 2.1% and initiator 1.4%.

Oil	S, %	S, %	GE, %	δ, %	P, %
Linseed	85	98	90	88	31
Olive	90	97	90	83	30
Sunflower seed	60	95	85	94	35

Physico-mechanical properties of the films were investigated involving the air dried films of graft copolymers of the 0.1 mm thickness. The film of initial starch could not be prepared because it was very friable.

Investigation of the elongation at the break of films showed, that it increases with the monomer concentration in the reaction mixture (Fig. 1, curve 1). At the same time, an increase in the starch concentration led to a decrease of elongation (Fig. 1, curve 2). Therefore, copolymer of methyl acrylate with natural oil plastified the starch containing film. An increase in the initiator concentration in the reaction mixture decreased the elongation at the film break although the monomer conversion and grafting efficiency increased (Fig. 1, curve 3). Evidently, it was due to cross-linking of polymers by a bimolecular termination of the macroradical chains. The swelling capacity of films in water decreased insignificantly when the initiator concentration in reaction mixture increased from 0.35 to 1.4%.

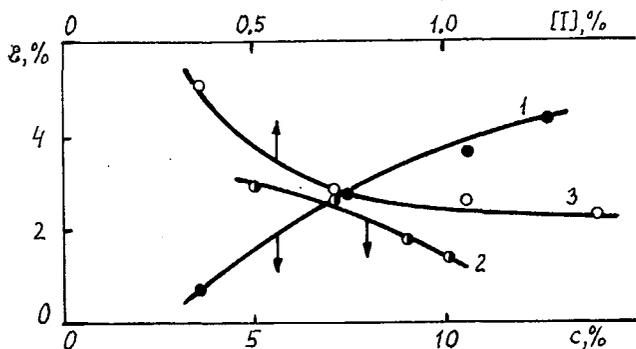


Fig. 1. Dependence of elongation at break of the graft copolymer of methyl acrylate and linseed oil with starch on reagent concentration in reaction mixture. Concentration of initiator was 0.7% (1,2), starch - 7% (1,3), methyl acrylate 7% (2,3), linseed oil 2.1% (2,3), mass ratio of linseed oil - methyl acrylate was 0.3 (1).

Decrease of the swelling capacity of film with the monomer concentration increase (Fig. 2, curve 2) and the starch concentration decreases (Fig. 2, curve 2) were observed. At the same time, an increase in the natural oil concentration in reaction mixture led only to insignificant swelling of the films (Fig. 2, curve 3). Evidently, that is the result of low conversion of oil.

Water vapor permeability of graft copolymers to starch increased with starch concentration (Fig. 3, curve 2). However, the water vapor permeability passed through the maximum, when the monomer concentration in reaction mixture increased at the constant ratio of methyl acrylate to natural oil (Fig. 3, curve 1). That could be explained as the result of decrease in the grafting efficiency.

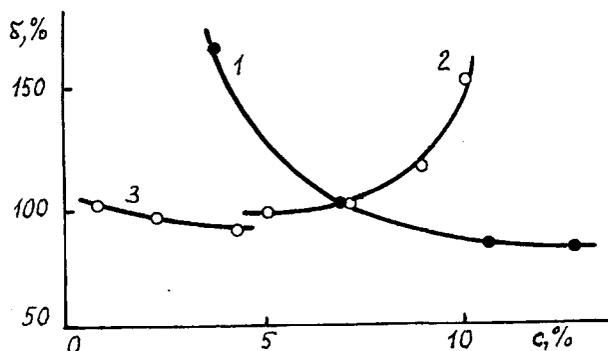


Fig. 2. Dependence of swelling capacity of the graft copolymer of methyl acrylate and linseed oil with starch on reagent concentration in the reaction mixture. Concentration of initiator was 0.7% (1,3), starch - 7% (1,3), methyl acrylate 7% (2,3), linseed oil 2,1% (2), mass ratio of linseed oil - methyl acrylate was 0.3 (1).

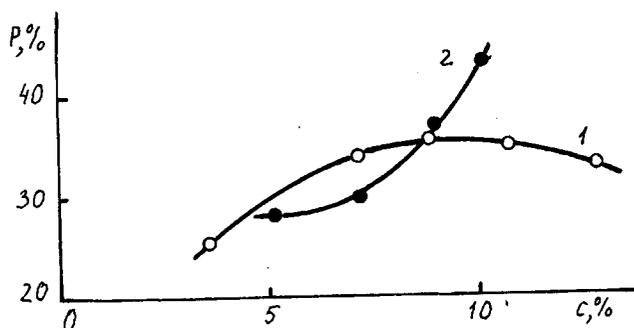


Fig. 3. Dependence of water vapor permeability of the graft copolymer of methyl acrylate and linseed oil with starch on reagent concentration in reaction mixture. Concentration of initiator was 0.7%, starch - 7% (1), methyl acrylate 7% (2), linseed oil 2.1 (2), mass ratio of linseed oil - methyl acrylate was 0.3 (1).

The breaking strength of the films insignificantly depended on the concentration of monomers and starch (Fig. 4, curves 1-3). An increase in the initiator concentration led to decrease in the breaking strength of the film (Fig. 4, curve 4). Oxidation of starch during graft polymerization could be involved leading to a change in the structure of the material.

The nature of oil had no influence on the physico-mechanical properties of the films of the graft copolymers of methyl acrylate and oil with starch.

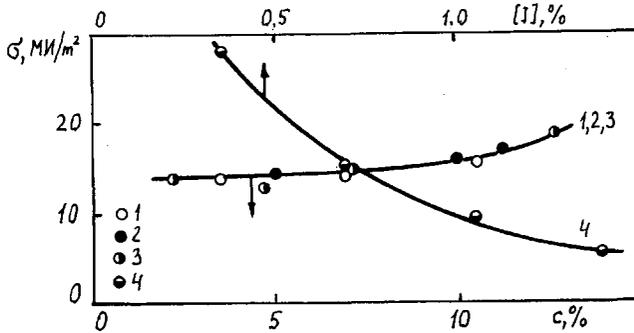


Fig. 4. Dependence of breaking strength of the graft copolymer of methyl acrylate and linseed oil with starch on reagent concentration in reaction mixture. Concentration of initiator was 0.7% (1-3), starch - 7% (1,2,3), methyl acrylate 7% (2-4), linseed oil 2.1% (2,4), mass ratio of linseed oil - methyl acrylate was 0.3 (1).

REFERENCE

- [1] Elesejeva V.I.: Polymer Dispersions. Chemistry, Moscow, 1980, 295.
- [2] Polymer Film Forming Substances. Ed. Elesejeva V.I. Chemistry, Moscow, 1971, 214.
- [3] Solomon D.G.: Chemistry of Organic Film Forming Substances. Chemistry, 1971, 318.
- [4] Biklz H., Segal L.: Cellulose and it's Derivatives. Mir, Moscow, v. 2, 1974, 510.
- [5] Cheronis N.D., Ma T. S.: Organic Functional Group Analysis by Micro and Semimicro Methods. Interscience. N.-Y., 1964, 483.
- [6] Avvakumov N.I., Budarin A.A., Dvignon S.M.: Handbook of Chemistry and Physics of Polymers. Chemistry, Moscow, 1990, 304.
- [7] Elesejeva V.I.: Polymer Film Forming Compounds for Leather. Gizlegprom, Moscow, 1961, 238.
- [8] Kislenko V.N.: Colloids and Surfaces, 152, 1999, 199.

SZCZEPIONE POLIMERY NIENASYCONYCH MONOMERÓW ZE SKROBIĄ

Streszczenie

Badano wpływ stężenia reagenta na konwersje monomeru i efektywność szczepiania w czasie inicjowanej peroksydisiarczanem amonu polimeryzacji akrylanu metylu i olejów roślinnych ze skrobią.

Konwersja i efektywność szczepiania wzrastała ze stężeniem inicjatora. Wzrost stężenia monomeru podnosi stopień jego konwersji, obniżając efektywność szczepiania. Efektywność szczepiania olejów roślinnych maleje w kolejności: olej oliwkowy > olej lniany > olej słonecznikowy. Stopień konwersji tych olejów maleje ze wzrostem ich stężenia w mieszaninie reakcyjnej.

Badano też wpływ stężenia reagenta na naprężenie wzdłużne w punkcie zerwania, wytrzymałość na zerwanie, zdolność pęcznienia i przepuszczalność dla pary wodnej filmów z tych materiałów. Wytrzymałość na zrywanie nie zależała od stężenia monomeru i skrobi i obniżała się ze wzrostem stężenia ini-

cyjatora. Względne naprężenie wzdłużne wzrastało ze stężeniem metakrylanu metylu i malało ze wzrostem stężenia inicjatora. Pęcznienie filmu malało ze wzrostem stężenia inicjatora i malało ze wzrostem stężenia skrobi. Nie zależało ono od stężenia oleju roślinnego. Przepuszczalność pary wodnej wzrastała ze stężeniem skrobi i przechodziła przez maksimum zależności od stężenia monomeru. ☒