

SYNTHESIS OF GRAFT COPOLYMERS OF SYNTHETIC RUBBERS WITH ACRYLIC MONOMERS INITIATED BY POTASSIUM PERSULFATE

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Abstract: Carried out graft copolymerization of synthetic rubbers with acrylic acid and methyl methacrylate in a solution of a mixture of benzene and dimethylformamide, in the presence of potassium persulfate as an initiator. The main parameters of grafting are determined: the degree and efficiency of grafting, the value of which depends on the nature of the rubber and monomer. The highest grafting efficiency (over 60%) was achieved in the case of grafting methyl methacrylate to polychloroprene rubber. Based on the results of FTIR spectroscopic studies, the scheme of the reaction between the polychloroprene macromolecule and potassium persulfate with the formation of active centers of a radical nature was determined. Thermogravimetry and differential scanning calorimetry were used to determine the thermal properties of the synthesized copolymers.

INTRODUCTION

Copolymerization of a monomer of a thermoplastic polymer with rubber makes it possible to synthesize thermoplastic elastomers (TPE), which combine the properties of elastomers during operation, and thermoplastics during processing [1, 2]. The composition, structure and properties of such polymers are inextricably linked with the method and patterns of their preparation.

Currently, there are several ways to obtain TPE. One of the methods is based on the reactions of graft and block copolymerization of thermoplastic polymer monomers with an elastomer macromolecule or elastomer monomers with a thermoplastic macromolecule. The applicability of thermoplastic elastomers is practically universal, therefore, the latest advances in science and technology related to their production and processing are becoming more and more relevant [3, 4, 5]. TPE is widely used in the production of footwear: as a shoe sole and an adhesive material. The development of technologies determines the development and research of new types of TPE products based on polyolefins [6], fibers and elastomers with magnetic properties [7], compositions with hydroxides [8]. Photo- and biodegradable thermoplastic elastomers of polybutadiene [9], oil-free polymer nanocomposite thermoplastic elastomers acrylic acid [10, 11] have been obtained.

Graft copolymerization of methyl methacrylate on natural rubber, initiated by the redox system hydrogen peroxide - sodium thiosulfate, has long been successfully carried out. The reaction was studied in an aqueous medium by varying the concentrations of the monomer, hydrogen peroxide, and sodium thiosulfate [12]. In order to improve the thermal and mechanical properties of natural rubber, it was grafted copolymerized with acrylic monomers by means of redox polymerization [13]. Grafting polymerization of methyl methacrylate onto polychloroprene rubber in the presence

of hydrogen peroxide as an initiator is carried out in order to improve the adhesion of adhesives [14]. The graft copolymerization of ethyl acrylate and methyl methacrylate onto polychloroprene was carried out in toluene using benzoyl peroxide as an initiator also in order to improve the adhesive ability of adhesives [15].

The possibilities of grafting polymerization of acrylic monomers, both in terms of determining the laws of synthesis and practical improvement of the properties of materials, are far from being exhausted. The aim of this study is to synthesize graft copolymers of synthetic rubbers with acrylic monomers in the presence of potassium persulfate as an initiator, to determine the grafting parameters, the interaction scheme, and the thermal properties of the grafted copolymers.

MATERIALS AND METHODS

Samples of synthetic rubbers PCH - polychloroprene rubber, PI - polyisoprene rubber, SRN-40 - nitrile butadiene rubber (40% acrylonitrile units), SRS-30 - styrene butadiene rubber (30% styrene units), produced by the Russian Federation, were provided by LLC "Tashkent-Rezina" (Republic of Uzbekistan).

Acrylic acid (AA, $CH_2 = CHCOOH$) was subjected to double distillation in vacuum before use.

Methyl methacrylate (MMA, $CH_2 = C(CH_3) - COOCH_3$) was purified by distillation at normal pressure. Potassium persulfate (PP, $K_2S_2O_8$) was purified from impurities by recrystallization from water.

The synthesis of graft copolymers was carried out in a three-necked flask equipped with a stirrer, thermometer and reflux condenser. The flask was charged with 20 ml of dimethylformamide (DMF), 30 ml of benzene and 5 g of synthetic rubber. The rubber first swells, then dissolves completely with vigorous stirring. A certain weighed amount of monomer and initiator (PC), which also dissolve in the reaction mixture, were added to the rubber solution. The flask was immersed in a thermostat with a temperature of 60 ° C. The synthesis of copolymers was carried out with constant stirring of the reaction mixture in solution for 6 hours. Then the reaction mixture was removed from the thermostat, cooled to room temperature, and poured into a glass with ethanol. Unreacted monomer dissolves in ethanol, copolymer and homopolymer precipitate. The non-grafted polymers were separated from the graft copolymer by multiple extraction. For a copolymer of rubber with polyacrylic acid (PAA), distilled water serves as an extracting agent, and for a copolymer with polymethyl methacrylate (PMMA), it is DMF. The extraction was continued until the termination of the decrease in the weight of the graft copolymer. The copolymer purified from unreacted monomer and homopolymer was dried at 60 ° C to constant weight.

The degree of grafting is defined as the ratio of the weight of the grafted chains (acrylic polymer) to the weight of the original synthetic rubber.

Grafting efficiency is defined as the ratio of the weight of the grafted chains to the weight of the acrylic monomer that has entered the polymerization.

IR spectra of polymer samples were recorded on an IRTracer-100 infrared Fourier spectrometer (SHIMADZU CORP., Japan, 2017). Spectrometer complete with a MIRacle-10 ATR attachment with a diamond / ZnSe prism (spectral range on the wavenumber scale - 4000 ÷ 400 cm⁻¹;

resolution - 4 cm⁻¹, sensitivity, signal-to-noise ratio - 60,000: 1; scanning speed - 20 spectra per second).

Thermoanalytical studies of polymer samples were carried out on a Netzsch Simultaneous Analyzer STA 409 PG device (Germany), with a K-type thermocouple (Low RG Silver) and aluminum crucibles. All measurements were carried out in an inert nitrogen atmosphere with a nitrogen flow rate of 50 ml / min. The temperature range of measurements was 22-390 ° C, the heating rate was 5 K / min. The amount of sample per measurement is 5-10 mg. The measuring system was calibrated with a standard set of substances *KNO₃, In, Bi, Sn, Zn*.

RESULTS AND DISCUSSION

To carry out the synthesis of the copolymer in a homogeneous solution, individual solvents and their mixtures were selected, which simultaneously dissolve the rubber, initiator (PC), and monomers. This solvent turned out to be a mixture of benzene and DMF at a volume ratio of 3: 2. Table 1 shows the results of the graft copolymerization of rubbers with AA. The initial mass of all rubbers is 5 g, AA - 5 g, PP - 0.05 g, synthesis temperature 60 ° C, synthesis time 6 hours.

TABLE 1. Parameters of AA grafting to synthetic rubbers macromolecules

Rubber	Weight after sedimentation and drying, g	Weight after extraction and drying, g	Degree of grafting,%	Grafting efficiency,%
PCH	8.91	5.79	15.8	20.2
PI	8.77	5.46	9.2	12.2
SRN-40	8.65	4.60	-	-
SRS-30	8.87	5.74	14.8	19.1

Table 2 shows the results of the graft copolymerization of rubbers with MMA. The initial mass of all rubbers is 5 g, MMA - 2 g, PC - 0.02 g, synthesis temperature 60 ° C, synthesis time 6 hours.

TABLE 2. Parameters of MMA grafting to synthetic rubbers macromolecules

Rubber	Weight after sedimentation and drying, g	Weight after extraction and drying, g	Degree of grafting,%	Grafting efficiency,%
PCH	6.76	6.18	23.6	67.0
PI	6.64	5.98	19.6	59.8
SRN-40	6.45	4.03	-	-
SRS-30	6.57	5.77	15.4	49.0

As can be seen from the data in Tables 1 and 2, the possibility and parameters of grafting depend on the nature of the rubber and, to a lesser extent, on the nature of the monomer. It should be noted that SRN-40 does not undergo graft copolymerization with either AA or MMA. Earlier it was shown that SKN-26 and SRN-40 enter into a graft copolymerization reaction with butyl methacrylate, but with another initiator, dinitrile ester of azoisobutyric acid (AIBN) [16]. The active centers of graft copolymerization are formed as a result of the interaction of the nitrile

groups of SRN with AIBN. Apparently, PC does not interact with the nitrile groups of the SRN. On the other hand, it cannot be said that active centers of initiation are not formed in the SRN – AA - PP or SRN - MMA - PP system. Monomers are converted to polymer, but separately, without the formation of a graft copolymer.

Other rubbers, especially PCH, react very well with PP to form initiating radicals on their macromolecules. In this case, the active sites to be reduced serve for the grafting of the acrylic monomer. The effectiveness of MMA grafting is especially high. In the literature, there is also a work that notes the high efficiency of grafting MMA to PCH in the presence of hydrogen peroxide as an initiator [14]. Due to what atoms or groups of atoms, bonds of rubber does it interact with PP? This is one of the main issues in these processes. Earlier, according to the results of IR spectroscopic studies, it was established that in the case of copolymerization of rubbers in the presence of AIBN, double bonds of rubber do not enter into the reaction. The formation of active centers of polymerization occurs due to the interaction of AIBN with hydrogen at an unsaturated carbon atom [17].

To determine the scheme of interaction of the components, IR-Fourier spectroscopic studies of AA, COD and their copolymer were carried out (Fig. 1-3).

The IR Fourier spectrum of AA shows absorption bands of stretching vibrations of the *OH* group at 3067 cm^{-1} , stretching vibrations of bonds of *C = O* groups at 1697 cm^{-1} , stretching vibrations of bonds of *C = C* groups at 1634 cm^{-1} , stretching vibrations of bonds = *CH*₂ and = *CH* – groups at 2986-2886 cm^{-1} . The absorption band of deformation vibrations of –*CH = CH*₂ bonds is observed in the region of 1429-1294-1236 cm^{-1} , the absorption band of stretching vibrations of bonds of the ester group *CO – O – C* is observed in the region of 1067-1043-976 cm^{-1} (Fig. 1).

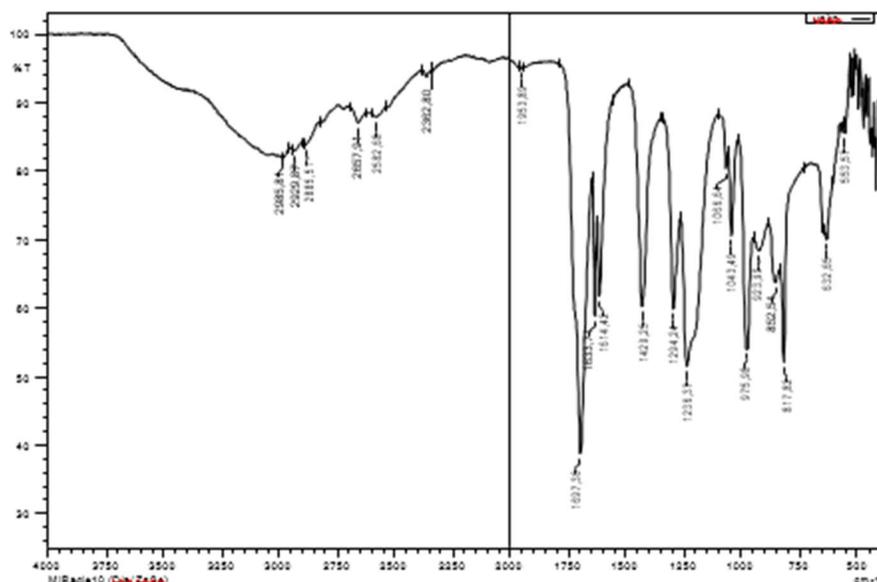


FIGURE 1. IR Fourier spectrum of AA

In the FTIR spectrum of PCH, an absorption band of stretching vibrations of bonds of = *CH*₂ and = *CH* – groups at 2920-2853 cm^{-1} , and deformation vibrations of the same bonds at 1445 cm^{-1} , stretching vibrations of bonds of *C = C* groups at 1693-1659 cm^{-1} . The absorption band in the

range of 1013-881-824-777 cm^{-1} , apparently, refers to stretching vibrations of polysubstituted $C - Cl$ bonds (Fig. 2).

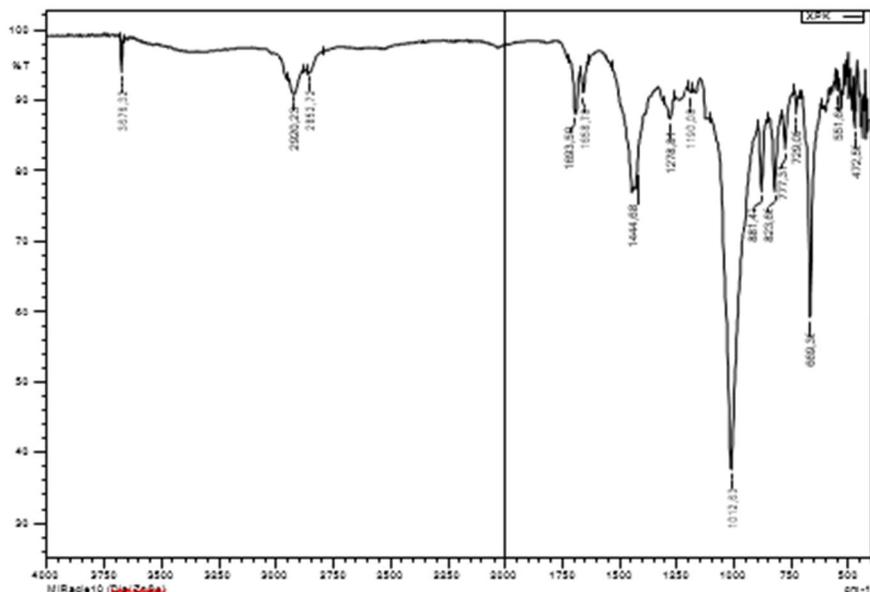


FIGURE 2. FT-IR spectrum of PCH

Now let us consider the FTIR spectrum of the PCH-AA graft copolymer (Fig. 3). The copolymer spectrum contains characteristic absorption bands of both PCH and PAA bonds, some of which are slightly shifted. The absorption band of stretching vibrations of $C = C$ bonds of PCH at 1655 cm^{-1} is retained, then the absorption band of $C = C$ bonds of AA at 1634 cm^{-1} disappears in the copolymer. In the copolymer, the number of absorption bands in the region of 2900-2800 cm^{-1} , referred to the stretching vibrations of bonds of $-CH = CH_2$ groups, also decreases.

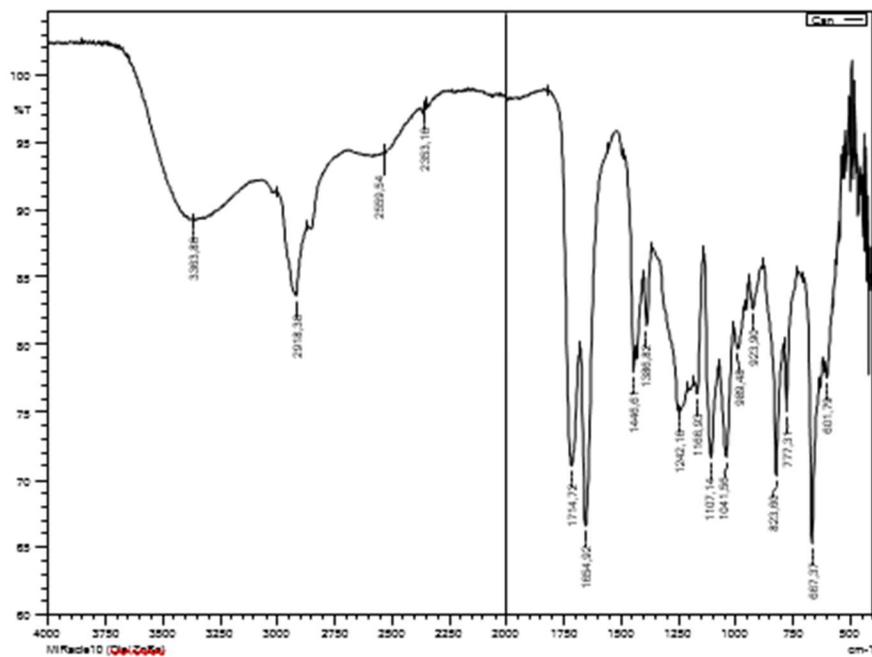


FIGURE 3. FT-IR spectrum of the PCH-AA copolymer

Judging by the results of FTIR spectroscopic studies, the active centers of graft copolymerization of a radical nature are formed after the detachment of a proton from the =CH–group of the PCH. The reaction of interaction of PCH with PP can be represented by the following scheme:



Free radicals are formed both in the PCH macromolecule and in the free state. The initiation and growth of the

graft copolymerization chain is carried out by radicals in the PCH macromolecule. Free radicals $KSO_3\cdot$ initiate PAA homopolymerization. Therefore, along with the graft copolymer, a certain amount of homopolymer is formed in the system.

For the use of a graft copolymer COD as a structural TPE and an adhesive material, their thermal properties are of great importance. Thermogravimetric analysis of COD and COD-AK copolymer showed that they remain thermally stable when heated to 200 °C (Fig. 4). At this temperature, the weight loss of the COD is only 16%, and that of its copolymer is 8%. Above a temperature of 230 °C, an intense weight loss of the samples begins, by 300 °C a significant weight loss was found - 40% of the COD and 25% of the copolymer, respectively. The processes occurring with polymer samples are characterized by DSC curves (Fig. 5).

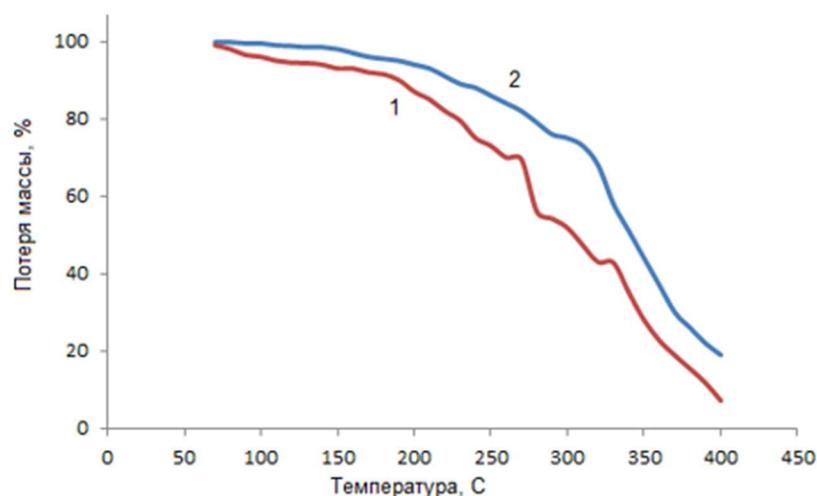


FIGURE 4. Curves of thermogravimetric PCH (1) and copolymer PCH-AA (2)

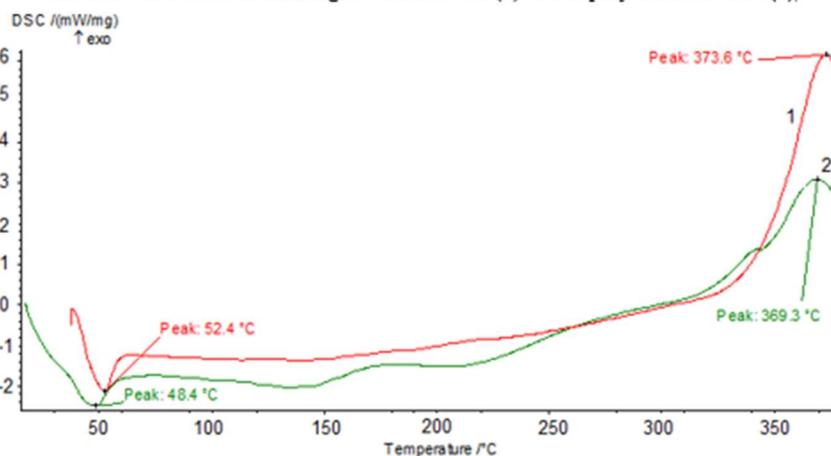


FIGURE 5. DSC curves of the PCH rubber (1) and the PCH-AA copolymer (2).

The first endothermic peak in the figure - 52.4 ° C for PCH and 48.4 ° C for PCH-AA copolymer corresponds to the melting process of the samples. This means that with moderate heating, you can get a hot melt glue for gluing shoe parts. Moreover, both PCH and its copolymer with AA have a high decomposition temperature, which correspond to exothermic peaks at 373.60C and 369.30C. The low melting point and high decomposition temperature make it possible to use the graft copolymers as a solution or melt adhesive.

CONCLUSIONS

A mixture of benzene and dimethylformamide in a volume ratio of 3: 2 is a suitable solvent for the synthesis of graft copolymers of synthetic rubber with acrylic monomers in the presence of potassium persulfate as an initiator. Grafting of acrylic acid and methyl methacrylate is carried out to chloroprene (PCH), isoprene (PI), butadiene- styrene (SRS-30) rubbers; acrylic monomer is not grafted onto butadiene-nitrile rubber (SRN-40). The grafting efficiency of methyl methacrylate is about 2-3 times higher than that of acrylic acid. The active centers of graft copolymerization are formed as a result of the elimination of the proton of the vinyl group of rubber during the interaction with potassium persulfate. The graft copolymer PCH-AA has a low melting point and high thermal stability, which makes it a potential adhesive for shoe parts.

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