

Synthesis and Application of Latex-Based Ethylene-Propylene Copolymer on Methacrylic Acid

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ABSTRACT

The latex synthesis in the presence of ethylene-propylene copolymer and methacrylic acid (MAA) was considered for this experiment. The kinetic regularities of the synthesis process were determined and the optimal quantities and ratios of the components were determined both experimentally and by mathematical modeling. It was determined that a modified latex with optimal values is obtained when the amount of methacrylic acid in the latex is 5 parts by weight. The absorbent composition was prepared latex-based based on synthesized EPC - + methacrylic acid. The prepared absorbent was impregnated with viscose (22B) and 222K kapron cord and a rubber-cord bond were determined.

KEY WORDS: ETHYLENE-PROPYLENE COPOLYMER (EPC), MODIFICATION, METHACRYLIC ACID (MAA), SYNTHESIS.

INTRODUCTION

Synthetic latexes are widely used in various industries. Latex is an important product used in the tire industry, in the production of rubber-technical products, in the medical industry, and in the construction industry (Shikhaliyev 1980; Shikhaliyev 2020). Latex is the main absorbent component in the production of carcass parts of tires in the tire industry, which provides a woven material-rubber adhesion bond (Bilalov 1973; Bilalov 2005; Bilalov 2008; Bilalov 2010). Recently, the production of latexes by synthetic methods is mainly obtained by the emulsion method (Ososhnik 2007; Nurmukhametova 2012; Amirov 2017; Shikhaliyev 2020).

New latexes are being purchased on an industrial scale and the equipment used for their synthesis is being updated. New emulsifiers and coagulation agents are used in technological processes. Synthetic latexes are widely used in various industries. Latex is an important product used in the tire industry, in the manufacture of rubber products, in the medical industry, and the n construction industry. Latex is the main adhesive in the tire industry, which provides a cord-rubber connection in the manufacture of the carcass part of the tire. Recently, the production of latexes by synthetic methods is mainly by emulsion. New latexes are currently being used on an industrial scale, and the equipment used to synthesize them has also been updated (Nabil et al. 2013;

Hayeemasaeetshal 2013). New emulsifiers, surfactants are used in technological processes (Koblov et al. 2012; Mikheeva et al. 2013; Mikheeva et al. 2014). However, none of these adhesives can fully ensure the rubber-cord connection. Taking all this into account, we have synthesized a latex based on EPC (Shikhaliyev 2020).

Recently, the ethylene-propylene copolymer has been used in the production of military tires. The adhesive that provides the cord-rubber connection of the EPC-based carcass part has not yet been synthesized. In the production of tires used in military aviation based on EPC, ensuring the cord-rubber connection of their carcass part, the synthesis of latex-based on EPC is the most pressing problem (Shikhaliyev 1980; Shikhaliyev 2020). The contact of non-woven goods (a cord, cloth, apron, etc.) with rubber is almost zero without adhesion. Therefore, it is necessary to use adhesives to ensure a rubber-woven bond (Bazenov 2010). Our literature review has shown that the production of synthetic latexes is the most pressing problem and material in demand on an industrial scale (Bilalov et al. 1973; Bilalov et al. 2004; Shikhaliyev 2020).

Korkut (2012) and Riyajan (2012) considered the sample to be the most popular butadiene-styrene latexes and therefore recommend the use of absorbent formulations with particularly active accelerators for vulcanization of latex products. The search for vulcanization systems will continue for a long time. n the tire industry, a latex-based absorbent is used to absorb cords and technical parts. For this purpose, an aqueous solution of various rubbers is used. However, the latex-based ethylene-propylene copolymer

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Received 30/10/2021 Accepted after revision 28/03/2022

Published: 30th March 2022 Pp- 60-64

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Available at: <https://bbrc.in/> DOI: <http://dx.doi.org/10.21786/bbrc/15.1.9>

has not been used so far. As it is known, some rubbers are mainly made of EPC. Taking all this into account, the object of research is the production of EPC + PMMA flat latex-based ethylene-propylene copolymer based on methacrylic acid (Shikhaliyev 2020).

MATERIAL AND METHODS

Ethylene propylene copolymer and methacrylic acid were used as raw materials for preparing an aqueous dispersion of EPC and modified EPS-PMMA latex. A residual pressure 4MPa was considered for this study. To obtain an aqueous dispersion of modified latex EPDM, a laboratory setup and a special experimental technique have been developed. Ethylene propylene copolymer and methacrylic acid were used as raw materials for preparing an aqueous dispersion of EPC and modified EPS-PMMA latex. residual pressure 4MPa (Shikhaliyev 1980; Shikhalizade et al. 2010; Shikhaliyev 2020). To obtain an aqueous dispersion of modified latex EPDM, a laboratory setup and a special experimental technique have been developed. The composition of the copolymer was determined by IR spectroscopy. The spectra were recorded on a UR-20 spectrometer in a special range from 400 to 3500 cm⁻¹. The crystallinity of the copolymers was determined by X-ray diffraction on a URS-50nm instrument. The intrinsic viscosity of copolymers was determined in decline at a temperature of 30 °C in Ebberson viscometers.

The adhesive is a key factor used in the formation of the rubber-cord system. Thus, after impregnation of the cord with an absorbent composition based on EPS, the fibers of

the woven product provide a high adhesion of the rubber-cord system, forming a strong adhesion bond with the rubber. Spills in the cord-rubber-adhesive system should be considered separately for each system. This is because spillage can occur between either cord-rubber or rubber-adhesive. In all cases, the strength of the cord-rubber-adhesive system has a biphasic property and Silva have high adhesion to both the textile product (Shikhaliyev 1980; Shikhalizade et al. 2010; Shikhaliyev 2020).

For the preparation of absorbent composition, the absorbent content should be 8.0% dry residue and pH 8.8-9.0. Technical carbon to a predetermined EPC latex to determine the dry residue of the absorbent composition. Phenol formaldehyde resin modified by Naibova (Naibova 2015) and. An absorbent drop was prepared by adding 10% NaOH. The liquid residue of the absorbing composition was calculated to the nearest 0.0012. The absorbent composition was placed in a drying cabinet at a temperature of 165-175 °C and dried until constant weight. The dry residue (p) is calculated as a percentage:

$$P_{\text{dry residue}} = \frac{m \cdot 100}{m_n}$$

where - m is the mass of dry residue, g; m_n – a mass of the absorbent composition. It was determined using a pH meter to determine the pH of the absorbent composition. The absorbent composition was prepared according to the recipe given in Table 1.

Table 1. Recipe for the optimal absorbent composition studied

Ingredient name	100 parts by weight parts by mass	Components	Dry residue of the component due to the absorbent composition
LateEPC+PMMA	100	240	63,2
Modified resorcinol			
formaldehyde resin	53,2	268	34,2
Technical carbon	37,2	509	13,1
10% of NaOH	25,9	-	“,6

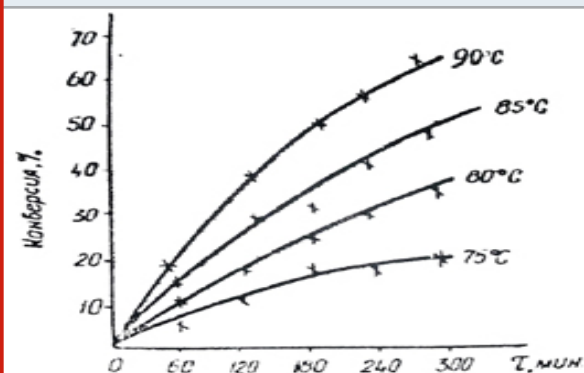
SF-282 resorcinol-formaldehyde resin is used in standard absorbent formulations. However, due to the economic inefficiency of this resin, Assoc. We used a synthesized and modified FFQ by Naibova (Naibova 2015). For this purpose, we used technical formaldehyde. In this case, we increased the dry residue of the absorbent to 5%. In this case, the absorbent composition easily penetrates between all the threads of the cord, soaks it thoroughly, and gives the threads a special softness, which led to a noticeable increase in the rubber-cord connection. The rubber-cord bond was determined by the standard H-method. After the cord was impregnated with an absorbent compound, it was rubberized

on a calendar with a thickness of 0.1 mm on both sides. A double-sided rubberized pattern was vulcanized by adding it to a specially prepared performance.

The vulcanization process was carried out at a temperature of 155°C -160°C for 20 minutes and a pressure of 3.5 Mpa was considered. The "whiskers" on the edges of the sample are cut with a knife. The sample should be 25 ± 1 mm. The sample was fixed in the tanks on the fighter and the machine was started. The breaking strength was determined by the moment on the scale when the cord pulls on the fighter.

The test was performed several times and the result was an average score. It was determined that the viscosity of the absorbent composition should be 5-8%. However, the concentration of EPC + PMMA copolymer in the used latex should not be less than 10%. Only in this case can the cord strands be thoroughly soaked in the absorbent composition (Naibova 2015).

Figure 1: Construction scheme of methacrylic acid to raise the temperature from 75°C to 90°C.



RESULTS AND DISCUSSION

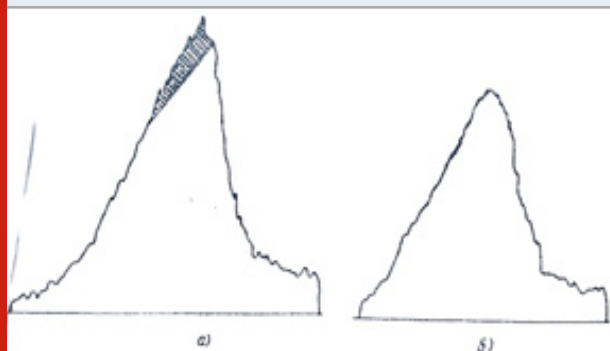
Investigation of the kinetics of graft copolymerization:

In the laboratory, a special device was installed to carry out the synthesis process and to obtain latex in this device, we first cut EPS into small pieces, put them in a three-necked flask, and stirred until completely dissolved in toluene. Once completely dissolved, we raised the temperature to 80°C and added methacrylic acid drop by drop to the mixture for 10 minutes. After transferring the methacrylic acid to the complete reaction flask, we performed a new synthesis by adding benzoyl peroxide. As a result of the synthesis, a new modified latex was obtained. Absorbent composition is prepared based on the obtained latex. EPS stable aqueous dispersion was modified with methacrylic acid in the presence of benzoyl peroxide and nitrogen at different temperatures (75°C to 90°C). General kinetic regularities of copolymerization reaction with EPC and methacrylic acid, copolymerization rate constants, reaction sequence and speed, monomer half-life and activation energy, monomer conversion, etc. was appointed.

Table 2. Monomer configuration, reaction temperature, and reaction time

Temperature, °C	Reaction time, hours	Monomer\ polymer	Monomer conversion, %	The viscosity of latex, seconds	Surface tension, din / sm
80	8	0,02	89	3,12	42,0
80	88	0,04	86	3,16	42,1
80	6,5	0,05	82	3,15	42,4
85	6,5	0,04	92	3,16	43,3
85	6,5	0,08	90	18	42,0
85	5	0,10	88	3,19	43,2
90	5	0,02	94	3,19	42,4
90	5	0,02	97,5	3,16	41,0
90	5	0,05	99,4	3,14	41,8

Figure 2. X-ray of the copolymer containing EPS (a) and EPS + PMMA (b) The proportions of components for latex production are given in Table 3



The rate of solidification of the monomer at different temperatures was determined from the dry residue sample of the reaction mixture. The results showed that the duration of the construction reaction of methacrylic acid depends on the temperature. EPC methacrylic acid builds very slowly at 70 ° C. Raising the temperature from 75 ° C to 90 ° C increased the reaction rate.

Use of modified EPC latex to increase the adhesion of rubber-cord bond:

The results of IR spectroscopy confirm the presence of -COOH groups in the copolymer chain. At 675, 1100, 1300, 1750, and 1800 cm⁻¹, peaks characteristic of carboxyl-containing polymers appear in the IR spectrum. These streaks were observed after 10 hours. X-ray studies showed that the EPS crystallization rate used in the study

was about 8%, but this was not the case with the original polymer. MAA helps to destroy the crystal grades present in vaccinated samples and causes a sharp increase in the

rate of conversion of methacrylic acid during the process (Figure 1).

Table 3. Ratios of components

System In ph.	Amount of sulfonyl,%	Amount of azeotropes,%	Surface tension Din/sm	Viscosity, Seconds
11	4	24	58	2,18
11	6	18	49	2,04
11	8	10	43	1,09
11	10	8	42	1,04
8	10	9,0	43	1,04
9,0	10	8,5	42	1,04
10	10	8	42	1,04
12	10	8	42	1,04

Table 4. Physical and mechanical properties of films.

Polymer	at the break, MPa	Relative extension, %	Residual elongation, %	Note
Original EPC	8,0	225	83	After holding for 3 days at 20 ° C, the samples of the films were thermostatic at 130 ° C for 30 min.
EPC precipitated from an aqueous dispersion	9,0	200	74	
Graft copolymer EPC + PMAA (5 wt.%)	24,0	285	38	

The missing properties of EPC were obtained by copolymerizing it with MAA to obtain a modified latex, and the kinetic regularities of the copolymerization reaction were determined. It is shown that the optimal mode: temperature - 90 ° C, time - 5 hours. In this section, the monomer conversion reaches 99%. To clarify the effect of the composition of the modified latex EPC on the foaming and strength properties of films and rubbers based on it, the physical and mechanical properties of films and rubbers were determined (Shixaliyev 2020; Bazhenov et al. 2021; Alizade 2022). The data obtained are shown in Table 4. The grafted EPC is distinguished by its high strength and elasticity, which gives the right to judge the structural ability of -UNC. The study of the physicochemical properties of rubbers made it possible to assume that the -COOH groups introduced into the copolymer as a result of grafting are involved in the formation of the vulcanization structure. Modified EPDM containing 5 wt% acids has higher strength (18.0 MPa) compared to unmodified EPDM (15.4 MPa). The physical and mechanical properties of the films are shown in table 4 (Alizade 2022).

After vulcanization of the samples, the analysis of their physical and mechanical properties showed that EPC latex provides the strength of the cord-rubber bond in the range of 10.5 kg / 2.5 cm, which was applied to the elastic polymer, cover meets the requirements.

CONCLUSION

The findings of the present study shows that the aqueous dispersions of EPC latex were synthesized using various emulsifiers with high technological stability. The presence of the main factors affecting the stability and adhesive properties of the EPC aqueous dispersion has been established. It has been shown that the best stability for 6 months is achieved at a pH value of 12. EPC water emulsion was modified in the presence of MAA by graft copolymerization. Gross kinetic regularities of EPC with MAA in the emulsion were determined. It is shown that the optimal conditions are: temperature - 90 ° C, time - 5 hours. Under these conditions, the monomer conversion reaches 99%. The physicochemical and adhesive properties

of modified latexes containing from 2 to 20 wt% of grafted PMAA have been studied. It has been established that the high bond strength of the cord with rubber is achieved by using EPDM latex containing 5 wt. % grafted PMAK. It is shown that the physical and mechanical properties of films and rubber compounds based on a graft copolymer significantly exceed those of unmodified copolymers.

Conflict of Interests: Author declare no conflicts of interests to disclose.

Data Availability Statement: The database generated and /or analysed during the current study are not publicly available due to privacy, but are available from the corresponding author on reasonable request.

REFERENCES

- Ali, A.F. and Seyfi, S.K., (2017). Obtaining and application of rubber mixtures based on isoprene (sri-3) and functional group polymers. *Austrian Journal of Technical and Natural Sciences*, (3-4), pp.27-31.
- Bazhenov S.L., Berlin A.A. and Kul'kov (2010). *Kompozitsionnyye materialy [Polymer composite materials]*. Dolgoprudnyy: Intellect Publ., 8, p.84-87.
- Beresnev V.N., Krainik S.V., Mishunin, L. V. et al. (2021). Macroradicals In The Process Of Synthesis, Storage, And Processing Of Synthetic Latexes And Polymers *Journal of Applied Chemistry*. 2021, Vol. 93, p.393-405.
- Bilalov Y.M. and Shikhaliev K.S. (1973). Investigation of the regularities of the reaction of grafted copolymerization of ethylene-propylene rubber and methacrylic acid in an emulsion. *Scientific notes Azineftekhim*, pp.36-47.
- Bilalov Y.M., Aliev V.M. and Shikhaliev K.S. (2005). Synthesis study of latexes of grafted copolymers of EPDM *Scientific notes Azineftekhim*, 6, p.53-57.
- Bilalov Y.M., Belyaeva N.V., Shikhaliev K.S. et al. (2004). Methods for producing EPDM latex and methods for its modification to increase the bond strength of the rubber-fabric system. *Scientific journal. Scientific notes*, 3, p.84-86.
- Bilalov Y.M., Seidov N.M. and Shikhaliev K.S., (2008). Impregnation compositions based on SCEP Abstract of works of the Institute of Chemical Physics of the Academy of Sciences of the USSR, p.55-57.
- Hayemasae N., Ismail H. and Azura A.R. (2013). The blending of natural rubber recycled ethylene- propylene diene monomer: Cure behaviors and mechanical properties. *Polym.-Plast. Technol. Eng.* 52 pp.501-509.
- Kablov E.N. (2012). Strategic directions for the development of materials and technologies for their processing for the period up to 2030. *Aviation materials and technologies*, p.7-17.
- Korkut, T. and Umac Z.I. (2012). Neutron equivalent dose rate measurements of gypsum - waste tire rubber layered structures. *Int. J. Polym. Anal. Charact.* 18 (6) pp. 423 - 429.
- Magg G. (2014). Vulcanizing systems for special rubbers // *Polymer materials*, 14, p. 22-29.
- Mikheeva V.A., Tkacheva E.N., Sofronova O.B. et al. (2014). Influence of the hexachloroparaxylylene modifier on the structure of ethylene-propylene rubbers depending on the copolymerization temperature. *Industrial production and use of elastomers*, No. 1, S.13-19.
- Mikheeva V.A., Tkacheva E.N., Sofronova, et al. (2013). Influence of technological parameters of production on the structure and properties of new grades of ethylene-propylene rubbers // *Industrial production and use of elastomers*, No. 2, S. 3-7.
- Misin V.M., Nikulin S.S. and Dyumayev (2013). *Kazanskogo tekhnologicheskogo universiteta [Bulletin of Kazan Technological University]*. vol. 16, 1, pp. 97-109.
- Nabil, H., Ismail H., and Azura A. R. (2013). Comparison of thermo-oxidative aging and thermal analysis of carbon black-filled NR, virgin EPDM and NR / recycled EPDM blends. *Polym*, p. 631 - 639.
- Naibova T.M. (2015). Study of physicochemical parameters of passive inhibitors based on modified phenol-formaldehyde oligomers. *J. News of Azerbaijan Higher Technical School ADNA*, 2 (96), p. 31-34.
- Nurmukhametova A.N. (2012). Rubbers based on ethylene propylene rubber filled with mineral fillers based on shungite: Author's abstract. dis. Ph.D. Kazan, p. 19-24.
- Ososhnik I.A. and Shutilin Y.F. (2007). Manufacturing of rubber technical products. Voronezh: Voronezh State technologist. Acad, 972.
- Riyajan S.A. and Pheweaw N. (2012). Modification of skim rubber blended with poly (vinyl alcohol) to be applied as a biodegradable pressure-sensitive adhesive: effect of 2,6-di-butyl-4-methyl phenol and hydrocarbon resin. *Rubber Chemistry and Technology*, vol. 85, no. 4, p. 547-558.
- Shikhalizade P.D., Bilalov Y.M. and Shikhaliev K.S. (2010). On the possibility of using pyrolysis resin in the impregnating composition of tire cord. *Az.Khim. Thur.* No. P. 89-95.
- Shixaliyev K.S., Mamedov F.B. and Mamedov M.M. (1980). The influence of rubber covering on the bond strength of rubber mixtures, impregnated with adhesive based on modified Latex SKEP. *Journal International Polymer Cov. And Tecnology.* firm British Lyborn. England, p. 384-598.
- Shixhaliev K.S. (2020). Development and implementation in industry technology of obtaining composite materials and products based on polyvinyl chloride (Article) *Journal of Advanced Research in Dynamical and Control Systems*.12, Special Issue, pp 359–370.
- Silva S.D., Marques C.L. and Cardozo N.S.M. (2012). Composition and performance of Styrene-Isoprene-Styrene (SIS) and Styrene-Butadiene-Styrene (SBS) hot melt pressure sensitive adhesives. *The Journal of Adhesion/vol. 88/ pp. 187-199.*