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FIRE-PROOF UNSATURATED POLYESTERS ON THE BASIS OF ANHYDRIDE OF HEXABROMOBICYCLO-[2,2,1]-HEPT-5-ENE-2,3-DICARBOXYLIC ACID, GLYCERIN AND METHACRYLIC ACID

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Abstract: *The paper deals with production of α, ω-methacryl-(bis-glycerin)-endomethylenehexabromotetrahydrophthalate (BNP) on the basis of anhydride of 1,4,5,6,7,7-hexabromobicyclo-[2,2,1]-hept-5-ene-2,3-dicarboxylic acid, glycerin and methacrylic acid. Kinetics of polycondensation is researched at 170-190^{0}C. It is ascertained that the acid number equal 30-50 mg of KOH per 1 g of unsaturated polyesters is obtained at 170^{0}C within 6 hours, at 180^{0}C within 3.5 hours and at 190^{0}C within 3 hours.The hardening of BNP samples with the acid number from 20 up to 80 mg of KOH per 1g of resin showed that gelatinization rate of the styrene solutions in the presence of 3% methylethylketone hydroperoxide and of 8% cobalt naphthenate considerably increases with the reduction of the acid number. It is ascertained that gelatinization time at 20^{0}C decreases in 6-6.5 times with the transition from BNP with the acid number of 20 mg of KOH per 1g of resin to BNP with the acid number of 80 mg of KOH per 1g of resin.*

Keywords: *polyester, self-extinguishing material, polycondensation, glycerin, methacrylic acid, gelatinization.*

INTRODUCTION

Production of fire-proof and self-extinguishing materials is one of the most important problems of the present-day materials science. An ability of material to flare up and burn heavily matters most in such areas of industry as the building industry, motor-car industry, shipbuilding and aircraft building. Assemblies and mechanical parts made from such materials are thermostable and heat-resistant ones. These properties are crucial when these materials are used in aviation. The use of items made from self-extinguishing polyester resins, particularly in closed space (subway etc.), is also very important from fire safety standpoint.

It should be noted that a great quantity of self-extinguishing materials containing chlorine, bromine, antimony oxides, aluminum hydroxide, etc. is produced worldwide. In comparison with chlorine-containing materials, the bromine-containing materials are rather harmless from environmental point of view, that is, a lesser quantity of toxic substances is formed at burning of bromine-containing materials than at burning of chlorine-containing compounds.

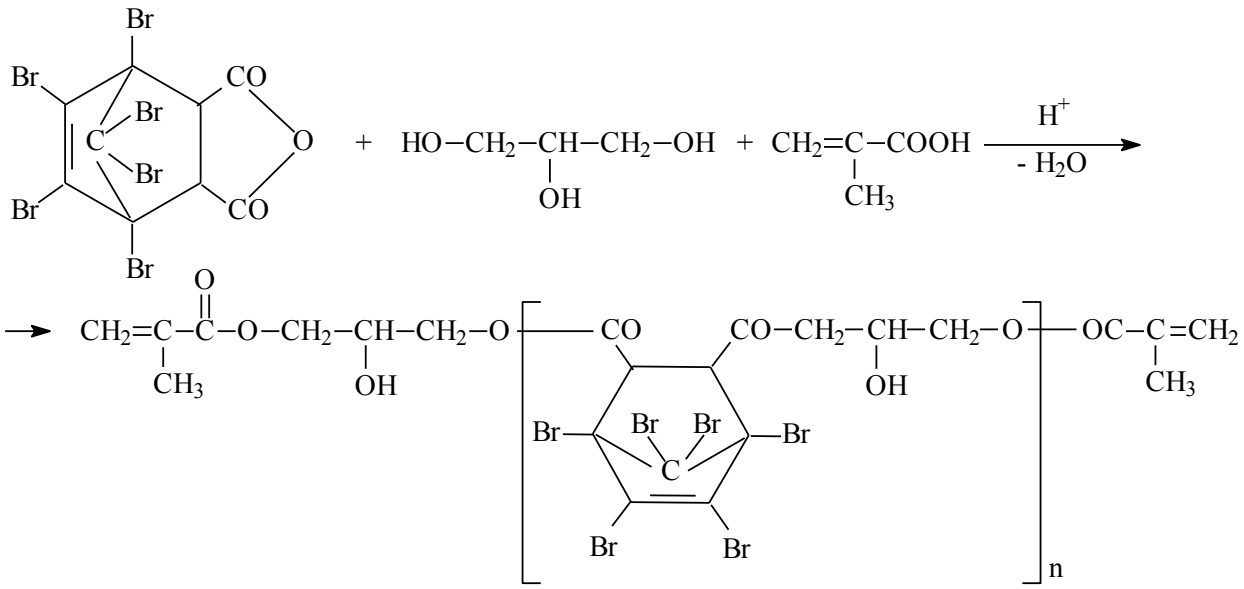
Fire-proof unsaturated polyester resins are mainly obtained by introducing halogen atoms into macrochain of polyester. Halogen is introduced into polyester resin either at the expense of halogen-containing initial substances or by way of the cross-linking monomer halogenation [1-4]. Bromine-containing resins are important representatives of halogen-containing unsaturated polyesters. Effectiveness of combustion deceleration of bromine-containing compounds is greater than effectiveness of chlorine-containing compounds of the same structure in 2.5-3 times [5].

Unsaturated polyesters simultaneously containing methacrylate end groups and polybromonorbornene links in main chain are of the great scientific and practical interest. At

selecting of anhydride of polybromonorbornene dicarboxylic acids, we supposed that the presence of large quantity of bromine atoms should contribute to the increase of fire-resistance of the obtained unsaturated polyester [5-7].

EXPERIMENTAL PART

Thus, the paper deals with obtaining of α, ω-methacryl-(bis-glycerin)-endomethylene-hexabromotetrahydrophthalate (BNP) on the basis of anhydride of 1,4,5,6,7,7-hexabromobicyclo-[2,2,1]-hept-5-ene-2,3-dicarboxylic acid, glycerin and methacrylic acid according to the below mentioned reaction:



The obtained BNP is a solid substance of dark-brown color and softening temperature of 65-70^{0}C. The yield of the above mentioned product makes up 90-94% of weight of initial constituents.

The synthesized BNP is well-soluble in monomers which are usually used for obtaining of polyester resins. At dissolving in styrene BNP forms low-viscous resins. Viscosity and special weight of BNP solutions in styrene were researched. Herewith a concentration of styrene made up 30, 40 and 50% mass.

Dependence of viscosity and special weight of solutions from the ratio of styrene and BNP is given in Table 1.

Table 1. Dependence of properties of unhardened solutions of α,ω-methacryl-(bis glycerin)-endomethylenehexabromotetrahydrophthalate with styrene from their concentrations

No.	Properties	Styrene concentration, %		
		30	40	50
1	Average molecular weight of BNP 2500±50	-	-	-
2	Density, kgm^{-3}	1540	1385	1290
3	Viscosity, centipoise	1580	270	85
4	Gelatinization time in the presence of 3% methylethylketone hydroperoxide and of 8% cobalt naphthenate used as accelerant, minute	190	260	315

Synthesis of α,ω-methacryl-(polyglycerin)-hexabromo-endo-methylenetetrahydrophthalate was carried out as follows: 31.1 g (0.05 mole) of anhydride of 1,4,5,6,7,7-hexabromobicyclo-[2,2,1]-hept-5-ene-2,3-dicarboxylic acid, 0.1 mole of glycerin, 0.05 mole of methacrylic acid, 0.2 g of hydroquinone and 0.2% of para-toluene sulfonic acid from weight of initial constituents were fed into four-neck flask equipped with mechanical stirrer, thermometer, backflow condenser and Dean and Stark trap placed into thermostat. Herewith para-toluene sulfonic acid is used as a catalyst.

The stock was heated during three hours at 190^0C in nitrogen atmosphere. Reaction course was controlled in line with the acid number of the product. Polycondensation reaction was discontinued when the acid number became equal to 25-40 mg KOH per gram. Upon completion of the synthesis, the flask content was neutralized by 2% water solution of soda; next it was washed by water up to neutral reaction and then dried up in the presence of sodium sulfate. The obtained light-brown resin was dried up in the vacuum desiccator at 50 ± 5^0C under residual pressure of 20-25 mmHg up to constant weight. Then it was dissolved in styrene.

RESULTS

On the basis of research results of polycondensation kinetics at 170-190^0C it was ascertained that the acid number equal to 30-50 mg of KOH per g of unsaturated polyesters is obtained at 170^0C within 6 hours, at 180^0C within 3.5 hours and at 190^0C within 3 hours. (Fiq.1)

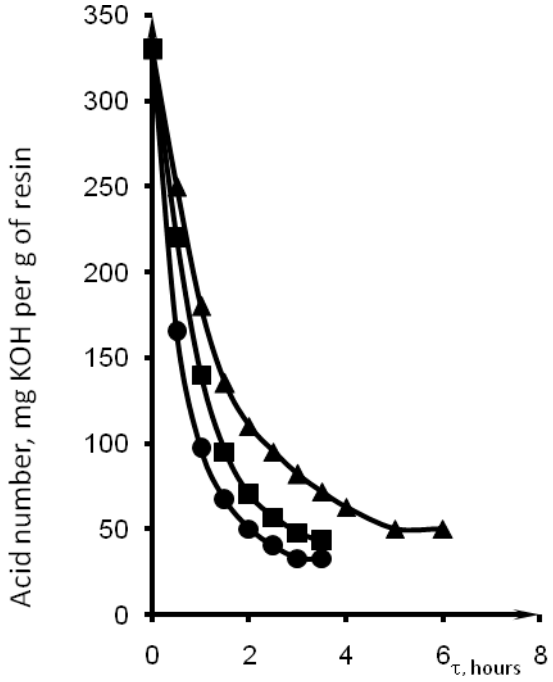


Fig.1. Kinetic curves of the synthesis of unsaturated polyesters on the basis of anhydride of 1,4,5,6,7,7-hexabromobicyclo-[2,2,1]-hept-5-ene-2,3-dicarboxylic acid and methacrylic acid with glycerin at molar ratio 0.5:1.1:0.5 : ▲- at 170^0C; ■- at 180^0C; ●- at 190^0C.

Time dependence of polycondensation degree is shown in Fig.2. Thus, it is clear from Fig.2 that obtained dependences have got a linear character.

Consequently, condensation of the mixture of 1,4,5,6,7,7-hexabromobicyclo-2,2,1]-hept-5-ene-2,3-dicarboxylic acid anhydride and methacrylic acid with glycerin occurs in keeping with mechanisms of reactions of the second order. Reaction rate constants (K) were determined with the help of these dependences. They are correspondingly

equal to $4.0 \cdot 10^{-2}$ (at 170^0C), $4.67 \cdot 10^{-2}$ (at 180^0) and $8.6 \cdot 10^{-2}$ g·mole^{-1}·minute^{-1}.

Mixtures prepared on the basis of styrene solutions of BNP were hardened both at room temperature and at 80-100^{0}C. Researches of hardening of BNP samples with the acid number from 20 up to 80 mg of KOH per 1 g of resin showed that gelatinization rate of styrene solutions in the presence of 3% methylethylketone hydroperoxide and of 8% cobalt naphthenate considerably increases with the decrease of the acid number.

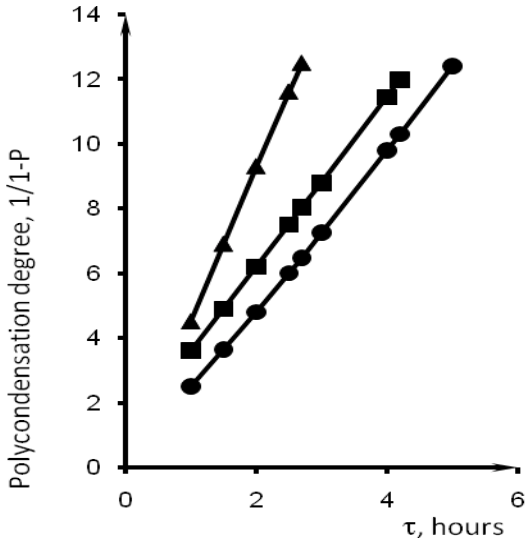


Fig.2. Time dependence of polycondensation degree of glycerin with anhydride of 1,4,5,6,7,7-hexabromobicyclo-[2,2,1]-hept-2-ene-5,6-dicarboxylic acid and methacrylic acid: ▲- at 190^{0}C; ■- at 180^{0}C; ●- at 170^{0}C.

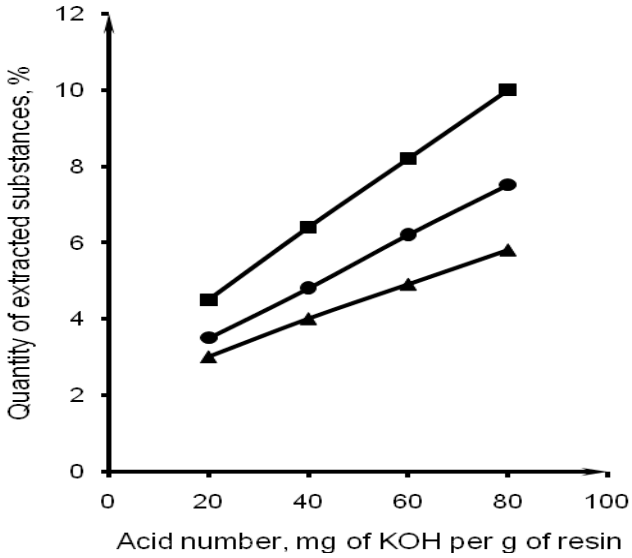


Fig. 3. Quantity of substance extracted by acetone within 8 hours from hardened BNP with varied acid numbers: ■- a hardening at 20^{0}C within 200 hours; ●- a hardening at 80^{0}C within 8 hours; ▲- a hardening at 100^{0}C within 5 hours.

Quantities of substances extracted by acetone hardened BNP with varied acid numbers in Soxhlet apparatus within 6-8 hours are shown in Fig.3. Hardening degree made up 96-98% in tested samples.

It is ascertained that gelatinization time at 20^0C is down in 6-6.5 times at transition from BNP with the acid number of 20 mg of KOH per 1g of resin to BNP with the acid number of 80 mg of KOH per 1g of resin. Probably, it is related to the fact that the BNP acidity influences the formation process of free radicals in the initiating system. Decreasing of gelatinization rate of BNP with high acid number can be explained by the deactivating effect of carboxylic fragments of BNP on the formation process of free radicals in the initiating systems.

Properties of the hardened styrene solutions with various concentrations of BNP are shown in Table 2.

Table 2. Physical-mechanical properties of hardened polybromine-containing unsaturated resins of BNP modified by anhydride of 1,4,5,6,7,7-hexabromobicyclo-[2,2,1]-hept-5-ene-2,3-dicarboxylic acids.

No:	Properties	Resin composition		
		I	II	III
1	Styrene concentration, %	30	40	50
2	Brinell hardness, kgf per mm^{-2}	20	10	18
3	Ultimate compression strength, kgf per sm^{-2}	1150	1000	880
4	Bending strength, kgf per sm^{-2}	350	320	300
5	Impact strength, kgf·sm·sm^{-2}	3.1	3.5	3.4
6	Shrinkage, %	5.9	7.9	8.8
7	Water absorption for 24 hours, %	0.028	0.039	0.045
8	Vicat softening temperature, ^{0}C	110	112	107
9	Time of self-maintained burning, sec	It is extinguished	It is extinguished	It is extinguished
10	Time of smouldering, sec	0	0	1.0
11	Weight loss at burning, %	3.2	3.4	3.7

It is ascertained that the increase of styrene concentration from 30% up to 50% considerably influences the viscosity of BNP but at the same time the physical-mechanical properties of the hardened resins depend little on concentration of styrene in initial mixture.

Fire resistance tests of samples in accordance with the fire-tube method showed that hardened resins of BNP are self-extinguishing materials.

Thus, synthesized polybromine-containing unsaturated polyester (BNP) can be used as self-extinguishing constructional material, potting compound, coverings and also as a component for binders used in the manufacture of laminated and pressed plastics with satisfactory physical-mechanical properties.

REFERENCES

1. Eva Kitsko-Valchik. Research into self-extinguishing unsaturated polyether. A brief review of industrial and new achievements. *Plast.massy – Poly Plastic.* 2002, no. 5, pp. 4. (In Russian).

2. Mustafayev A.M., Mustafayev C.G., Orudzhev K.D., Zarbaliyev M.M. Self-extinguishing polyether based on anhydride 1,2,3,4,11,11-hexabromtricyclo [6,2,1,$0^{5,10}$]-2-undecene-7,8-dicarboxylic acid. *SDU. Elmi xeberler - Scientific publications. Sumgayit State University.* 2006, vol. 6, no. 2, pp.5. (In Azerbaijan).

3. Shaov A.H., Alarhanova Z.Z. Latest achievements in polymer materials (review). Part 1. *Plast.massy – Poly Plastic.* 2005, no. 6, pp. 7-20. (In Russian).

4. Shaov A.H., Alarhanova Z.Z. Latest achievements in polymer materials (review).

Part 2. *Plast.massy – Poly Plastic.* 2005, no. 7, pp. 9-12. (In Russian).
5.Aseeva R.M., Zaikov G.E. *Gorenie polimernyh materialov* [Combustion of polymer materials]. Moscow: Nauka Publ., 1981, 280 p.
6.Herman V. Boenig. Unsaturated polyesters structure and properties. Elsevier Publishing Company. Amsterdam. London. New-York. 1964, p. 253.
7.Mustafaev A.M., Gusejnov I.A., Karaeva A.M. et al. Unsaturated polyether on the basis of anhydride of norbornene dicarbon acid, ethyleneglycol and metacrylic acid. *Processes of Petrochemistry and Oil Refining.* 2007, no.1(28), p. 68. (In Azerbaijan).

ОГНЕСТОЙКИЕ НЕНАСЫЩЕННЫЕ ПОЛИЭФИРЫ НА ОСНОВЕ АНГИДРИДА ГЕКСАБРОМБИЦИКЛО [2,2,1]-ГЕПТ-5-ЕН-2,3-ДИКАРБОНОВОЙ КИСЛОТЫ, ГЛИЦЕРИНА И МЕТАКРИЛОВОЙ КИСЛОТЫ

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Данная работа посвящена получению α, ω-метакрил-(бис-глицерин)-эндометиленгексабромттетрагидрофталата на основе ангидрида 1,4,5,6,7,7-гексабромбицикло-[2,2,1]-гепт-5-ен-2,3-дикарбоновой кислоты, глицерина и метакриловой кислоты. Изучена кинетика поликонденсации при 170-190^{0}C. Установлено, что кислотное число, равное 30-50 мг КОН на 1г ненасыщенного полиэфира, достигается при 170^{0}C в течение 6 часов, при 180^{0}C - в течение 3.5 часов, а при 190^{0}C - в течение 3 часов. Отверждение образцов α, ω-метакрил-(бис-глицерин)-эндометиленгексабром-тетрагидрофталата с кислотным числом от 20 до 80 мг КОН на г смолы показало, что скорость желатинизации растворов стирола в присутствии 3% гидропероксида метилэтилкетона и 8% нафтената кобальта значительно увеличивается при уменьшении кислотного числа. Обнаружено, что время желатинизации при 20^{0}C уменьшается в 6-6.5 раз при переходе от образца с кислотным числом 20 мг КОН на г смолы к образцу с кислотным числом 80 мг КОН на г смолы.

Ключевые слова: *полиэфир, самозатухающий материал, поликонденсация, глицерин, метакриловая кислота, желатинизация.*

HEKSABROMBİTSİKLO [2,2,1]-HEPT-5-EN-2,3-DİKARBON TURŞUSUNUN ANHİDRİDİ, QLİSERİN VƏ METAKRİL TURŞUSU ƏSASINDA ODADAVAMLI DOYMAMIŞ POLİEFİRLƏR

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Təqdim olunan iş 1,4,5,6,7,7-heksabrombitsiklo-[2,2,1]-hept-5-en-2,3-dikarbon turşusu, qliserin və metakril turşusu əsasında α, ω-metakril-(bis-qliserin)-endometilenheksabrom-tetrahidroftalatın (BNP) alınmasına həsr olunub. Polikondensləşmə kinetikası 170-190^{0}C temperaturlarda öyrənilibdir. Müəyyən olunub, ki 1 q doymamış poliefirdə 30-50 mq KOH bərabər turşuluq ədədi 170^{0}C-də 6 saat ərzində, 180^{0}C-də 3.5 saat ərzində və 190^{0}C-də 3 saat ərzində əldə edilir. 20-80 mq KOH/(q qatran) turşuluq ədədi olan BNP nümunələrin bərkiməsi göstərdi ki, turşuluq ədədinin azalması 3% metiletilketonun hidroperoksidi və 8% kobalt naftenatının iştirakı ilə stirol məhlullarının jelatinləşmə sürətinin əhəmiyyətli dərəcədə artmasına səbəb olur. Aşkar olunub ki, turşuluq ədədi 20 mg KOH/ (q qatran) olan BNP-dən turşuluq ədədi 80 mq KOH/(q qatran) olan BNP-ə keçdikdə jelatinləşmə vaxtı 6-6.5 dəfə azalır.

Açar sözlər: *poliefir, öz-özünə sönən material, polikondensləşmə, qliserin, metakril turşusu, jelatinləşmə.*

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