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STUDY OF THE PHYSICO-CHEMICAL PROPERTIES OF OLIGOMERS BASED ON EPICHLORHYDRIN

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Abstract: The purpose of this work is the synthesis and study of Thiokol oligomer (EAF-9) based on sodium polysulfide, epichlorohydrin, and ammonium phosphate, intended for use as the main component of Thiokol sealing substance. To achieve this goal, a thiokol oligomer based on sodium tetrasulfide, epichlorohydrin, and ammonium phosphate was studied and the optimal conditions for the synthesis of a thiokol oligomer were determined. The influence of the molar ratios of starting materials on the composition and physicochemical properties of the synthesized Thiokol oligomer has been studied. The temperature of the optimal polycondensation reaction was equal to 80°C, the reaction time was 1.5–2 h, and the yield of the target product reached 94%. The thiol oligomer with the best efficiency was obtained at a molar ratio of sodium tetrasulfide, epichlorohydrin, and ammonium phosphate of 1:1:1, respectively. Based on the results of IR spectroscopy and differential scanning calorimetry, a reaction for the formation of a thiokol oligomer was proposed.

Keywords: thiokol, polysulfide oligomer, polycondensation, IR spectroscopy, thermal analysis.

1. Introduction

In Japan, thiocol oligomers are undoubtedly of interest in the production of sealing and protective coatings. The use of hermetic materials in construction today reaches 50% of their total production. In recent years, hermetic materials based on thiocol oligomers have become widespread [1].

Polysulfide polymers are an important class of polymers used as sealants, adhesives, coatings, etc. in various forms. They are usually synthesized by reacting sodium polysulfides with dihalogen compounds to form liquid or solid polymers. Their most important advantages are excellent adhesion to various surfaces, ease of use of sealants even under load and pressure, resistance to fuels and solvents, very low gas and vapor permeability, as well as resistance to ozone and ultraviolet radiation and aggressive environments [2,3, 4.5].

In industry, the synthesis of liquid thiocols is carried out by polycondensation of aqueous solutions of sodium polysulfide with organic halides to obtain a high molecular weight rubber dispersion, followed by its cleavage at disulfide bonds and liquid thiocols with SH-groups at the end of the chain are obtained [6,7]. For the preparation of thiocol oligomers, organic di- and trihaloid derivatives and sodium polysulfides of various compositions are widely used as starting monomers [8]. Unlike carbochain rubbers, thiocol oligomers contain a significant amount of sulfur atoms in the main chain, and there are no unsaturated bonds in the macromolecules.

In recent years, new oligomeric thiocols with improved properties have been synthesized and put into production. For example, dithiol polyester and its derivatives open new opportunities for semi-

crystalline thiocol materials [9,10]. The use of oligomeric thiocols has the distinct advantage of low shrinkage and reduced stress during the depolymerization process [11] or lower glass transition temperatures and homogeneous materials [12] . Another work used thiocarbamate oligomers used in the preparation of photovoltaic or thermoset films with high glass transition temperatures to improve hardness and impact resistance [13].

2. Experimental part

2.1. Synthesis of EAF-9 thiocol oligomer based on epichlorohydrin. 31.5 g (0.40 mol) of sodium sulfide is placed in a 500 ml three-necked flask equipped with a metal stand, stirrer, reflux condenser, thermometer, and dropping funnel and dissolved in 200 ml of distilled water. Then 37.5 g (1.17 mol) of sulfur is added to the flask, the mixture is heated with stirring for 1 hour. The solution was then filtered and 0.22 g (0.0013 mol) of ionic liquid (tetraethylammonium chloride) was added to increase the reaction yield and stirred for 10 minutes.

After that, 27.8 g (0.30 mol) of epichlorohydrin is poured into the flask with stirring at 700C for 1 hour. Then 0.2 g (0.0013 mol) of ammonium phosphate is added and the reaction mixture is heated again at 80-85 0 for 1 hour. Then, the resulting mixture is cooled, and the resulting yellow viscous mass is separated from the aqueous phase, washed three times in boiling water, and left to dry. The mass of the resulting oligomer is 63.5 g (94% theoretical). Sulfur content is 50.8%.

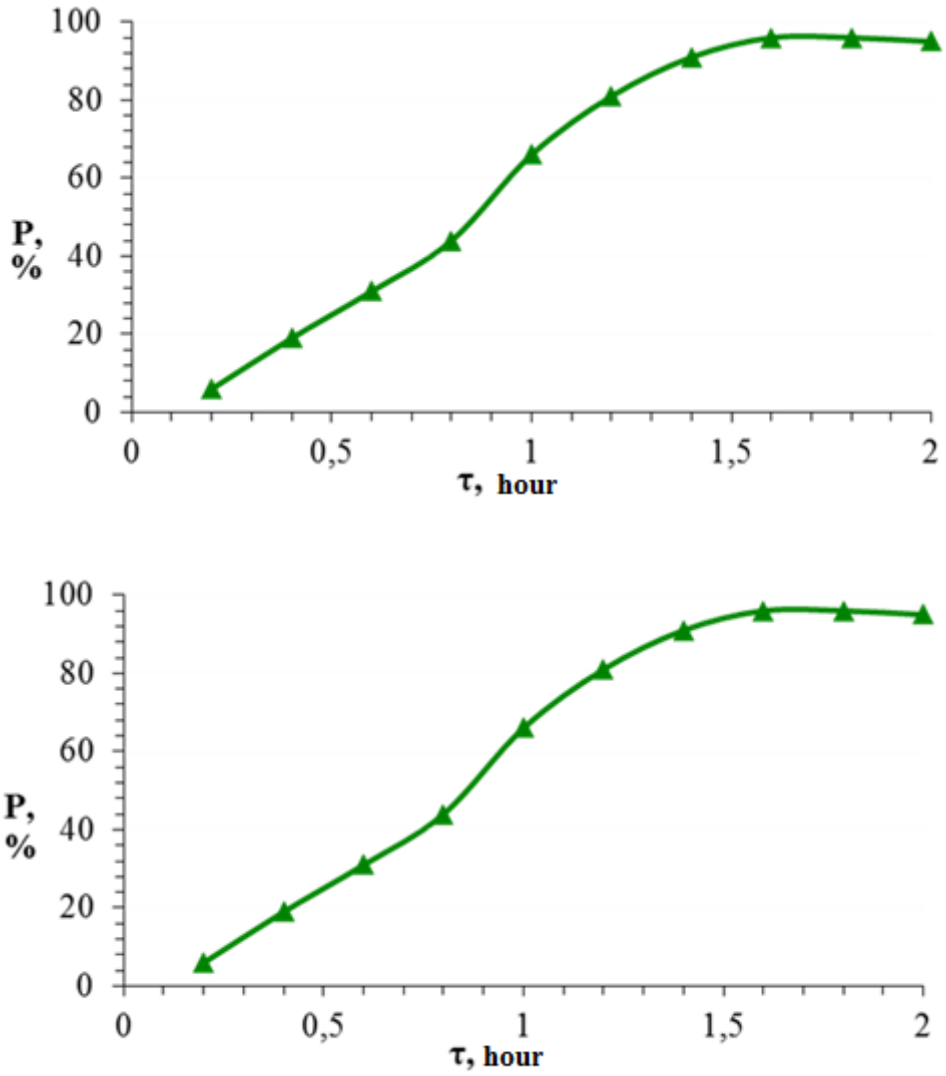

Figure 1. Time dependence of reaction productivity. 800-85°C

During the synthesis of thiocol oligomers, the dependence of the reaction yield on the reaction time at a temperature of 80°-85°C was studied. It was found that the reaction yield is at the maximum value in the time interval of 1.5 hours [14].

3. Results and Discussion

This study is devoted to the preparation of the main component of thiocol sealants based on oligomers containing sulfur, nitrogen, and phosphorus. Experiments have shown that in order to obtain a high yield of thiocol oligomer, it is necessary to obtain an equimolar ratio of monomers according to Table 1. The data are presented in Table 1.

Table 1. Dependence of the thiocol oligomer reaction product on the molar ratio of initial monomers (80¬0- 85°C, τ=1,5-2 s)

Ratio of monomers, mol	Reaction yield, %	Average molecular weight (cryoscopic)	External appearance	The amount of sulfur, %	
				Calculated	Found
1:1:1	94	3730	Viscous brown color	51,4	50,8
1:2:1	78	4610		37,7	37,2
1:2:2	67	4460		33,1	33,4

3.1. Infrared spectrum analysis. The IR spectrum of EAF-9 has absorption lines confirming the presence of -CH2- groups in the 2854-2918 cm-1 region and absorption lines confirming the presence of the -SONH2 group in the 1651 cm-1 region. Deformational vibrations of all active groups appear in the form of strong intensive lines between typical bending vibration zones –CH2 – CO– in the range of 1440 - 1400 cm-1.

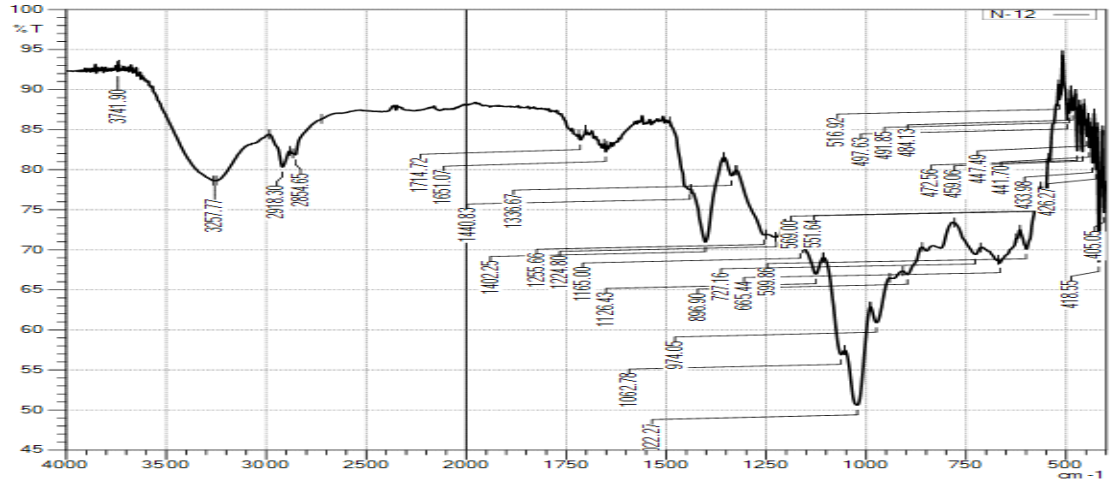

Figure 2. IR spectrum of thiocol oligomer EAF-9.

Absorption lines at 1022 and 1332 cm-1 confirm the presence of -NH2 groups. The presence of groups containing phosphorus P = O and P - O - C in the 1165 cm-1 region is confirmed by broad intense lines and sulfur-containing vibrations in the 900-400 cm-1 and 1060-1040 cm-1 vibration. In addition, in the IR-spectroscopy in the ranges of 450-550 cm-1 and 1460 cm-1, narrow lines of low intensity, containing bonds of the sulfur-containing compound.

3.2. Thermal stability analysis. Thermal stability of EAF-9 oligomer containing sulfur, nitrogen and phosphorus was studied by scanning calorimetric (DSC) method [15, 16]. The thermal decomposition data for the resulting thiocol oligomer is shown in Figure 3.

It can be seen that the mass of the EAF-9 sample does not change up to 200oC. In the temperature range of 20-200 °C, one small endothermic peak (171 °C) is observed in the DSC curve, which may correspond to sample dilution or structural change. At a temperature of 200°C, the sample begins to decompose in one step-(7% / min in the range of 200-270°C, 66% mass loss is completed, and the decomposition reaction is endothermic, the total energy of decomposition is -261 J/g.

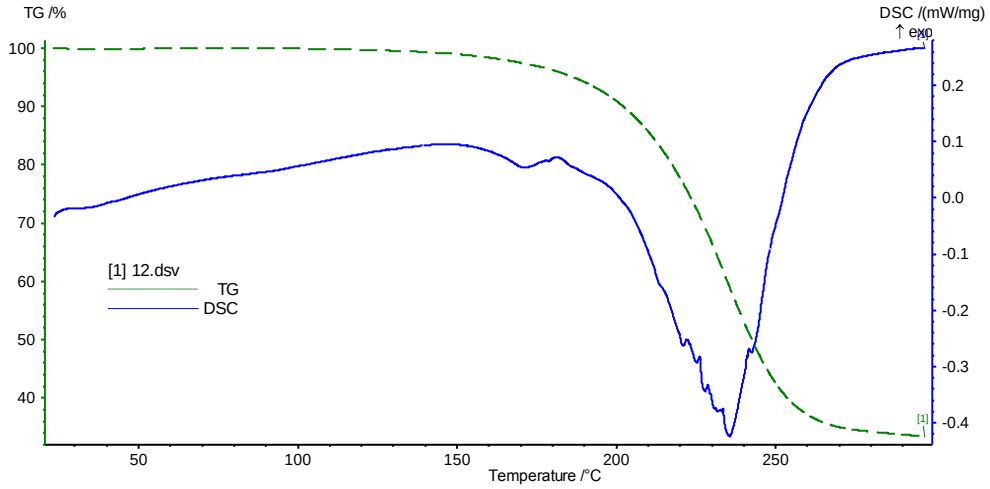

Figure 3. Differential scanning calorimetric results of EAF-9 thiocol oligomer.

Physico-chemical properties of obtained thiocol oligomer: density, melting point, solubility were studied. Data on the physicochemical characteristics of the synthesized thiocol oligomer EAF-9 are presented in Table 2.

Table 2. Physico-chemical properties of thiocol oligomer

Indicators	Thiocol oligomer
	EAF-9
Density, g/sm^3 ГОСТ 15139-69	1,42
T_{liq}, ^oC	135
$\eta_{хв}$, sm^3/g	0,069
Solvent	Dimethylsulfoxide, dimethylformamide
Appearance and color	Dark brown color

4. Conclusion

Nitrogen, phosphorus, sulfur-preserving thiocol oligomer EAF-9 was synthesized. In the process of synthesis, the influence of various factors on the synthesis of new thiocol oligomers, including temperature, the ratio of starting materials and the study of the physicochemical properties of oligomers, showed the possibility of obtaining thiocol oligomers with complex properties. Reactions for the preparation of thiocol oligomer based on sodium polysulfide, epichlorohydrin and ammonium phosphate were proposed using IR-spectroscopy and DSC data.

References

1. Normurodov B.A., Turaev H.Kh., Nabiev D.A., Suyunov Zh.R., Khayitalieva H.A. Study of synthesized nitrogen and phosphorus-containing thiokol oligomer // Universum: chemistry and biology: –-2019. No. 11(65). -pp.71-73.

2. Pirayesh A., Salami-Kalajahi M., Roghani-Mamaqani H., Najafi F. Polysulfide polymers: synthesis, blending, nanocomposites, and applications //Polymer Reviews. – 2019. – Т. 59. – №. 1. – С. 124-148. doi.org/10.1080/15583724.2018.1492616
3. Normurodov B.A., Tozhiev P.Zh., Jalilov A.T., Turaev H.Kh. KH. Synthesis and IR-spectroscopic study of sulfur-containing oligomers //Universum: chemistry and biology. – 2018.– no. 2 (44).
4. Zhang G.Z., Fan Z.K., Quan Y.W., Chen Q.M. The preparation and physical properties of polysulfide-based elastomers through one-pot thiolene click reaction // Express Polymer Letters, -2013. -Vol.7, -No.7 –pp.577–584.
5. Carioscia J. A., Lu H., Stanbury J. W., Bowman C. N.:Thiolene oligomers as dental restorative materials. Dental Materials, -2005. –V.21, -pp.1137–1143 doi: 10.1016/j.dental.2005.04.002
6. Clark T., Kwisnek L., Hoyle C. E., Nazarenko S.: Photopolymerization of thiol-ene systems based on oligomeric thiols. Journal of Polymer Science Part A: Polymer Chemistry, -2009. –V.47, -pp.14–24. doi: 10.1002/pola.23089
7. Li Q., Zhou H., Wicks D. A., Hoyle C. E.: Thiourethane-based thiol-ene high Tg networks: Preparation, thermal, mechanical, and physical properties. Journal of Polymer Science Part A: Polymer Chemistry, -2007. –V.45, -pp.5103–5111. doi: 10.1002/pola.22252
8. Usmani A. M.: Chemistry and technology of polysulfide sealants. Polymer-Plastics Technology and Engineering, -1982. –V.19, -pp.165–199. doi: 10.1080/03602558208067730
9. Normurodov B.A., Turaev Kh.Kh., Jalilov A.T., Nurkulov F.N., Rasulova S.M. Study of the physicochemical properties of the resulting polysulfide oligomer based on sodium tetrasulfide and ammonia phosphate // Universum: technical sciences, -2018. -No. 7(52), -p. 34-37.
10. Kadirov D.M., Nefediev E.S., Kadirov M.K. Differential scanning calorimetry of thiokol composite //Structure and dynamics of molecular systems. - 2016. - S. 55-55.
11. Ostanov U. Yu., Beknazarov Kh. S., Dzhalilov A. T. Study by DTA and TGA of the thermal stability of polyethylene stabilized by produced gossypols //Plastic masses. – 2010. – no. 8. - S. 27-29.
12. Normurodov B.A., Tozhiyev P.Zh., Turayev Kh.Kh., Dzhalilov A.T., Kiyomov Sh.N., Pardayeva N.Zh. Highly filled thiokol oligomers for polyolefin compositions //Chemistry and chemical technology: achievements and prospects. - 2018. - S. 224.1-224.4.
13. Kochergin Yu.S., Grigorenko M.A., Grigorenko T.I., Loiko D.P. Properties of epoxy-thiokol mixtures subjected to a preliminary reaction of thioetherification // Questions of chemistry and chemical technology. – 2011. – no. 6. - P. 83.
14. Normurodov B.A. Synthesis of modified thiokol oligomers based on local raw materials and their applications: Cand. on the soy. uch. step. Doctor of Philosophy (PhD) in Technical Sciences, - Termez State University, 2019. - P.141.