

MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Influence of the Nature of Curing Agents on Properties of Polyetherurethanethiol Composites

A. V. Kulikov, A. I. Kurkin, and Ya. D. Samuilov

Kazan State Technological University, Kazan, Tatarstan, Russia

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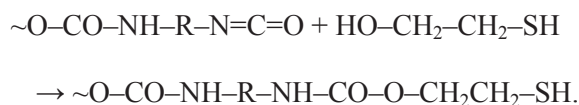
Abstract—The effect of the nature of curing agents on the properties of sealants based on polyetherurethanethiols was examined.

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HS-Terminal oligomers are widely applied for preparing mastics and sealants used in machine and ship building, aviation industry, and construction [1–4]. However, preparation of such oligomers, Thiokols, is extremely hazardous for the environment. Production of 1 t of Thiokol involves formation of 60 t of highly toxic aqueous–organic salt solutions requiring utilization. Therefore, of increased interest are procedures for preparing SH-containing oligomers that do not involve formation of so large amounts of wastewater. Principally, such routes exist. For example, the reaction of polyetherdiols or –triols with diisocyanates yields preisocyanates:



The reaction of preisocyanates with mercapto alcohols allows preparation of polyetherurethanethiols (PEUTs):



These compounds contain terminal mercapto groups, which can be oxidized to disulfide groups or converted to metal mercaptides. In so doing, the material will be cured with the formation of a 3D structure. This procedure is environmentally clean. The PEUT synthesis process is single-step. All these advantages attract attention. However, until now, only scarce patent information concerning this approach was available, and there are virtually no data on the properties of sealants based on PEUT [5, 6].

The goal of this study was to examine the proper-

ties of sealants prepared on the basis of PEUT, in particular, to reveal the dependences of the physicochemical properties of the vulcanizates on the nature of the curing agents, because it is well known that this factor strongly affects the properties of sealants [1–4, 7].

EXPERIMENTAL

The substances used in this study met the requirements indicated in Table 1.

Laprol used for preparing PEUT was preliminarily dried in a vacuum at a residual pressure of 2600 Pa and

Table 1. Grades of substances used^a

Name	GOST, TU no.
Toluylene diisocyanate T-80	TU 113-03-12-17-85
Laprol 3603-2-12	TU 2226-015-10488057-94
2-Mercaptoethanol	BASF product (Germany), 99.99% main substance
Finely dispersed chalk MTD-2	TU 5743-008-05 346 453-97
Diphenylguanidine (DPH)	TU 6-14-22-269-90
Manganese dioxide	TU 6-09-01-775-90
Sodium bichromate	GOST 2651-78
Zinc oxide	GOST 202-84
Chloroparaffin KhP-470B	TU 2493-379-05 763 441-2002

^a (TU) Technical specification and (GOST) State standard.

a temperature of 90–100°C for 4 h. Then the hydroxyl number of the dry polyether was determined in accordance with GOST (State Standard) 25 261–82. The preisocyanate was synthesized in a four-necked flask equipped with a power-driven stirrer, a thermometer, and a reflux condenser with a calcium chloride tube and a tube for introducing an inert gas (nitrogen or argon). First the dried polyether and toluylene diisocyanate (T-80 grade) were charged to the flask with stirring at 40–45°C. The reactant ratio should correspond to the HO : NCO ratio of 1 : 2. An inert atmosphere was provided by feeding nitrogen at excess pressure. The flask contents were heated to 80±5°C, and this temperature was kept for no less than 2 h with stirring of the reaction medium. The reaction completion was judged from the attainment of a constant content of isocyanate groups in the reaction medium. The amount of isocyanate groups in aliquot portions was determined in accordance with TU (Technical Specification) 38.103 137–78.

Mercaptoethanol can react with isocyanates via both hydroxy and mercapto groups. When performing this step, we took into account the results of a thermodynamic analysis of the reaction of phenyl isocyanate with methanol and methyl mercaptan [8], which showed that thiourethanes at 100°C virtually completely decompose into the starting reactants, whereas urethanes remain stable at this temperature. Our experiments showed that, when this reaction step is performed at temperatures below 100°C, the reaction mixture rapidly transforms into a rubber-like mass.

The preisocyanate from the previous step was mixed with mercaptoethanol at 60–70°C. The molar ratio of the isocyanate and hydroxy groups was kept equal to 1 : 1. Then the reaction mixture temperature was increased to 100±5°C, and the mixture was stirred in an inert atmosphere for no less than 6 h up to complete exhaustion of the isocyanate groups. The resulting PEUT is a viscous colorless liquid at room temperature. The content of SH groups in PEUT was determined in accordance with TU 38.103 636–87 to be 2.30 wt %. The IR spectrum of PEUT (film on KBr, Perkin-Elmer 16PC-FT-IR device) contains amide absorption bands (1720, amide I; 1540, amide II; 1280 cm⁻¹, amide III), a band of N–H stretching vibrations (3335 cm⁻¹), bands of antisymmetric and symmetric vibrations of C–H bonds in methyl and methylene groups (2960, 2940, 2970, 2860 cm⁻¹), bands of bending vibrations of C–H bonds in methylene and methyl groups (1470, 1350 cm⁻¹), a strong absorption

Table 2. Formulas of PEUT-based compounds

Component	Content, wt proportion		
Base paste			
PEUT		20	
Chalk		55	
Chloroparaffin		15	
Curing paste	1	2	3
Sodium bichromate		0.3	
Zinc oxide			5
Manganese dioxide	2		
Chloroparaffin	2	2.0	3
Chalk	3	4.7	0.5
Water	2	2	0.5
DPH	1	1	1

band of C–O–C antisymmetric stretching vibrations (1150 cm⁻¹), and a weak bond of H–S stretching vibrations (2560 cm⁻¹).

The vulcanizates of PEUT-based sealants were prepared by mixing the base paste with a curing paste containing curing agents. The compositions of the base and curing pastes are given in Table 2.

To reveal the influence of the curing agent content in the sealant compound on the physicomechanical properties of the vulcanizates, we varied the relative amounts of the base and curing pastes in the compound. The preparation of the vulcanizates consisted of the following steps.

(1) Preparation of the base paste by manually mixing the components in a porcelain mortar with a putty knife, according to the formula given in Table 2.

(2) Preparation of the curing paste by manually mixing the components in a porcelain mortar with a putty knife, according to the formula given in Table 2.

(3) Preparation of vulcanizates by manually mixing the base and curing pastes in a porcelain mortar with a putty knife and keeping the compound for 1 day at room temperature and for 3 h in an oven at 70°C. The samples obtained were kept for 1 day at room temperature, and their physicomechanical parameters were determined.

The physicomechanical parameters of the vulcanizates were determined in accordance with the procedures given in TU 5772-042-05 766 764 "Building Sealant 1m." The tensile strength σ , stresses at 100 and 300% elongation σ_{100} , σ_{300} , relative elongation ϵ , and elongation set ϵ_{set} were determined with a 2166R-55 tensile-testing machine, and the Shore hardness (scale A), with a TIR hardness meter, GOST 7761-55.

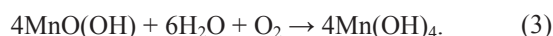
The working life of sealant compounds was determined at room temperature as the time within which the compound can be uniformly applied to any surface. The water absorption of sealant vulcanizates was determined by the procedure described in [9].

We studied the vulcanization of PEUT-based sealant compounds under the action of manganese dioxide, sodium bichromate, and zinc oxide. The first two agents are oxidative curing agents, and the third is a salt-forming agent.

The use of manganese dioxide for vulcanization of oligomers with HS fragments is based on the reaction [1-4, 7]

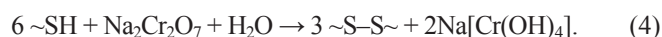


This reaction step is catalyzed by bases. For this purpose, diphenylguanidine is added to the curing paste. The resulting white manganese(II) hydroxide is then readily oxidized to brown manganese(III) oxyhydroxide and then to manganese(IV) hydroxide [10, 11]:

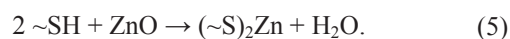


The occurrence of the last two steps requires the presence of water, which is introduced into the curing paste. Manganese(III) compounds are less powerful oxidants than Mn(IV) compounds [10]. Principally, oligomers containing HS groups could be vulcanized by catalytic amounts of manganese dioxide. However, in this case the process becomes too long, which is unacceptable. Therefore, in practice manganese dioxide is introduced into sealant compounds in increased amounts (>2 wt %). The vulcanization mainly occurs owing to the direct reaction of mercapto groups with manganese dioxide [reaction (1)]. We made experiments to determine what amounts of manganese dioxide should be introduced into PEUT-based compounds to attain the best physicomechanical parameters of the sealing agents under the common vulcanization conditions.

Bichromates are six-electron oxidants, and in the presence of water Cr(VI) compounds are readily reduced to Cr(III) compounds [11]:



The reaction of aromatic [12] and aliphatic [13] mercaptans with zinc oxide is a preparative route to zinc mercaptides:



In the latter two cases, it was also necessary to elucidate the influence of the amount of curing agents on the properties of the sealants obtained.

The physicomechanical properties of sealants cured in the presence of curing agents of different chemical nature are given in Table 3.

As seen from the data obtained, the physicomechanical parameters of the vulcanizates in all the cases increase with an increase in the content of the curing agents in the compounds. For complete exhaustion of mercapto groups in vulcanization of the sealant compound in accordance with Eq. (1), the required content of MnO_2 is 2.63%; that of sodium bichromate [Eq. (4)], 1.51%; and that of zinc oxide [Eq. (5)], 5.30%.

The use of zinc oxide leads to formation of vulcanizates with unsatisfactory properties. Introduction into the compound of superstoichiometric amounts of zinc oxide failed to give a positive result. We believe that this fact is due to a weak oxidizing action of ZnO on SH groups.

Sodium bichromate is a more effective curing agent than manganese dioxide. Good properties of the sealants are attained when the bichromate is taken in a substantially smaller amounts relative to the stoichiometry [Eq. (4)]. This fact suggests that chromium in higher valence states can be formed from Cr(III) under the action of atmospheric oxygen. Indeed, Cr(III) compounds are oxidized with atmospheric oxygen to Cr(IV) compounds, and these reactions are catalyzed by variable-valence heavy metal ions [14, 15]. Note that an increase in the sodium bichromate concentration in the compound leads to substantial changes in the physicomechanical parameters of the vulcanizates: the tensile strength and hardness increase and the elongation set decreases. Similar trends are observed in vulcanization with manganese dioxide.

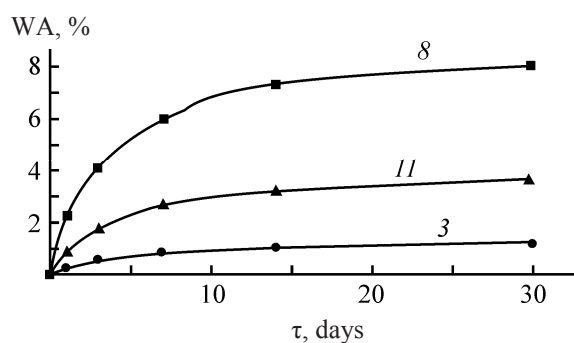
The consumer's properties of sealants are determined by their behavior toward water. Low water ab-

Table 3. Physicomechanical properties of vulcanized PEUT-based compounds

Sample no.	Vulcanizate concentration, g/100 g compound	σ	σ_{100}	σ_{300}	ϵ	ϵ_{set}	Shore hardness <i>A</i>	Working life, h
		MPa						
Manganese dioxide								
1	1.5	0.7	0.1	0.3	976	90	2	6
2	1.75	0.79	0.22	0.38	610	4	10	2.5
3	2	0.84	0.25	0.42	560	2	20	1
4	2.25	0.88	0.33	0.57	353	2	24	0.5
Sodium bichromate								
5	0.1	0.2	0.2	–	100	12	10	30
6	0.2	0.57	0.38	–	200	10	14	4
7	0.3	0.9	0.4	–	250	10	24	1
8	0.5	1.0	0.44	0.93	320	8	26	0.5
9	0.6	1.05	0.48	1.05	300	8	28	0.08
Zinc oxide								
10	2.5	0.16	0.16	–	100	10	2	40
11	5	0.25	0.18	–	250	10	12	10
12	7.5	0.4	0.2	–	280	8	12	5

sorption is the necessary condition of their practical use. Therefore, we evaluated the water absorption of the sealants. In so doing, we examined samples whose properties, from our viewpoint, are the best in the series. The results are shown in the figure.

The sealant obtained with manganese dioxide exhibits the lowest water absorption. It is two times lower than that of the common Thiokol sealants. Vulcanizates based on zinc oxide exhibit moderate water



Water absorption WA of vulcanizate samples as a function of the exposure time τ . Figures at curves are sample nos. in Table 3.

absorption. The highest water absorption is observed with the sealants vulcanized with sodium bichromate. Only in the latter case, both the curing agent and its transformation products are water-soluble. Presumably, the increased water absorption in this case is due to formation of solvation shells around species formed in transformations of sodium bichromate.

Thus, sealants with acceptable service properties can be prepared on the basis of PEUT. Their production is simple and waste-free. Therefore, the new oligomers show much promise for practical use.

CONCLUSIONS

(1) Vulcanization of polyetherurethanethiol-based sealant compounds can be effected by oxidative (manganese dioxide, sodium bichromate) and condensation (zinc oxide) types. The best results are obtained with oxidative curing agents.

(2) Sodium bichromate is a more effective cross-linking agent for polyetherurethanethiol-based compounds than manganese dioxide.

(3) The water absorption of polyetherurethanethiol-based sealants depends on the nature of the curing agent used. The use of agents capable of solvation with water increases the water absorption of the vulcanizates.

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