The Regularities of Polyurethane Foam Chemical Degradation with Thiodiglycol

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Received July 7, 2011

Abstract—A pattern was studied of the process of chemical degradation of elastic polyurethane foam under the action of thiodiglycol and its mixture with oxypropylated oligopolyol. It was established that in the systems simulating the process of polyurethane degradation the introduction of sulfur atoms in the hydrocarbon chain of glycol reduced its activity in the reaction with the urethane and reduced the thermodynamic stability of the urethanes formed. On the basis of recycled sulfur-containing oligoether-urethane a polyurethane sealant resistant against oil and petrol was obtained.

DOI: 10.1134/S1070363212090162

Recycling of plastic waste can solve the problem of environmental protection and shortage of raw material. A lot of research concerns the chemical processing of polyurethane waste [1–3]. One of the reasonable and efficient ways of processing the waste is the method of alcoholysis based on the thermochemical interaction of polyurethane with hydroxy compounds [4]. To date a number of such compounds is known, but they do not include polyols. The use of the latter would lead to the formation in the process of alcoholysis of the reactive oligomers containing in the chain, for example, atoms of sulfur, phosphorus, and silicon. Such oligomers in the future might be of interest for polymer composites with a complex of special properties.

This idea formed the basis of the present study of the pattern of chemical degradation of the elastic polyurethane foam waste under the action of thiodiglycol and its mixture with oxypropylated oligopolyol, and of the application of the alcoholysis products in the synthesis of polyurethanes. The presence of a sulfur atom and hydroxy groups in the structure of thiodiglycol, as well as relatively high thermal stability (bp 283°C) make this compound promising for use in the chemical degradation of elastic polyurethane foam waste.

The process of destruction was carried out by the action both of individual thiodiglycol, and mixtures thereof with Laprol 3603. The replacement of a part of thiodiglycol by Laprol 3603 was dictated by the need

to reduce the concentration of hydroxy groups in the degradation product. Use of the Laprol 3603 for these purposes was due to the identity of its structure with that of the oligoether block of the foam to be destructed, which simplifies the structure of the products. This fact contributes to a better reproducibility of the technology of recycled raw materials and the quality of the products based on it.

Quantum-Chemical Study of the Thermodynamic Regularities in the Reactions of Alcoholysis of the Model Compounds

To determine the effect of glycols on the equilibrium in the reaction of the foam alcoholysis we carried out quantum-chemical calculations of the thermodynamic parameters in the model transformations, the reactions of thiodiglycol, dithiodiglycol, diethylene glycol, and butanediol with phenyl-N-phenylurethane [Eqs. (1)–(4)]. The data obtained are compiled in Table 1.

$$\begin{split} &\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{NHC}(\text{O})\text{OC}_6\text{H}_5 \\ &\rightarrow \text{C}_6\text{H}_5\text{NHC}(\text{O})\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{OH}, \quad (1) \\ &\text{HOCH}_2\text{CH}_2\text{S}-\text{SCH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{NHC}(\text{O})\text{OC}_6\text{H}_5 \\ &\rightarrow \text{C}_6\text{H}_5\text{NHC}(\text{O})\text{OCH}_2\text{CH}_2\text{S}-\text{SCH}_2\text{CH}_2\text{OH} \\ &+ \text{C}_6\text{H}_5\text{OH}, \quad (2) \\ &\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{NHC}(\text{O})\text{OC}_6\text{H}_5 \\ &\rightarrow \text{C}_6\text{H}_5\text{NHC}(\text{O})\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{OH}, \quad (3) \\ &\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{NHC}(\text{O})\text{OC}_6\text{H}_5 \\ &\rightarrow \text{C}_6\text{H}_5\text{NHC}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{OH}, \quad (3) \end{split}$$

All the considered reactions are characterized by small transformation entropy. This is primarily due to the fact that during the interaction the number of translational and rotational degrees of freedom of movement does not change but only the numerical values alter. Enthalpies of the same reactions were significantly more sensitive to the changes in the structure of glycols. The reaction with butanediol is exothermic and is characterized by the highest values of the equilibrium constants (Table 1). In all other cases the transformation is endothermic. While in the reactions with butanediol an increase in the temperature leads to a decrease in the equilibrium constant, in the reactions with other glycols the opposite trend is observed: an increase of the equilibrium constants with increasing temperature. The lowest values of equilibrium constants occur in the transformation with dithiodiglycol. These data suggest that the use of dithiodiglycol for the process of polyurethane foam alcoholysis is problematic.

Kinetic Study of the Model Alcoholysis Reactions with Phenyl-N-phenylurethane

The thermodynamic parameters of reactions do not allow us to estimate the activity of the considered glycols in the process of alcoholysis of phenyl-*N*phenylurethane. Therefore, we carried out a study of the kinetics of the alcoholysis process in model reactions of phenyl-*N*-phenylurethane with thiodiglycol, dithiodiglycol and butanediol. These transformations may proceed in two directions [10]. The first path involves the thermal dissociation of phenyl-*N*-phenylurethane to form phenyl isocyanate and phenol, followed by reaction of phenyl isocyanate with glycol to form urethane. The second path is the direct replacement of the phenol group at the carbonyl carbon atom in the phenyl-*N*-phenylurethane [Eqs. (5)–(7)].

 $C_6H_5NHC(O)OC_6H_5 \rightleftharpoons C_6H_5NCO + C_6H_5OH, \qquad (5)$

$$C_6H_5NCO + ROH \rightarrow C_6H_5NHC(O)OR,$$
 (6)

$$C_{6}H_{5}NHC(O)OC_{6}H_{5} + ROH$$

$$\rightarrow C_{6}H_{5}NHC(O)OR + C_{6}H_{5}OH.$$
(7)

To estimate the temperature range of the monomolecular decay of phenyl-*N*-phenylurethane to phenylsocyanate and phenol, we performed the DSC-TGA study of the process (Fig. 1).

The DSC curve of phenyl-*N*-phenylurethane includes two endothermic peaks. The first one corresponds to the melting of phenyl-*N*-phenylurethane at 125°C, the second to its intense decomposition into

Table 1. Enthalpy (ΔH_r^0) , entropy (ΔS_r^0) , and the equilibrium constant (K_{eq}) of the reactions of phenyl-*N*-phenylurethane with thiodiglycol, dithiodiglycol, diethylene glycol, and butanediol in the gas phase at 298, 333 and 473K

Reaction	$\Delta H_{\rm r}^0,$ kJ mol ⁻¹	$\Delta S_{\rm r}^0, \\ \rm J~K^{-1}~mol^{-1}$	<i>K</i> _{p298}	<i>K</i> _{p373}	<i>K</i> _{p473}
1	7.11	24.66	1.11	1.99	3.21
2	10.58	21.11	0.17	0.41	0.86
3	5.77	24.20	1.84	2.94	4.27
4	-30.01	23.00	3.1×10^{6}	3.47×10 ⁵	3.43×10^{4}

phenol and phenyl isocyanate at 147°C. After 125°C begins immediately the mass loss by phenyl-*N*-phenylurethane due to the transition into the gas phase of the produced phenyl isocyanate and phenol. These data give grounds to assume that at temperatures below 125°C the reaction of glycols with phenyl-*N*-phenylurethane will mainly occur along the second pathway.

The kinetic studies were performed at 80°C. We found that the non-catalyzed conversion proceeds very slowly. Therefore, the reaction of the glycols with phenyl-*N*-phenylurethane was carried out in the presence of tin(II) octanoate as a catalyst. Table 2 lists the second order reaction rate constants of the studied reactions of glycols with phenyl-*N*-phenylurethane.

Under these conditions, dithiodiglycol reacts so slow that the rate constant of its reaction could not be described quantitatively. The highest rate constant was found in the reaction involving butanediol. It follows



Fig. 1. DSC (1) and TGA (2) curves of phenyl-*N*-phenyl-urethane.

1	
Glycol	$k_{\rm H} \times 10^4 1 {\rm mol}^{-1} {\rm s}^{-1}$
Dithiodiglycol	b
Thiodiglycol	9.64
Butane-1,4-diol	3.7

Table 2. The second order reaction rate constants of phenyl-*N*-phenylurethane with glycols in chlorobenzene in the presence of tin(II) octanoate at $80^{\circ}C^{a}$

^a Initial concentration: [c(phenyl-N-phenylurethane)]₀ = 0.1 M, [c(glycol)]₀ = 0.1 M, [c(tin(II) octanoate)]₀ = 0.01 M. ^b Reaction proceeds very slowly.

from the data in Tables 1 and 2 that the introduction of sulfur atoms into the glycol structure and the increase in their number lead to a decrease in the kinetic and thermodynamic feasibility of the reactions as compared with the butanediol.

Patterns of Chemical Degradation of Elastic Polyurethane Foam

Further we studied the alcoholysis of polyurethane foam at the action of thiodiglycol and its mixture with Laprol 3603. An important technological parameter that allows the control of the process of the chemical degradation and the recycling the alcoholysis products is the concentration of terminal functional groups. In the tested substance their role play the hydroxy and amino groups. Their formation is due to the alcoholysis of urethane and urea bonds in the polyurethane foam [Eqs. (8), (9)].

 $R^{1}NHC(O)OR^{2} + R^{3}OH \rightarrow R^{1}NHC(O)OR^{3} + R^{2}OH,$ (8)



Fig. 2. Dependence of the total concentration of OH and NH₂ groups $[c(OH+NH_2)]$ in the alcoholysis products on the degradation time (t_D) at 180°C: (1) polyurethane foam + thiodiglycol, (2) polyurethane foam + thiodiglycol + Laprol 3603.

$$R^{1}NHC(O)NHR^{1} + R^{2}OH$$

$$\rightarrow R^{1}NHC(O)OR^{2} + R^{1}NH_{2}.$$
(9)

Due to the complexity of the separation of amino and hydroxy groups, the monitoring of the alcoholysis process extent was carried out by the determination of their total concentration $c(OH+NH_2)$ in the system. The determination of $c(OH+NH_2)$ in the initial period of decomposition showed a wide variation of this value. Given that the concentration of OH and NH₂ groups in the system should remain unchanged because the decomposition proceeds by the reactions of the exchange type, the changes in the content of these groups in the early hours of alcoholysis are of tentative character. Obviously, this is due to the lack of homogeneity of the system when analyzed samples contain along with the products of alcoholysis the particles of undestructed polyurethane foam. Therefore in the figures we used dotted lines for this time interval.

At higher conversions, the $c(OH+NH_2)$ value stabilized in time, and for the system (polyurethane foam + thiodiglycol) it was 20.2 wt. %, and for the system (polyurethane foam + thiodiglycol + Laprol 3603), 12.2% wt. (Fig. 2). The reduction of the plateau level in the second case is due to the replacement of thiodiglycol by Laprol 3603, having a low concentration of hydroxy groups. This increases the duration of the establishment of the equilibrium in the system. A further increase in the destruction time leads to a decrease in the content of OH and NH₂ groups, connected obviously with the beginning of the process of secondary structization. Raising the temperature has almost no effect on the $c(OH+NH_2)$ equilibrium value, but can significantly reduce the time needed to achieve it (Fig. 3).

Another sensitive indicator of the impact of degradation conditions on the state of the system is the dynamic viscosity. This characteristic made it possible for us to cover the entire time range of the studied process, including the initial period when the products of the alcoholysis are still heterogeneous and contain gel-like inclusions of polyurethane foam.

Investigation of dynamic viscosity at the alcoholysis (Fig. 4) showed its monotonic decrease in the initial steps of the process due to the deepening of the processes of destruction. Over time, the viscosity stabilized. Further heating, coinciding with the fall in $c(OH+NH_2)$, led to an increase in viscosity, connected obviously with the negative impact of the process of



Fig. 3. Dependence of the total concentration of OH and NH₂ groups [c(OH+NH₂)] in the products of alcoholysis of (polyurethane foam + thiodiglycol + Laprol 3603) vs. the time of degradation (t_D) at different temperatures: (1) 180°C, (2) 200°C.

polycondensation of the formed products of alcoholysis.

IR spectroscopic study of the products obtained showed the presence of the absorption bands characteristic of an ether bond (1074 cm⁻¹), C–S bond (800–600 cm⁻¹), vibrations of the C–C bond of aromatic fragment (1636–1600 cm⁻¹), and urethane bonds (1540, 1718 cm⁻¹), as well as hydroxy and amino groups (region of 3360–3340 cm⁻¹). The presence of these groups in the spectrum allow us the characterization of the recycled raw material as a mixture of compounds with terminal hydroxy and amino groups containing in the backbone sulfide, urethane, and ether bonds.

Properties of the Polyurethane Sealants on the Basis of a Sulfur-Containing Recycled Oligoether-Urethane

On the basis of a sulfur-containing recycled oligoether-urethane a protecting-sealant composition was developed with the properties listed in Table 3.

The developed sealant, due to the presence in its structure of the sulfur atoms and the additional amount of urethane fragments through the application in the synthesis of recycled oligoether-urethane is superior to the commercially available polyurethane analogs (UG-2, and Forsage) in oil and fuel resistance. In comparison with thiocol compositions (U30M), the developed composition surpasses them in strength properties and water resistance, but exhibits less resistance to hydrocarbon solvents.



Fig. 4. Dependence of dynamic viscosity ($\eta_{50^{\circ}C}$) of the products of alcoholysis of (polyurethane foam + thiodiglycol + Laprol 3603) vs. the time of degradation (t_D) at different temperatures: (1) 180°C, (2) 200°C.

EXPERIMENTAL

The quantum-chemical calculations of the thermodynamic parameters of the model reactions were carried out by nonempirical hybrid method B3LYP in the extended basis STO-6-31G(d) with full geometry optimization of compounds using the software package Gaussian-03 [5].

Synthesis of phenyl-*N*-phenylurethane was performed in accordance with the method of [6].

DSC-TGA studies of phenyl-*N*-phenylurethane were carried out with a Simultaneous DSC-TGA thermoanalyzer Q Series TM. The heating rate was 2 deg min⁻¹ in the temperature range 25–300°C.

Kinetic studies of reactions of thiodiglycol, 1,4butanediol, and dithiodiglycol with the phenyl-*N*phenylurethane were carried out using infrared spectroscopy on a Perklin-Elmer instrument in a cell with windows of KBr ($d_{cell} = 0.22$). The reaction was monitored by the change in intensity of the absorption band of the stretching vibrations of the carbonyl group at 1757 cm⁻¹ (the original phenyl-*N*-phenylurethane) and 1730 cm⁻¹ (stretching vibrations of the carbonyl group of the formed urethane). The process was carried out at 80°C in chlorobenzene medium at equimolar ratio of the reagents in the presence and absence of tin(II) octanoate catalyst. The initial concentration of phenyl-*N*-phenylurethane and glycol were 0.1 M, catalyst concentration, 0.01 M.

	Sealants				
Property	proposed	industrial			
		U30M	UG-2	forsage	
Conditional tensile strength, MPa	6.2–7.3	1.2-2.0	8-12	1.5-2.0	
Elongation, %	250-350	150-300	350-450	300–400	
Relative residual deformation, %	0–2	0–8	2–4	10-12	
Adhesion to metal at peeling, kN m ⁻¹	1.5–2.5	0.3–0.5	2.1	0.3–0.5	
Elasticity, %	24–28	_	15–18	_	
Hardness, conventional units	60–65	50–60	55-60	-	
Equilibrium swelling degree, %					
Water	2	12	2	3	
Gasoline	5	<1	13	15	
Transformer oil	4	<1	9	10	

Table 3. Properties of the developed and commercial sealing compositions of the thiocol and polyester-urethane nature

The rate constants were calculated from the initial rates determined from the kinetic curves of phenyl-*N*-phenylurethane consumption and the accumulation of the urethane produced in the reaction, according to a second order equation.

Alcoholysis was carried out in a flask equipped with a stirrer and a reflux condenser at 180 and 200°C. In this temperature range the urethane fragments do not decompose to isocyanates and alcohols, and alcoholysis reactions proceed along the mechanism of substitution at the carbonyl carbon atom [7]. The flask was charged with degrading agent: thiodiglycol or its mixture with oxypropylated oligopolyol Laprol 3603 $(M \sim 3600)$, the functionality with respect to the OH group was three). Then the temperature was adjusted to a predetermined level and a crumb of elastic polyurethane foam with nominal diameter of 3-5 mm was continuously injected. The feed rate of the foam crumb was adjusted in accordance with the rate of its dissolution. The weight ratio of polyurethane foam:degrading agent was 40:60, which was chosen experimentally on the basis of calculating the maximum amount of waste foam and a minimum of degrading agent. To prevent the development of the processes of thermal oxidative degradation, the alcoholysis was carried out in a flow of nitrogen. The start of the process of destruction was the moment of the introduction of the polyurethane foam crumb to the degrading agent. In the course of alcoholysis of the polyurethane foam samples for analysis were taken. The total content of hydroxy and amino groups $[c(OH+NH_2)]$ in the samples was determined by chemical method [8]. The dynamic viscosity $(\eta_{50^{\circ}C})$ of

the products of alcoholysis was determined on a Heppler viscometer at 50°C.

The chemical structure of products of alcoholysis was determined by IR spectroscopy on a Perklin-Elmer spectrometer. To obtain spectra a sample drop was sandwiched between KBr glasses.

The sealant was synthesized by the reaction of the isocyanate component with a sulfur-containing recycled oligoether-urethane [9]. The molar ratio NCO:(OH+NH₂) was 1:1. Carbon black was used as a filler. To accelerate the curing, the tin octanoate catalyst was injected. Physical and mechanical tests of the sealants were carried out according to the following standards: conventional tensile strength, elongation at break, residual elongation at break according to GOST 2151-76, the strength of adhesion to the metal (steel 3) at peeling by the GOST 21981-76, the hardness by the GOST 263-75, elasticity rebound according to GOST 6950-73, the equilibrium degree of swelling by GOST 421-59.

ACKNOWLEDGMENTS

This work was financially supported by the Federal Target Program "Research and scientific-pedagogical personnel of innovation in Russia" for 2009-2013, state contract no. P478

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