

SOME PHYSICAL PROPERTIES OF BROMINATED POLYISOCYANATES

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SUMMARY : Rigid polyurethane was prepared from alcoholized castor oil and toluene diisocyanate. Modification of polyurethane was carried out by treating with bisphenol (4,4'-dihydroxy diphenyl propane) and brominated bisphenol (tetrabromo 4,4'-dihydroxy diphenyl propane) to improve its physical properties. The probable quantities of bisphenols for alcoholized castor oil to form cross-linked network structure of polyurethane are given. These two structures have high level tensile strength, elongation and excellent electrical resistivity. All samples can be used in mechanical and electrical fields. In addition the brominated samples act as flame retardants.

Key Words : Polyurethane, brominated bisphenol, flame retardant.

INTRODUCTION

Although rigid-cell polyurethanes are excellent thermal (1) and electrical (13) insulators, they do suffer from a limited and often unsatisfactory level of fire resistance even in the presence of halogen containing fire retardance. The flame retardant activity was found to be greatly enhanced by a number of compounds. This is considered as synergist (8). As flame retardant antimony oxide is of little value alone, but it displays very pronounced activity when used in conjunction with halogen compounds. Several comparisons of the relative effectiveness of bromine, chlorine (14), fluorine (15) and phosphorus (13) derivatives on the flame retardant activity of some polymers are reported.

A particularly effective synergist in the case of rigid polyurethane foam, hexabromobenzene, nylon, polyester fiber, polystyrene foam, polyester resin, and polyolefin is antimony oxide (11) as well as aluminum hydroxide (14).

EXPERIMENTAL MATERIALS

Castor oil; commercial, M. W. 842, Equivalent wt. 311.67, Sp. gr., 0.966, Vis. at 25°C, 312.15 C. St., Acid number 1.34 and Hydroxyl number 180.

Isocyanates, (TDI), mixture of toluene 2,4-diisocyanate (80%) and 2,6 diisocyanate (20%).

All other chemicals are technical grade.

METHODS

Preparation of alcoholized castor oil (Polyol, ACO)

Castor oil (84.15 g) was treated with glycerol (9.2 g) in presence of lead monoxide (0.01% of the mixture weight) at 130°C for 2 hours under vigorous stirring to produce alcoholized castor oil (ACO). Its specifications are characterized as follows : Average M. W. 535, Equivalent wt. 303.24, Vis at 25°C 671.39 C. St., Acid number 1.21 and Hydroxyl number 185.

Preparation of bisphenol, 4,4'-dihydroxy diphenyl propane (Polyol, Bis)

A mixture of acetone (1 mole) and phenol (4 mol) was covered with dry toluene and stream of dry hydrogen chloride gas was passed through the mixture and the experimental work was carried out according to the method described in (9). The obtained bisphenol was collected and its characteristics are given in Table 1.

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Table 1: Characteristics of the bisphenols.

Bisheno Symbol	Formula	Molecular Weight	Melting Point °C	Elemental Analysis, %		
				C	H	Br
Bis	C ₁₅ H ₁₆ O ₂	228	155	72.0	7.1	-
Br Bis	C ₁₅ H ₁₂ O ₂ Br ₄	598	141	36.0	2.45	50.82

Preparation of brominated bisphenol, tetrabromo, 4,4'-dihydroxy diphenyl propane (Polyol, Br Bis)

Bromine (0.4 mole) was added to a solution of bisphenol (Bis, 0.1 mole) in acetic acid (120 ml), following the procedure described (6). The brominated bisphenol (Br Bis) was collected and its characteristics are given in Table 1.

Preparation of rigid polyurethane

The mixture of polyols (calculated amount, in Table 2), TDI (5 g), triethanolamine (TAE, 0.1% of the weight of polyols as accelerator) and toluene (10 ml) was vigorously stirred at 50 ± 5 °C under nitrogen gas according to the procedure described in (Saunders, 1962).

Preparation of rigid polyurethane films

A blend of the prepared polyurethane (20 g) and antimony oxide Sb₂O₃ (0.25 g) was vigorously stirred at room temperature in presence of toluene (5 ml) and butyl acetate (5 ml) till complete homogeneity. The mixture was poured into petri-dish and left to dry at room temperature to give the required film samples.

RESULTS AND DISCUSSION

According to some preliminary investigations (2, 5), the most preferable NCO/OH ratio to prepare rigid polyurethane in the present work was (0.9-1.0). So it was planned to prepare some rigid polyisocyanates having the above mentioned ratio from various polyols and (TDI) with expected high mechanical, excellent electrical resistivity and flame retardancy.

Previous works reveal that the introduction of more than one phenyl ring in the polyurethane structure develops its physical properties (16). For this reason we try to prepare modified polyisocyanate structure with the previous NCO/OH ratio from mixture of the polyols ACO and Bis (9) samples of group II in Table 2. Replacement of the phenyl in the polyisocyanate structure by brominated

phenyl ring Br Bis (3), samples of group II in order to modify the mechanical and electrical properties as well as flame resistancy of the formed polyurethane was also attempted.

MECHANICAL PROPERTIES

The results in Table 2 show that, in general modified samples in groups I and II have higher tensile strength (Ten. Str.) than the unmodified sample (sample No. 1). This effect is due to the introduction of bisphenols in the urethane structure. On the other hand, the data show that, the Ten. Str. of brominated samples of group II are higher than the Ten. Str. of modified samples of group I. This phenomena seems due to the bigger molecular weight in Br Bis than in the Bis.

The results of group I samples also show that the Ten. Str. and elongation of these samples increase with increasing the quantity of Bis in the samples till they reach maximum level with sample 5, then after the above mentioned properties of the other samples containing more quantity of Bis (samples 6 and 7) begin to decrease again. This may be attributed to the formation of complete cross-linked network structure (5) of polyurethane in sample 5 having suitable amount of Bis and ACO whereas the presence of higher quantity of Bis in sample 8 converts it to brittle structure. The same trend is found true for the same properties of the brominated samples in group II. In this case the sample No. 12 has complete cross-linked network structure.

FLAMMABILITY

Halogen, particularly bromine compounds, occupies an important position among the fire-extinguishing and fire-retardant agent (7). The mechanism of the inhibitory action

of halogen compounds is believed to be based on the interaction of the halogen with some of the reactive moieties of the flame itself (12). Certain ingredients can be incorporated into the flame retarding systems which can combine chemically with the halogen components to increase their residence time in the burning mass (8). Accordingly in this work, formulation of the formed polyurethane's with antimony oxide which acts as fire retardants improver was used (Table 2). The data in Table 2 indicate that all the samples containing bromine in their structure are non-flammable while the reverse is true for non-brominated samples.

ELECTRICAL RESISTIVITY

Due to the basic toughness and high elongation at break of the urethane structures, they find application as a thermoplastic in cable sheathing. Also, it is well recognized that the chemical composition of the polyols used can effect on electrical properties due to its water absorption properties. Considering these bases, the results in Table 2 indicate that the electrical resistivity of all modified samples in groups I and II are higher than the unmodified samples

No. 1. The high level of resistivity can be obtained with the modified samples 5 and 12 due to the expected formation of complete cross-linked network structure of polyisocyanate. The study also clarifies that the introduction of bromine atoms in the urethane structure gives high electrical resistivity.

From the above results it can be concluded that the brominated compounds not only have a good resistance to burning and flame spread and excellent electrical resistivity but are also able to withstand service temperature of up to 150°C.

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Table 2: The quantities of reacted polyols with TDI (5 g) and TEA (0.1% of the weight of Polyols) to prepare Polyurethanes and its Physical properties.

Group No		---	Group I							Group II						
Sample No.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Reacted Polyols, g	ACO	17.48	16	14	12	10	8	6	4	16	14	12	10	8	6	4
	Bis	---	0.52	0.72	1.48	2.24	3.0	3.76	4.48	--	--	--	--	--	--	--
	Br Bis	---	--	--	--	--	--	--	---	1.28	3.07	4.88	6.68	8.44	10.24	12.04
Physical	Tensile * strength N/cm ²	300	481	535	658	787	522	198	Britte	510	653	764	833	598	216	Brittle
Properties	Elongation %	45	63	69	78	86	59	43	----	65	75	89	94	69	53	----
	Resistivity x** 10 ¹³ Ω cm	0.60	0.73	0.95	2.40	3.78	1.16	0.31	----	0.94	2.18	4.65	5.46	3.75	1.3	----
	Flammability ***	F	F	F	F	F	F	F	F	----	NF	NF	NF	NF	NF	NF

F= Flammable, NF= Non Flammable.

* According to ASTM-D 638-779 (1980), using Instron Mode 1026, Cross head speed 100 mm/min. Chart speed 100 mm/min.

** According to ASTM-D 257, using direct current supply unit GMU 516/01 (Philips) and multimeter URL BN 1050 Rhode Schwarz.

*** According to ISO-R 305 and DIN 51-381/2.

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