

Moisture-Cured Polyurethane Based on Polyester and Polycarbonate Polyols

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Synopsis

Moisture-cured polyurethanes were prepared by reacting toluene diisocyanate and sebacic acid-based hydroxy esters such as ethylene glycol sebacate, propylene glycol sebacate, diethylene glycol sebacate, and polyester polyols such as poly(ethylene glycol sebacate), poly(propylene glycol sebacate), poly(diethylene glycol sebacate), and poly(butane diol sebacate). The effect of molecular weight of the esters on film properties and the catalytic effect of 3–5% triethylamine, triethanolamine, and 2-diethylaminoethanol on curing of such films were investigated. Polyurethanes were also prepared using a blend of poly(butane diol carbonate) polyol with polyester polyols. Best polyurethane compositions were obtained when sebacic acid-based polyester polyols were blended with poly(butane diol carbonate) polyol in the ratio of 3:2. These polyurethanes show good tensile strength (120–215 kg/cm²) and elongation (340–460%) properties, having high melting points (247–268°C) and good resistance to solvents and chemicals. Moreover, they are colorless and transparent.

INTRODUCTION

Polyester polyol-based polyurethanes have already been studied by many workers.^{1–4} Reports on the use of sebacic acid-based polyester polyols are limited. Iwamura et al.⁵ used poly(ethylene glycol sebacate) to obtain polyester-urethane block copolymers. Adhesives for coated metal surface were prepared by Lester using poly(ethylene glycol sebacate) and 4, 4'-diphenylmethane diisocyanate.⁶ Barcelona⁷ used sebacic acid-based polyester for synthesis of poly(ester amide) urethane. Besides these scattered experiments a systematic study of sebacic acid-based moisture-cured polyurethanes has yet to be made.

In our present series of investigation on extending the use of castor oil and its derivatives in polyurethane compositions,^{8–11} we have studied several sebacic acid-based hydroxyl esters and polyester polyols as polyurethane components. The effect of catalysts such as triethylamine, triethanolamine, and 2-diethylaminoethanol on curing of these polyurethane films has been studied.

Pank¹² made use of polycarbonate polyol in polyester polyol-based polyurethane. This blending gives a hard, flexible polymer. Since polyurethane films obtained from sebacic acid-based polyester polyols have been found to be generally brittle, studies have been made on the effect of similar blending with poly(butane diol) carbonate with a view to obtain a moisture-cured flexible polyurethane composition.

The effect of solvent and chemicals on these films has also been noted.

TABLE I
Properties of Low-Molecular-Weight Sebacic Acid Esters. Acid Chloride Method^a

Product	Acid value	Hydroxyl value	Equivalent weight (based on acid values and OH value)	Appearance
Ethylene glycol sebacate	37	372.57	137	waxy solid
Propylene glycol sebacate	39	256.8	189.7	pale-yellow liquid
Diethylene glycol sebacate	20.3	196.7	258.5	semisolid

^a Mole ratio of glycol/acid = 8.

EXPERIMENTAL

Materials

Chemically pure-grade ethylene glycol (Pfizer); 1,2 propylene glycol (British Drug House); diethylene glycol (BDH); 1,4 butane diol (BDH); sebacic acid (BDH); diethyl carbonate (BDH); triethylamine (BDH); triethanolamine (BDH); 2-diethylaminoethanol (BDH); dimethylformamide (Merck); xylene (Merck); ethyl acetate (BDH); and toluene diisocyanate, 80/20 (Bayer) were used in the present investigation.

Preparation of Ethylene Glycol, Propylene Glycol, and Diethylene Glycol Hydroxy Esters

A mixture of sebacic acid and thionyl chloride was allowed to react by heating on a water bath. Heating was continued till evolution of SO₂ and HCl ceased. The mixture was distilled to remove any residual thionyl chloride, and the sebacic acid chloride was allowed to cool. Glycol was heated on a water bath and the acid chloride (acid chloride/glycol mole ratio 1:8) was added dropwise during 30 min. under stirring. Heating was continued for about 30 min after evolution of hydrochloric acid ceased, and the mixture was allowed to stand overnight at room temperature. The ester was extracted with ether, followed by washing with water. Ether extract was dried over anhydrous sodium sulfate, and ether was distilled off. Properties of the esters obtained are given in Table I.

Preparation of Sebacic Acid-Based Polyester Polyols from Ethylene Glycol, 1,2 Propylene Glycol, Diethylene Glycol, and 1,4 Butane Diol

Polyester polyols were prepared by direct heating of the reaction mixture without any catalyst, except in the case of poly(butane diol sebacate), where phosphoric acid was used as catalyst (0.5%). Reaction was conducted in a three-necked flask provided with a stirrer, thermometer, and nitrogen gas inlet tube. Reaction time and the mole ratio of the reactants used are listed in Table II.

After the reaction was over, the product was allowed to cool to room temperature and used as such for the urethane reaction.

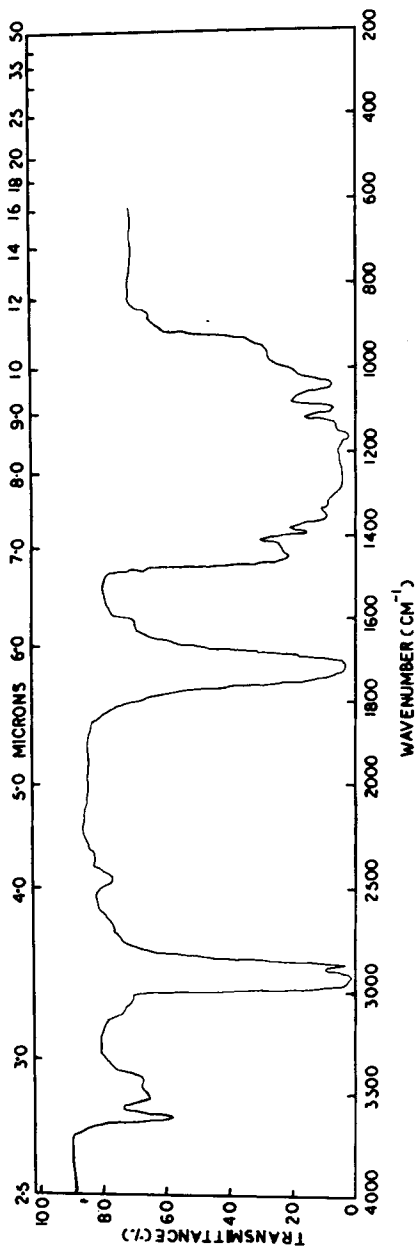


Fig. 1. IR Spectrum of poly(butane diol sebacate) polyol.

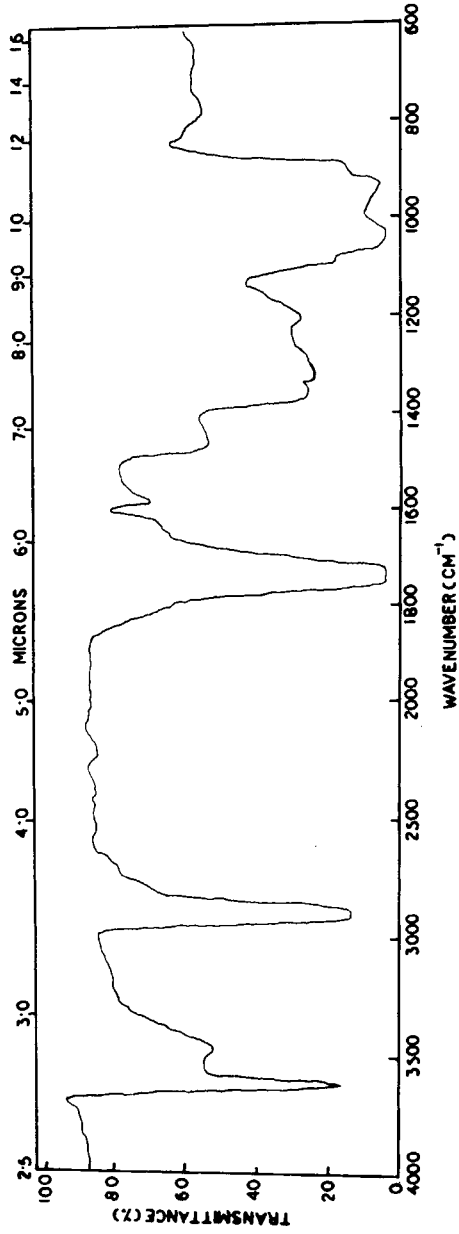


Fig. 2. IR Spectrum of poly(butane diol carbonate) polyol.

TABLE II
Reaction Conditions and Properties of Different Sebacic Acid-Based Polyester Polyols. High-Temperature Esterification Method

Product	Mole ratio glycol/acid	Reaction time, hr	Temperature, °C	Acid value	OH value	OH value (based on OH value + acid value)	Melting point, °C	Appearance
Poly(ethylene glycol sebacate) polyol	1.38	5	180-185	10.1	129.0	403.3	50	waxy solid
Poly(propylene glycol sebacate) polyol	1.4	6	170-175	16.8	104.4	462.9	—	pale-yellow liquid
Poly(diethylene glycol sebacate) polyol	1.2	5	180-190	15.2	49.4	868.3	—	semisolid
Poly(butane diol sebacate) polyol	1.4	3.5	160-180	5.8	98.62	537.2	44	waxy solid

TABLE III
 Effect of Catalyst on Moisture-Cured Poly(ester Urethane)

Hydroxyl-terminated Esters	TDI/polyol (equiv/equiv)	Catalyst 3-5%	Melting point, °C	Appearance
Ethylene glycol sebacate	2	trimethylamine	285	brittle, opaque
Ethylene glycol sebacate	2	triethanolamine	—	pasty mass
Poly(ethylene glycol sebacate)polyol	2	triethylamine	270	brittle, opaque ^a
Poly(ethylene glycol sebacate) polyol	1.5	none	265	brittle, opaque ^a
Poly(ethylene glycol sebacate) polyol	2	triethanolamine	—	pasty mass
Propylene glycol sebacate	2	none	270	tough, brittle, opaque
Propylene glycol sebacate	2	triethylamine	255	soft, opaque
Propylene glycol sebacate	2	triethanolamine	—	pasty mass
Poly(propylene glycol sebacate) polyol	2.4	none	270	opaque, brittle
Poly(propylene glycol sebacate) polyol	2	triethylamine	267	opaque, brittle
Diethylene glycol sebacate	1.8	triethylamine	268	opaque, brittle
Poly(diethylene glycol sebacate) polyol	2	triethylamine	256	opaque, brittle
Poly(diethylene glycol sebacate) polyol	1.5	triethanolamine	—	pasty mass
Poly(butane diol sebacate) polyol	2	triethylamine	256	hard, opaque ^b

^a Tensile strength, 45 kg/cm²; % elongation at break, 50.

^b Tensile strength, 38 kg/cm²; % elongation at break, 30.

Synthesis of Poly(butane Diol Carbonate) Polyol

Synthesis of polycarbonate polyol was conducted in a three-necked flask, using 25 g diol, 29.5 g diethyl carbonate, and 0.05 g sodium metal. Initially, sodium metal was allowed to react with glycol to obtain a sodium alcoholate catalyst. Then diethyl carbonate was added at once to the reactor, which had a fractionating column, a thermometer, and a nitrogen gas inlet tube. The reaction was allowed to continue at a bath temperature of 140–160°C (internal reaction temperature 100–110°C) for 3 hr under a continuous stream of nitrogen gas. The ethanol formed during the reaction was distilled off. After the initial 3-hr reaction time at atmospheric pressure, the reaction was continued under vacuum (7 mm) for 1 hr, at 140–160°C.

After keeping the reaction mass overnight at room temperature, a white waxy

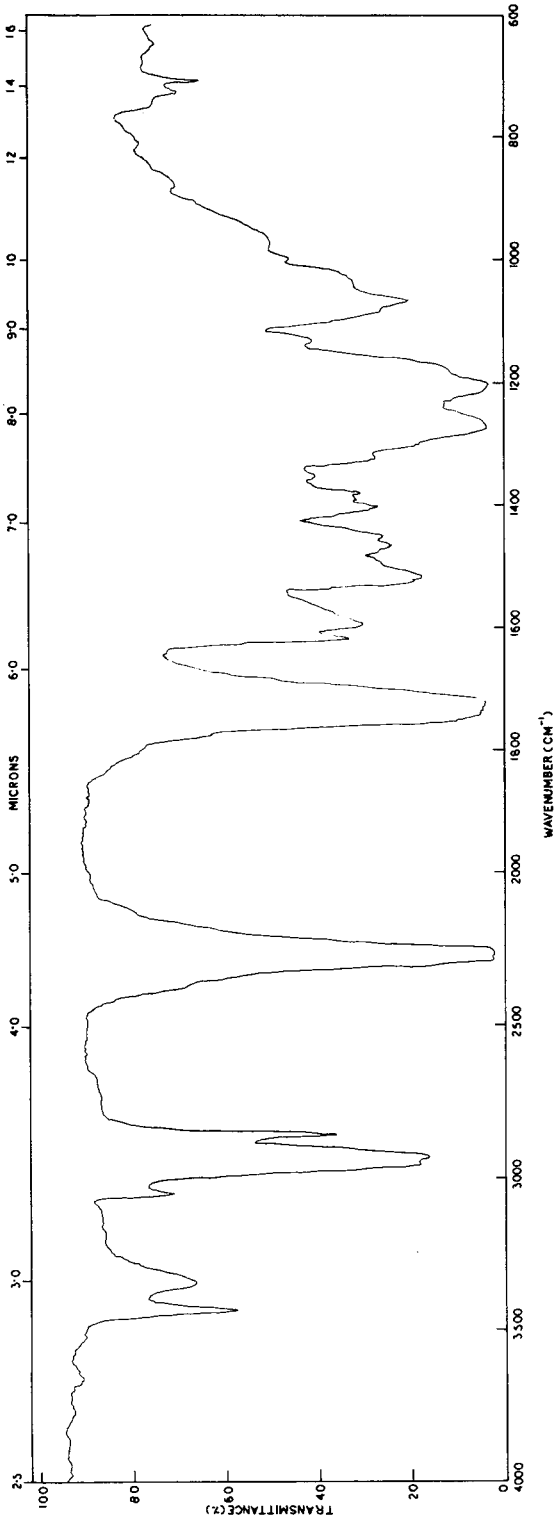


Fig. 3. IR spectrum of TDI prepolymer [TDI with poly(butane diol sebacate) polyol and poly(butane diol carbonate) polyol].

TABLE IV
Effect of Poly(butane Diol Carbonate) Polyol on Moisture-Cured Poly(ester Urethane)^a

Components (weight ratio;3/2)	Tensile strength, kg/cm ²	%		Melting point, °C	Appearance
		Elonga- tion at break			
Poly(butane diol carbonate) polyol	307	200	244	opaque, hard	
Poly(ethylene glycol sebacate) polyol + poly(butane diol carbonate) polyol	120	340	247	transparent, elastic	
Poly(propylene glycol sebacate) polyol + poly(butane diol carbonate) polyol	142	375	250	opaque, elastic	
Poly(diethylene glycol sebacate) polyol + poly(butane diol carbonate) polyol	160	410	248	transparent, elastic	
Poly(butane diol sebacate) polyol + poly(butane diol carbonate) polyol	215	460	268	transparent, elastic	

^a 2-Diethylaminoethanol catalyst, 3–5%.

solid mass was obtained, having a melting point of 43–45°C and hydroxyl value of 286.6–328 (two samples).

Preparation of Urethane Derivatives

The urethane prepolymer of sebacic acid-based polyester polyols is soluble best in a mixture of solvents, such as xylene/ethyl acetate/DMF in the ratio of 4:4:1, while dichloroethane is a good solvent for polycarbonate-based urethane prepolymer.

An amount of solvent calculated to make a 15–20% solution of the resulting urethane prepolymer was taken in a three-necked flask, and the required amount of toluene diisocyanate was added. The flask was fitted with a sealed stirrer, a thermometer, and a dropping funnel through which the polyol solution was added dropwise. The flask was heated at 60–70°C for 4 hr with stirring. Finally, the product was cooled to room temperature.

Evaluation of Polyurethane Film

Moisture-cured films were cast on mercury by following the method reported earlier.⁸ A small amount of dry acetone was poured over mercury; the pan was covered and allowed to stand for a few minutes. A 10–15% solution of the adduct was added to the layer of acetone (which contains the required amount of catalyst). The pan was again covered and allowed to stand undisturbed at room temperature to be cured.

The tensile and elongation properties of the films six to eight weeks old were determined using a stretching rate of 10 in./min for high tensile value specimens and 20 in./min for low tensile value specimens. The testing was done in a "Good

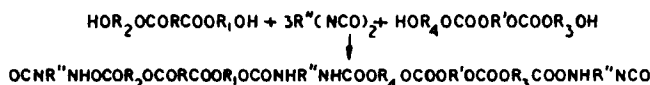


Fig. 4. Backbone of urethane prepolymer (TDI with polyester polyol and polycarbonate polyol).

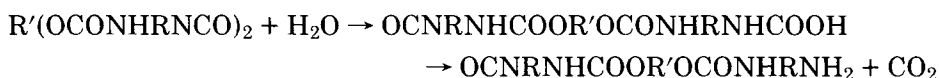
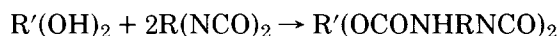
Brand" Tensile Tester. The melting points were determined on a Fischer Johns melting point apparatus, using a heating rate of about 15–20°C/min. The effect of solvent and chemicals was observed by immersion of strips of the film in the appropriate reagent for 100–150 hr at room temperature.

RESULTS AND DISCUSSION

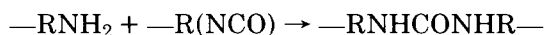
Table I lists the properties of the different polyols made from sebacic acid and glycols by the thionyl chloride method. Although this method was found suitable for the synthesis of low molecular weight hydroxy-terminated esters by using a large excess of glycol and maintaining proper reaction conditions, the products were found to have high acid values. Polyester polyols obtained by the direct high-temperature esterification method have lower acid values. The reaction requires 5–6 hr; however, the reaction time may be lowered to 3½ hr by using phosphoric acid as catalyst (0.5%), as has been found in case of poly(butane diol sebacate), which has also a lower acid value (5.8). Table II illustrates the mole ratio of the reactants used and reaction conditions together with the physico-chemical properties of the different polyester polyols prepared.

Ethylene glycol sebacate and poly(ethylene glycol sebacate) polyol are waxy solids, whereas propylene glycol sebacate and poly(propylene glycol sebacate) polyol are liquids. This liquid character of the 1,2 propylene glycol esters may be due to the secondary hydroxy group of the glycol. Similarly, the semisolid nature of diethylene glycol sebacate and poly(diethylene glycol sebacate) polyol may be due to the ether linkages present in these glycols. The residual acid of the polyester polyols may promote their hydrolytic decomposition on storage and changes in their properties. This is presently under investigation.

In moisture-cured polyurethane, polyol reacts with diisocyanate, leaving a slight excess of NCO groups which react with atmospheric moisture for curing of the prepolymer. The curing reaction is believed to proceed according to the following equation:



The amine formed reacts immediately with isocyanate to form a substituted urea:



Since we are using polyesters, the free carboxy groups of these polyesters may also take part in the reaction giving an amide linkage:



The following crosslinking reactions may also take place, and the corresponding groups may be present in the final polyurethane structure depending on the

TABLE V
Effect of Solvent and Chemicals on Poly(ester Carbonate) Urethane^a

	Water	Acetone	Benzene	DMF	Xylene	Methanol	10% HCl	3% NaOH	Normal hexane
Poly(ethylene glycol sebacate) polyol + poly(butane diol carbonate) polyol	NE	FB	LS	FB	NE	LS	NE	NE	NE
Poly(diethylene glycol sebacate) polyol + poly(butane diol carbonate) polyol	NE	LS	LS	Sw	NE	SLS	NE	NE	NE
Poly(propylene glycol sebacate) polyol + poly(butane diol carbonate) polyol	NE	FB	FB	S	LS	FB	NE	NE	SLS
Poly(butane diol carbonate) polyol + Poly(butane diol sebacate) polyol + poly(butane diol carbonate) polyol	NE	FB	LS	S	LS	LS	NE	NE	NE
Poly(butane diol carbonate) polyol	NE	LS	LS	S	NE	FB	NE	NE	NE

^a NE = No effect; FB = film breaks; LS = loss of strength; SLS = slight loss of strength; S = soluble; Sw = swelling.

availability and concentration of moisture:

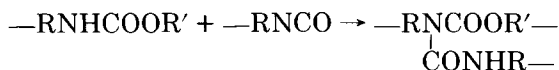
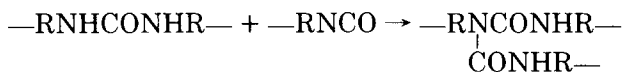
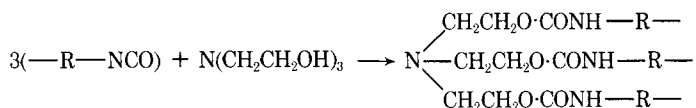


Table III illustrates the effect of catalyst on the curing of poly(ester urethane) films of sebacic acid-based hydroxy esters and polyester polyols. In general, it has been observed that triethylamine is a good catalyst for curing these polymers, whereas triethanolamine gives a pasty mass. This may be explained by the fact that three hydroxyl groups of triethanolamine also take part in the reaction during curing; as a result less free NCO groups are available for the reaction with atmospheric moisture and for the curing of the prepolymer:



Regarding the effect of molecular weight of the esters, in general, lower-molecular-weight esters give polyurethanes having higher melting points than those of the corresponding higher-molecular-weight polyester polyols of the same glycol. This increase in melting point may be due to the presence of a higher percentage of relatively stiff segments of aromatic groups in hydroxy ester-based urethane than in polyester polyol-based urethane. Similarly, no significant change in polymer properties, except a slight increase or decrease in melting point, is observed by varying the proportion of diisocyanate (1.5–2.4 equivalents). In general, sebacic acid-based hydroxy esters or polyester polyol give polyurethanes having brittle film characteristics. A somewhat flexible polyurethane film is obtained from polyester polyols, such as poly(ethylene glycol sebacate) polyol and poly(butane diol sebacate) polyol. This may be due to the presence of a large number of moderately flexible long, linear polyester segments.

Since urethane from sebacic acid-based polyester polyol does not give good film properties, an attempt was also made to obtain a better product by blending with an aliphatic polycarbonate polyol.

Poly(butane diol carbonate) polyol gives polyurethane with TDI having good tensile and elongation properties, but the film is opaque. Table IV illustrates the effect of blending poly(butane diol carbonate) polyol with polyester polyols to get a polyurethane film. Addition of poly(butane diol carbonate) is found to improve the film properties considerably. These films are flexible and elastic in nature, having higher elongation value than that in case of polycarbonate polyol-based polyurethane films. However, the tensile strength decreases.

Poly(ester carbonate)-based urethane has a slightly lower melting point than the corresponding polyester polyol-based polyurethane. This may be due to the fact that aliphatic polycarbonates have low intermolecular forces which may reduce the melting point of the blend.

Table V shows the effect of solvent and chemicals on poly(ester carbonate) urethane films. These films are only slightly affected by acetone, benzene, and methanol, but they have poor resistance toward dimethylformamide, in which some of the films are soluble.

The best film in this series of experiments was obtained from poly(butane diol carbonate) polyol and poly(butane diol sebacate) polyol when blended in the ratio of 2:3 (w/w). The film is transparent and colorless. It has high elongation as well as good tensile strength properties. 2-Diethylamino ethanol was found to be a suitable catalyst for this blended composition.

Infrared spectra of the monomers, polyester polyol, and polycarbonate polyol as well as of the prepolymer shown in Figures 1, 2, and 3, respectively, give some indication of the urethane prepolymer structure, which may be as suggested in Figure 4. The characteristic bonds of OH (3440 and 3350 cm^{-1}) indicate the presence of unreacted polyol in the prepolymer.

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