Urethane Foams from Animal Fats: X. Urethane Polyols from Epoxidized Tallow, Trimethylolpropane, and Propylene Oxide[1]

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ABSTRACT AND SUMMARY

A convenient three-stage reaction has been developed for the preparation of polyols from epoxidized tallow (ET), trimethylolpropane (TMP), and propylene oxide (PO), without the previously required water washing step. ET is first heated with excess TMP under catalysis by BF_3, causing rapid ring opening of the oxirane function. In the second stage, KOH catalyzes ester interchange of TMP with the triglyceride. Finally, PO is caused to react with free TMP and with other available hydroxylic components, to produce a homogeneous mixture of polyols. The polyols, all liquid at room temperature, were adjusted to equivalent weights of 100 and 120 with added triisopropanolamine and reacted with a polymeric isocyanate in the presence of a blowing agent to give low-density rigid foams. Densities ranged from 1.6 to 1.8 lb/ft^3 and compressive strengths from 21 to 30 psi.

INTRODUCTION

Previous contributions from this laboratory described the preparation of polyols by reaction of epoxidized tallow (ET) with trimethylolpropane (TMP), TMP-HBr, or with diethanolamine (1,2). Several of these polyols gave low-density rigid urethane foams with superior properties (3). ET is a mixture of an "active" portion, containing oxirane groups, and an "inert" portion (about 14%) made up of fully saturated triglycerides. Under acid catalysis the oxirane reacted rapidly with TMP to give ether-linked triol derivatives. Under basic catalysis the TMP reacted more readily with glyceride linkages to give a mixture of products including diglycerides, monoglycerides, and esters of TMP. A previous study showed that the hydroxyl content of the polyol products increased with the increase of the functional ratio of reactants employed, that is, the molar ratio of hydroxyl groups from TMP to moles of oxirane and ester available from ET. A typical product mixture was a blend of polyalcohols of moderate hydroxyl content and of appropriate plasticizing character to give good quality rigid urethane foams on reaction with isocyanates in the presence of a blowing agent. A disadvantage of this procedure is that unreacted TMP separates as a solid on standing at room temperature. In the laboratory this unreacted TMP could be largely eliminated by water-washing a solution of the polyol in a hydrocarbon solvent. In industrial practice the necessary washing, drying, and subsequent solvent removal would constitute added troublesome steps. To circumvent the washing step, we have developed the present three-stage procedure. In this process ET is first caused to react with TMP in the presence of BF_3. After removal of the catalyst, by evaporation with N_2, KOH is introduced to effect transesterification. The reaction mixture is then treated with propylene oxide (PO) to give a homogeneous mixture of polyols that is stable on storage.

EXPERIMENTAL PROCEDURE

Materials

The materials listed below were used as received: tallow, fancy (Mutual-Shoemaker Co., Philadelphia, PA), iodine value 55.8; liquid tallow (Fraction 2), iodine value 62.9, a product developed in our Physical Chemistry Laboratory (4); trimethylolpropane (Celanese Corp., New York, NY); propylene oxide and boron trifluoride etherate, 50%, (Eastman Organic Chemicals, Rochester, NY); triisopropanolamine (TIPA) and silicone L-530 (Union Carbide Corp., New York, NY); Dabco-33-LV, 33% solution of triethylenediamine in dipropylene glycol (Houdry Process and Chemical Co., Marcus Hook, PA); Freon 11, trichlorofluoromethane (Matheson Gas Products, New York, NY); polymethylene polyphenylisocyanate (Upjohn Co., Kalamazoo, MI).

Reaction of ET with TMP and PO

Experiment A, functional ratio 1.4: TMP, 167.9 g (1.25 mole), was melted in a 1 liter three-necked flask equipped with thermometer, mechanical stirrer, reflux condenser, and addition funnel. A heated oil bath controlled by an electronic thermoregulator provided the necessary heat. Boron trifluoride etherate, 50%, (10 ml) was diluted with 15 ml ether to form a 20% solution. Seventeen ml of this solution of BF_3 catalyst was dissolved in the TMP. This represented a 0.5% concentration of catalyst based on the weight of the total reaction mixture. Melted ET, 500 g

TABLE I

Polyol Properties as Functions of Reactant Compositions

Run	Functional ratio[a]	Reactants, wt %			Polyol properties		
					Hydroxyl		Viscosity cps, 25 C
		ET[b]	TMP[b]	PO	%	No.	
A	1.4	60.8	20.4	18.8	8.0	264	7,950
B	2.1	50.9	25.6	23.6	9.3	307	5,825
C	4.2	34.0	34.3	31.8	12.7	419	4,650
D	6.6	25.2	40.1	34.7	13.6	449	3,725
LET[b]	6.6	23.8	39.5	36.7	14.4	475	3,475

[a]Moles OH/moles (oxirane + ester).

[b]ET = epoxidized tallow; TMP = trimethylolpropane; LET = liquid epoxidized tallow.

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TABLE II

Formulation for Low-Density Rigid Foam

	Parts
Epoxidized tallow-TMP-propylene oxide polyol (OH No. 449; OH equiv. 125)	7.20
Triisopropanolamine (OH No. 850; OH equiv. 66)	2.80
Triethylenediamine	0.25
Trichlorofluoromethane	4.11
Polymethylene polyphenylisocyanate	14.70
Silicone L-530 surfactant	0.16

TABLE III

Properties of Low-Density Foams

Polyol	Polyol OH equiv.	OH equiv.^{a}	Density lb/ft^3	Comp. str.^{b} psi
A	213	100	1.7	29
		120	1.6	29
B	183	100	1.7	24
		120	1.6	21
C	134	100	1.7	21
		120	1.6	25
D	125	100	1.8	28
		120	1.7	30
		125^c	1.7	30
LET^d	118	100	1.7	24
		118^c	1.7	25

^{a}Adjusted with triisopropanolamine.

^{b}10% of compression.

^{c}Without adjustment.

^{d}LET = liquid epoxidized tallow.

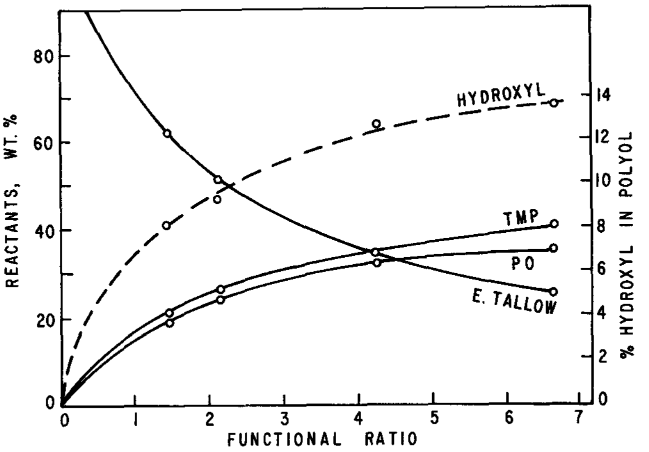

FIG. 1. Reactant composition vs. given functional ratio.

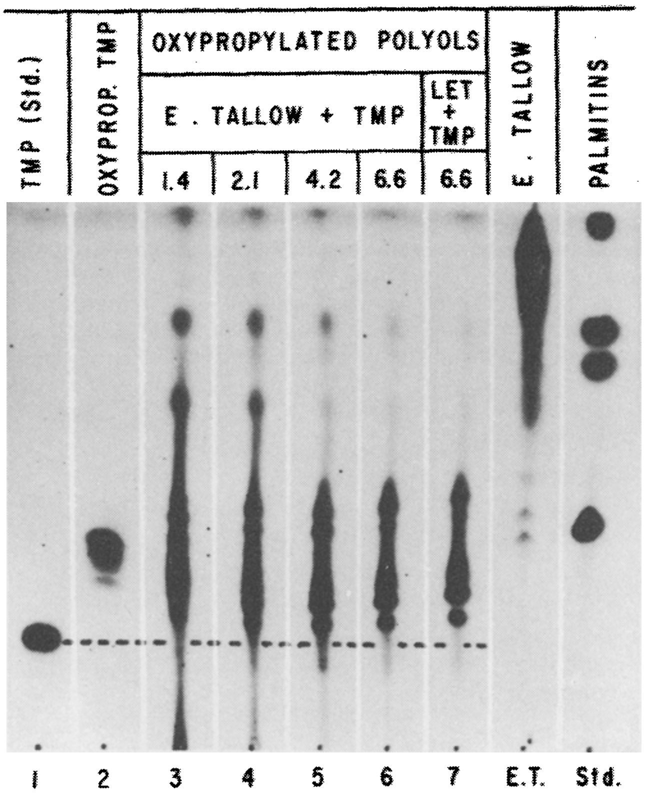

FIG. 2. Thin layer chromatography on silicic acid, developed with benzene-chloroform-ethanol (70:15:15). The standards are, from bottom to top, 1-monopalmitin, 1,2- and 1,3-dipalmitin and tripalmitin.

[oxirane 3.28% by the Durbetaki method (5), saponification no. 189.5, acid no. 2.6], prepared as described previously (6), was added slowly at 70 C. The temperature of the mixture was raised gradually to 120 C and held at this level for 1 hr. Oxirane analysis at this time showed that all epoxy groups had been consumed. The BF_3 catalyst was now removed at 120 C by bubbling nitrogen through the reaction mixture until the mixture was neutral, and 6.7 g (0.119 moles) of KOH was added (providing 1% concentration of KOH based on the weight of the total mixture). Stirring at 120 C was continued for an additional 4 hr. The temperature of the mixture was then raised to 150 C, and 165.0 g (2.84 moles) of PO was added dropwise at the rate of 2 ml per minute, under a nitrogen atmosphere. The product mixture was neutralized with concentrated hydrochloric acid and dried in a rotary evaporator under 0.25 mm pressure. The final product, weighing 831.9 g (containing 8.9 g of KCl, formed from the neutralization of the KOH catalyst), was an amber colored liquid at room temperature. The weight increase, based on the weight of ET, was 66.4%. During the oxypropylation reaction, 155.1 g (2.67 moles) of PO was fixed (0.71 moles of PO per mole of OH from TMP). The final product had a hydroxyl content of 8.0%, viscosity (Brookfield) 7,950 cps, at 25 C. Thin layer chromatography (TLC) showed no unsubstituted TMP in the final product.

Experiments B, C, and D: This series of polyols was prepared by following the reaction procedure described above. The amounts of reactants, TMP and ET were chosen in terms of their functional ratios (the molar ratio of hydroxyl available from TMP to oxirane plus ester from ET). These ratios were: Experiment B, 2.1; Experiment C, 4.2; Experiment D, 6.6. The polyol derived from liquid epoxidized tallow (LET) was prepared by reaction of the epoxidized material with TMP and PO, under the conditions of Experiment D. The properties of polyols A, B, C, D, and LET are tabulated in Table I. The amount of PO reacted was kept at 0.71 moles PO per mole of OH from TMP to maintain this constant for all polyols.

Foam Preparation and Testing

The polyols described above were used in formulating low-, medium-, and high-density rigid urethane foams. In this paper, the formulation and properties of only the low-density foams are described. The procedure for the preparation and physical testing of low-density rigid urethane foams was described previously (3). The adjustment to an equivalent weight of 100 or 120 was made by incorporation of the adjuvant TIPA. As catalyst, a small amount of Dabco was used. A typical formulation is given in Table II. Physical properties are reported in Table III.

RESULTS AND DISCUSSION

In the reaction of ET with TMP, under acid catalysis, the oxirane was consumed within 1 hr; however, under basic catalysis, the oxirane groups underwent slower reaction, leaving considerable amounts of unreacted epoxy groups (2). To obtain complete reaction, we employed the three-stage procedure. We used BF_3 catalyst instead of the p-toluenesulfonic acid utilized in earlier experiments because it is easier to remove from the reaction mixture. Thus, the need for catalyst neutralization in preparation for the subsequent step was minimized. The KOH catalyst used in the next two stages effectively catalyzed the alcoholysis reaction and the oxypropylation of hydroxyl bearing components (7). Increasing the functional ratio of reactants resulted in an increase in the hydroxyl content of the polyol (Table I). A decrease of ET in the polyols was accompanied by an increase in two other components, the TMP and PO. This also caused a corresponding lowering ot the viscosity of the polyols prepared. The properties of polyol D, prepared by reaction of ET with TMP and PO, are similar to those of the polyol from LET in which the "inert" portion of fully saturated triglycerides had previously been separated by a crystallization from acetone (4). The alkali-catalyzed reaction of PO with hydroxyl bearing components of the polyol mixture yields secondary alcohols predominantly (8). This is due to the nucleophilic attack by alkoxide ion on the terminal carbon atom of the epoxide. Figure 1 shows a plot of percent composition of the mixture of reactants versus their functional ratio as defined above and the hydroxyl content of the final polyol obtained for a given functional ratio. Thus Figure 1 can be used to select the reagent ratio to achieve a desired hydroxyl content.

Polarity of Polyol Components

The polyols were examined by TLC. Separations are shown in Figure 2. ET itself has components with R_f values in the range of 1,3-dipalmitin and tripalmitin. We found the polarities of the polyols prepared to be related to the hydroxyl content of the individual components. As expected, the fractions with higher hydroxyl concentration are more polar than those with less hydroxyl content. The polyols contain much material having an R_f value approximating that of monoglycerides. At a functional ratio of 6.6, components of polarity similar to that of tripalmitin are virtually absent. TLC also shows no unsubstituted TMP in the products.

Foam Properties

Table III compares the foam properties realized, at hydroxyl equivalents adjusted to both 100 and 120. Formulated at OH equivalent of 100, these polyols gave foams of densities ranging from 1.7 to 1.8 lb/ft^3. Compressive strengths ranged from 21 to 29 psi. At the equivalent weight of 120, densities ranged from 1.6 to 1.7 lb/ft^3, and compressive strengths from 21 to 30 psi. The foams prepared without adjustment with TIPA, have properties in the same range as those with TIPA (Table III).

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