Urethane Foams from Animal Fats. IV. Rigid Foams from Epoxidized Glycerides[1]

F. SCHOLNICK, E. J. SAGGESE, A. N. WRIGLEY, W. C. AULT, H. A. MONROE JR., and M. ZUBILLAGA, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

Abstract

Liquid polyols have been prepared from epoxidized glyceryl trioleate, glyceryl mono-oleate, lard oil, neatsfoot oil, and soybean oil by hydration with 24% fluoboric acid. Upon adjustment of the equivalent weight to 100 with tri-isopropanolamine, the polyols were foamed by reaction with a prepolymer made from oxypropylated sorbitol and tolylene diisocyanate. The resulting rigid foams had densities between 1.66 and 2.34 lbs/ft^3 and compressive strengths ranging from 23 to 39 psi (10% compression).

The same polyols were used in one-step systems with PAPI as the isocyanate. In general, foam properties were comparable with those obtained from the prepolymer systems.

Introduction

A LARGE POTENTIAL MARKET exists for polyols from natural sources in the rapidly expanding urethane foam industry. Predictions are that by 1970 use of rigid urethane foam will increase to 280 million pounds, more than double the consumption in 1965 (1).

Although urethane foams have been obtained from polyol derivatives of glucosides from corn starch (2,3), and from natural glycerides such as castor oil (4,5), until recently little work has been done on the utilization of fatty derivatives of animal fat origin. However Saggese et al. have reported the preparation and properties of rigid urethane foams by using, as polyols, oxyethylated or oxypropylated 9,10-dihydroxystearic acid (6,7).

In the present work polyols were prepared from epoxidized glycerides such as glyceryl trioleate, glyceryl mono-oleate, lard oil, neatsfoot oil, and soybean oil by acid-catalyzed hydration of the epoxy groups. Fluoboric acid was used as the catalyst for the hydration according to the procedure described by Maerker and co-workers (8a). Thus hydration of epoxidized triolein will furnish a polyol with six reactive hydroxyl groups as shown in Fig. 1.

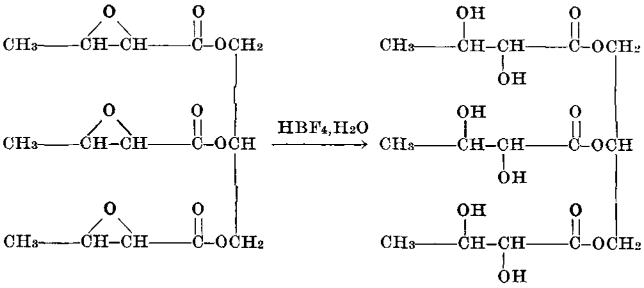

FIG. 1. Epoxidized glyceride (left) and hydrated glyceride.

Hydration of esters with two epoxy functions on the same hydrocarbon chain, such as methyl 9,10; 12,13-diepoxystearate, leads primarily to the formation of dihydroxy derivatives of substituted furans and pyrans rather than the expected methyl tetrahydroxystearate (8b). Similarly epoxidation and hydration of glycerides of polyunsaturated acids would be expected to lead to polyols with lower hydroxyl content than theoretically possible.

TABLE I

Analytical Data for Epoxidized Glycerides

Glyceride	% Oxirane		Residual iodine value	Saponification value
	Theory[a]	Found		
Triolein	5.07	4.54	0.12	184.9
Mono-olein	4.02	3.94	4.28	156.0
Lard oil	3.90	3.65	0.85	193.0
Neatsfoot oil	4.80	4.57	4.50	187.5
Soybean oil	......	7.19	0.91	176.8

[a] Based upon original iodine value.

In the present work, polyols prepared by hydration of the epoxidized glycerides had sufficient hydroxyl functionality to make them suitable for urethane foam formation. No difficulties were encountered in their use in either two-step systems with an isocyanate-terminated prepolymer or in one-step systems with PAPI as the isocyanate.

Experimental Section

The materials listed below were used as received.

Glyceryl trioleate over 90% purity (Hormel Institute), iodine value 84.8.

Glyceryl mono-oleate (Eastman Organic Chemicals), iodine value 66.4.

Lard oil (Armox Extra Winter Strain), iodine value 64.3.

Neatsfoot oil (Reilly-Whiteman Walton Company), iodine value 80.0.

Epoxidized soybean oil (Union Carbide Chemicals), % oxirane 7.19.

Fluoboric acid, purified, 48–50% (J. T. Baker Chemical Company).

Procedures

Epoxidation of Glycerides. Conventional epoxidation procedures (9) with peracetic acid were used with all of the unsaturated glycerides listed above. Analysis of the products led to the data summarized in Table I.

Hydration of Epoxidized Glycerides. All of the epoxidized glycerides were hydrated with diluted (24%) fluoboric acid in dioxane solution. The following general procedure was used in each case.

TABLE II

Polyols from Epoxidized Glycerides

Hydrated epoxidized glyceride	% Hydroxyl		% Residual oxirane	Saponification value
	Theory[a]	Found		
Triolein	8.80	7.75	0	168.3
Mono-olein	14.35	13.00	<1.00	158.8
Lard oil	7.20	6.18	<1.00	189.3
Neatsfoot oil	8.85	6.50	0	182.4
Soybean oil	13.26	8.20	<1.00	170.8

[a] Based upon original oxirane content, assuming formation of two hydroxyl groups from each oxirane.

---

[1] Presented at the AOCS Meeting, New Orleans, 1967.

[2] E. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE III

Two-Step Foam Formulation

Component		Weight, g	Percentage (exclusive of blowing agent)
Hydrated triolein (7.00%OH)	Cup A	4.70	17.79
Triisopropanolamine		5.30	20.06
Dabco-33		0.45	1.70
TDI-prepolymer (amine equivalent 151)	Cup B	15.80	59.83
Freon-11		4.10	....
Silicone L-520		0.16	0.61

To a solution of 50.0 g of epoxidized glyceride in 400 ml of 1,4-dioxane maintained at 15C, there was added a solution of 100 g of commercial (48%) fluoboric acid in a mixture of 100 ml of water and 200 ml dioxane over a period of 45 min. Stirring was continued for 2 hr at the same temperature, whereupon 100 ml of water were added and agitation was continued for 1 hr at 15C. The mixture was poured into one liter of benzene, and the benzene solution was washed successively with 50-ml portions of sodium bicarbonate (5%) and several 100-ml portions of water. After the benzene solution was dried over anhydrous magnesium sulfate, the solvent was removed and the polyol analyzed. Results are given in Table II. In general, all polyols were low-melting, waxy solids.

Foam Preparations.

a) Prepolymer systems—The hydrated glyceride was warmed in an aluminum cup with sufficient triisopropanolamine to give 10.0 g (0.100 equivalent) of liquid polyol of equivalent weight 100. To this was added 0.45 g of Dabco-33 catalyst. In a plastic-coated paper cup were mixed 16.5 g (0.105 equivalent) of an isocyanate-terminated prepolymer which was prepared by the reaction of excess tolylene diisocyanate with oxypropylated sorbitol (5), 0.16 g of silicone oil L-520 (Union Carbide Corporation), and slightly more than 4.1 g of Freon-11.

After the excess blowing agent had evaporated, the polyol-catalyst mixture was added to the prepolymer and the reactants were mixed for 8 sec at 1,500 rpm by a 4-quadrant stirrer, 44 mm in diameter. Creaming was evident after 10–15 sec; the foam was allowed to rise and was tack-free after 50–150 sec. A typical formulation is given in Table III.

b) One-step systems—The hydrated glyceride was adjusted to an equivalent weight of 100 by addition of triisopropanolamine. Ten grams of the polyol mixture (0.100 equivalent) were mixed, as described above, with a slight excess (0.105 equivalent) of a polymeric polyisocyanate (PAPI), silicone oil, triethylenediamine catalyst (Dabco-33), and blowing agent (Freon-11). A typical formulation is given in Table IV.

Test Methods. Density and compressive strength (at 10% compression) were measured by methods used previously (6). The percentage of open cells was measured by Tentative ASTM Method D-1940-62, with the use of the Beckman Air Comparison Pycnometer.

TABLE IV

One-Shot Foam Formulation

Component	Weight, g	Percentage (exclusive of blowing agent)
Hydrated triolein (7.75%OH)	4.80	19.70
Triisopropanolamine	5.20	21.35
Silicone L-520	0.16	0.66
Dabco-33	0.60	2.46
Freon-11	4.10	....
PAPI	13.60	55.83

TABLE V

Foam Properties (Prepolymer Process)

Hydrated substrate	Density (lb/ft³)	Compressive strength (at 10% compression, psi)	Open cells (%)
Triolein	2.03	25	36.4
Mono-olein	2.34	26	56.7
Lard oil	2.04	23	47.0
Neatsfoot oil	1.86	39	20.3
Soybean oil	1.66	27	31.2

Discussion

The physical properties of the foams derived from hydrated glycerides are given in Tables V and VI. Foams prepared by the two-step prepolymer process had densities between 1.66 and 2.34 lb/ft^3, with compressive strengths ranging from 23 to 39 psi. Lowest open-cell content was displayed by foams derived from neatsfoot oil and was greatest with those from mono-olein. Neatsfoot oil provided foams with the highest rigidity and compressive strength.

One-shot foams prepared from hydrated mono-olein were highly fragile and friable, with a high percentage of open cells. It should be noted that the open-cell content of the remaining foams was consistently about 25%, in contrast to the range of values obtained with two package systems. Once again, neatsfoot oil yielded foams with the highest compressive strength. It is obvious that adjustment of the formulation to give foams of higher density, such as 2.00 lb/ft^3, would be accompanied by higher compressive strengths comparable with those reported for the two-step foams.

All of the foams prepared by hydration of epoxidized glycerides were found to burn readily; however, treatment of the same epoxidized glycerides with dilute hydrobromic acid led to bromohydrins which yielded foams with self-extinguishing characteristics. The latter are currently under investigation.

TABLE VI

Foam Properties (One-Shot Process)

Hydrated substrate	Density (lb/ft³)	Compressive strength (10% compression, psi)	Open cells (%)
Triolein	1.73	20	25.5
Mono-olein		←Not satisfactory→	
Lard oil	1.77	19	25.5
Neatsfoot oil	1.86	24	24.5
Soybean oil	1.53	17	24.7

ACKNOWLEDGMENTS

Cutting of foams was done by W. Eglinton and R. R. Calhoun Jr. of the Instrument Shop, compressive strength measurements by G. R. Riser.

REFERENCES

1. Modern Plastics *43*, 135 (1966).
2. Yeates, T. E., and C. L. Mehltretter, Modern Plastics *39*, 151,225 (1961).
3. Otey, F. H., C. L. Mehltretter and C. E. Rist, JAOCS *40*, 76–78 (1963).
4. Goldblatt, L. A., and C. K. Lyon, JAOCS *40*, 157–161 (1963).
5. Lyon, C. K., V. H. Garrett and L. A. Goldblatt, JAOCS *41*, 23–25 (1964).
6. Saggese, E. J., M. Zubillaga, A. N. Wrigley and W. C. Ault, JAOCS *42*, 553–556 (1965).
7. Saggese, E. J., F. Scholnick, M. Zubillaga, W. C. Ault and A. N. Wrigley, JAOCS *44*, 43–45 (1967).
8. a) Maerker, G., E. T. Haeberer and W. C. Ault, JAOCS *41*, 585–588 (1964). b) Maerker, G., unpublished results.
9. Findley, T. W., D. Swern and J. T. Scanlan, J. Am. Chem. Soc. *67*, 412–414 (1945).

[Received September 5, 1967]