Rigid Urethane Foams from Hydroxymethylated Linseed Oil and Polyol Esters

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ABSTRACT

Rigid urethane foams were prepared from hydroxymethylated linseed oil and its esters of glycerol, trimethylolpropane and pentaerythritol. These polyols were made by selective hydroformylation with a rhodium-triphenylphosphine catalyst followed by catalytic hydrogenation with Raney nickel. Although the hydroxymethylated linseed monoglyceride by itself yielded a satisfactory foam, better foams were made from all hydroxymethylated linseed derivatives when blended with a low-molecular weight commercial polyol. Linseed-derived foams were compared with foams from equivalent formulations of hydroxymethylated monoolein and castor oil. Hydroxymethylated products yielded polyurethane foams meeting the requirements of commercial products with respect to density, compressive strength and dimensional stability.

INTRODUCTION

During the past 10 years, rigid urethane foams have been prepared from castor oil and from various polyols derived from castor oil (1-4), from corn starch glycosides (5,6), from animal fats (7-9) and from fish oils (10). Recently polyformyl vegetable oils were prepared by selective hydroformylation with a rhodium-triphenylphosphine catalyst (11). The polyhydroxymethyl derivatives made by hydrogenation of polyformyl linseed oil should be particularly suitable for urethane foams because of their highly reactive primary hydroxyl groups.

This paper describes the preparation and evaluation of foams made from hydroxymethyl derivatives of linseed oil, linseed monoglycerides and the corresponding monoesters of trimethylolpropane and pentaerythritol. These polyols were compared with castor oil and with hydroxymethyl monostearin made by hydroformylation-hydrogenation of monoolein.

EXPERIMENTAL PROCEDURES

Materials

The linseed oil was commercially refined and bleached. Esters of glycerol, trimethylolpropane and pentaerythritol were prepared by alcoholysis (12). Hydroxymethylated derivatives of linseed oil, linseed esters and monoolein were prepared in two steps by selective hydroformylation with rhodium-triphenylphosphine catalyst (11), followed by catalytic hydrogenation with Raney nickel (13). Reaction conditions and analyses of hydroxymethylated products are summarized in Table I.

Other commercial materials used included castor oil (Baker AA standard OH number 167); monoolein (technical grade, 80%, Eastman); trimethylolpropane (Celanese Corp.); pentaerythritol (Celanese Corp.); N,N,N',N'-tet-

TABLE I

Hydroxymethylated Oils and Esters[a]

	Samples					
	1	2	3	4	5	6
Analyses	HM-LSO[b]	HM-LSO	HM-LMG	HM-LTP	HM-LPE	HM-MO
Gas liquid chromatography,[c] relative %						
Palmitate	5.0	4.7	4.9	6.6	4.5	7.3
Stearate	3.6	3.9	4.0	3.8	3.4	3.0
Other fatty esters	—	0.4	—	2.2	0.6	10.3
HM-mono esters	23.7	21.6	29.7	33.3	23.6	79.4
HM-di esters	24.8	26.6	33.3	36.1	37.5	—
HM-tri esters	42.8	42.8	28.1	18.1	30.4	—
Hydroxyl number[d]	301	336	360	295	344	380
Viscosity,[e] Cp. x 10^3	70.4	70.0	56.0	30.0	278	—

[a] Prepared by hydroformylation followed by hydrogenation. Hydroformylation conditions (11): 1% Rh/C (5%), 0.5% Ph_3P; 110 C–2000 psi H_2 + CO for all samples except for sample 1, 90 C–3500 psi H_2 + CO. Hydrogenation conditions (13): ca. 10% Raney nickel, 100 C–1000 psi H_2.

[b] Abbreviations: HM = hydroxymethylated; LSO = linseed oil; LMG = linseed monoglycerides; LTP = linseed trimethylolpropane ester; LPE = linseed pentaerythritol ester; MO = monoolein.

[c] Analyses of samples 1-5 were made as the acetate esters after saponification, methylation (diazomethane) and acetylation. Sample 6 was acetylated directly. Analytical details in Reference 13. Peak assignments for HM esters are only tentative for samples 3, 4 and 5.

[d] AOCS Official Method Cd 13-60.

[e] Determined at 73 F with Brookfield viscometer (Model RVF).

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TABLE II

Preparation and Properties of Foams from Hydroxymethyl Derivatives of Linseed Oil

Formulations[a] and evaluations	HM-LSO[b]					HM-LMG[b]				HM-LTP			HM-LPE		HM-MO			
Sample:	1	1	2	2	2	3	3	3	3	4	4	4	5	5	6	6	Castor oil	
Foam:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Foams																		
Equivalent weight	110	120	110	120	167	110	110	120	156	110	110	120	110	120	110	120	110	120
HM component, g	33.2	38.5	35.8	41.9	70.0	34.7	38.1	44.1	70.0	32.8	32.8	38.1	38.1	42.6	40	46.6	25.8	30.0
Quadrol, g	26.8	21.5	24.2	18.1	0.0	20.3	21.9	15.9	0.0	27.2	27.2	21.9	21.9	17.5	20	13.4	34.2	30.0
PAPI, g	76.2	70.0	76.2	70.0	59.5	70.0	76.2	70.0	63.7	76.2	76.2	70.0	76.2	70.0	76.2	70.0	76.2	70.0
Evaluations																		
Density, lb/ft^3	1.91	2.01	1.97	2.00	2.41	1.76	1.87	1.95	2.04	1.74	1.87	1.92	1.89	1.85	2.13	2.15	1.89	1.96
Compressive strength, psi																		
Parallel	32.1	26.6	28.5	25.0	19.3	28.9	28.5	25.8	21.1	29.4	34.2	28.7	36.0	27.4	34.5	22.9	25.4	24.2
Perpendicular	12.9	14.4	15.8	14.9	—	12.6	14.6	12.4	12.7	11.1	15.7	15.0	15.9	12.8	18.1	15.2	12.1	12.0
Open cells, %	4	6	7	6	5	3	3	7	8	6	7	6	5	6	5	6	4	7
Humid aging, 158 F																		
Volume change (ΔV), %																		
Days: 1	2.9	3.8	2.8	4.1	7.0	5.1	3.7	4.1	10.2	4.0	1.9	2.2	4.6	4.5	5.8	13.7	2.4	3.8
7	3.8	4.8	3.5	4.3	1.8	8.8	4.8	5.7	9.6	5.6	4.0	3.6	5.9	5.8	6.2	13.7	2.8	3.8
14	5.5	7.5	5.2	7.3	-2.0	12.3	7.1	9.5	11.9	7.8	5.6	5.6	7.3	8.3	9.0	16.0	3.4	4.3
21	5.6	7.3	5.2	7.0	-2.3	12.6	7.4	9.5	10.9	8.2	5.9	6.0	7.7	8.4	8.7	15.2	3.2	4.0
28	5.1	7.1	5.3	6.7	-2.7	11.9	7.6	9.6	10.2	8.6	6.2	6.2	8.0	8.4	8.5	14.6	3.0	3.5
Weight change, %, 28 days	-3.5	-5.2	-4.2	-6.4	7.4	-3.5	-3.1	-3.9	-1.2	-3.2	-2.4	-3.1	-1.7	-1.0	-5.9	-9.0	-6.2	-7.7
Dry aging (ΔV), %, 212 F, 7 days	2.9	4.9	2.7	2.7	—	4.5	3.7	4.6	6.4	4.0	2.1	2.6	2.6	2.7	5.2	16.6	2.1	1.9

[a] Included in addition to the polyols and PAPI the following components: dibutyltin dilaurate 0.03-0.10 g, silicone surfactant (DC 193):1.1-1.2 g, Freon 11:19-20 g. Formulations without Quadrol (Foams 5,9) included also triethylenediamine: 0.60 g, and dimethylethanolamine: 0.60 g.

[b] See Table I for abbreviations.

rakis(2-hydroxypropyl)ethylenediamine ("Quadrol," Wyandotte Chemicals Corp.); polymethylene polyphenylisocyanate (PAPI, Upjohn); dibutyltin dilaurate (Alfa Inorganic, Inc.); trichlorofluoromethane ("Freon 11," E.I. DuPont de Nemours & Co., Inc.); dimethylethanolamine (Union Carbide); triethylenediamine ("Dabco 33," Houdry Process and Chemical Co.); and silicone surfactant (DC 193, Dow Corning Corp.).

Foam Preparations

Polyol mixtures were reacted with PAPI at an NCO/OH ratio of 1.05. Foam formulations are given in Table II. Foams were prepared by adding PAPI to a mixture containing the polyols, catalyst, silicone surfactant and blowing agent (Freon 11). The mixture was blended with a high speed air stirrer and allowed to foam to a creamy appearance at which time it was poured into a 7 x 7 x 3 in. mold. Foams were stored at least 4 days at ambient conditions before being cut into suitable test specimens for evaluation.

Foam Testing

Density was determined by the standard ASTM 1622-59T method. Compressive strength was measured on an Instron tensile tester (Model TTCM). The procedure to determine open cell volume by water displacement was as follows: A measured volume of foam was placed in a closed chamber and evacuated to 4 mm Hg. The evacuated chamber was filled with water. The volume of open cells represents the difference between the calculated foam volume and the observed displacement.

For dimensional stability under humid aging conditions (70 C at 100% relative humidity), the original volume was compared with those after 24 hr and after 1, 2, 3 and 4 weeks of aging. Dry aging stability was determined by exposing samples to 100 C in a forced air oven for 1 week (ASTM D2126-62T).

RESULTS AND DISCUSSION

Foam Preparations

Formulation techniques and compositions were limited to those expected to give the best results based on the study of Leitheiser et al. (14) on castor oil. The hydroxymethylated derivatives of linseed oil have hydroxyl numbers ranging from 295-380 (Table I). These are too low for sufficient crosslinking to produce low density foams of acceptable dimensional and strength properties. Formulations of higher hydroxyl number were achieved by blending the hydroxymethylated oils with Quadrol having a hydroxyl number of 770. Triisopropanolamine and other suitable commercial polyols have been used with castor oil which performed best in blends of equivalent weights of 90-110 (14). For our study hydroxymethylated products and Quadrol were blended to equivalent weights of 110 (OH number 510) and 120 (OH number 467) in the polyol mixtures. Decreasing the equivalent weight reduces the amount of linseed oil polyol that can be added but generally improves the foam formulation.

Hydroxymethylated oil-Quadrol blends were compared with castor oil-Quadrol blends that had equivalent weights of 110 and 120. Control foams were also prepared from hydroxymethylated oils without incorporation of Quadrol.

At any given hydroxyl equivalent weight more hydroxymethylated linseed oil can be incorporated into a foam than castor oil (Table II). This is an important advantage of the new hydroxymethylated oils over castor oil. Another advantage provided by the hydroxymethylated oils is the higher reactivity of their primary hydroxyl groups. Less catalyst was required than is generally used for polyether foams. Handling and mixing characteristics of the hydroxymethylated linseed oil formulations were comparable to the polyether-type formulations (5,6). The rise, cream and tack-free times were within an acceptable range for machine foam equipment. Although some of the hydroxymethylated linseed oils have undesirably high viscosities (Table I), they dissolve readily in the blowing agent, which reduced viscosity to an acceptable level for foam formulation.

Foam Properties

Foams of acceptable densities and compressive strengths were obtained from all formulations blended with Quadrol (Table II). All foams had a high percentage of fine, uniform, closed cells, and none of them were friable.

A foam of poor dimensional stability exposed to the high temperature and high humidity storage test will first expand rapidly and then shrink to near or below its original volume through cell rupture. Good hand-mixed polyether foams generally expand 10-15% of their original volume during 4 weeks of the humid aging test. Foams made from hydroxymethylated oils blended with Quadrol exhibited excellent resistance to the drastic conditions of the humid aging test. Almost all samples expanded less than 10%. Of the two hydroxymethylated oils tested without Quadrol (foams 5 and 9), one sample derived from linseed monoglycerides (foam 9) gave a surprisingly good foam of acceptable compressive strength, density and aging stability. The compressive strength of foam 9 was 21.1 psi compared to 25.8-28.9 psi for the same sample blended with Quadrol (foams 6-8); their densities were 2.04 and 1.73-1.95 lb./ft^3, respectively. Foams from hydroxymethylated linseed oil (foam 5) and monoolein (data not given) without Quadrol were too soft, shrank and increased in density. Poor dimensional stability was also indicated in these foams by shrinkage before or during humid aging.

Results of the 28 day humid aging test show that the addition of Quadrol improved all foams significantly. Foams from blends of equivalent weight of 110 were generally more stable than those from blends of equivalent weight of 120. Foams from castor oil and hydroxymethylated monoolein showed slightly more volume and weight decrease on humid aging than the hydroxymethylated linseed oil derivatives blended with Quadrol at an equivalent weight of 110. The hydroxymethylated linseed oil samples blended with Quadrol at an equivalent weight of 120 were better than the corresponding blends from castor oil and hydroxymethylated monoolein in showing higher compressive strength and less volume increase or weight loss during humid aging.

The urethane foams prepared in this study from hydroxymethylated linseed oil derivatives meet the requirements of commercial products in having low open-cell structure (less than 10%), low density, high compressive strength and dimensional stability (15). These foams would be suitable thermal insulating materials.

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