· Technical

Rigid Urethane Foams from Hydroxymethylated Castor Oil, Safflower Oil, Oleic Safflower Oil, and Polyol Esters of Castor Acids

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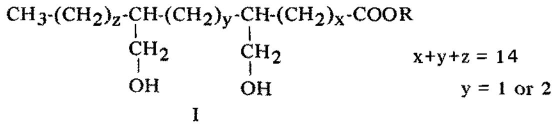
ABSTRACT

Castor, safflower, and oleic safflower oil derivatives with enhanced reactivity and hydroxyl group content were prepared by hydroformylation with a rhodium-triphenylphosphine catalyst, followed by hydrogenation. Rigid urethane foams prepared from these hydroxymethylated derivatives had excellent compressive strengths, closed cell contents, and dimensional stability. Best properties were obtained from hydroxymethylated polyol esters of castor acids.

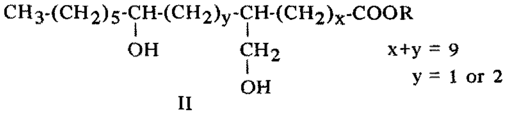
INTRODUCTION

Castor oil can be used to formulate commercially acceptable rigid urethane foams for such uses as thermal insulation and structural support (1). However, it should be possible to prepare superior foams, containing a higher proportion of potentially low cost fatty acid derivatives, by using castor or other oils in which the content of hydroxyl groups has been increased. It has been shown (2,3) that polyols prepared by hydroxymethylating linseed or other unsaturated oils and derivatives are suitable for the preparation of rigid urethane foams. This article describes the evaluation of foams made from hydroxymethyl derivatives of castor, safflower and oleic safflower oils and from some hydroxymethylated polyol esters of castor acids. The dihydroxymethylstearate (I) prepared from linoleate, the principal fatty ester in safflower oil, has been characterized (4). The expected structure of hydroxymethylhydroxystearate (II) obtained from ricinoleate, the principal fatty ester in castor oil, is indicated:



$$CH_3\text{-}(CH_2)_z\text{-}\underset{\substack{|\\ CH_2\\ |\\ OH}}{CH}\text{-}(CH_2)_y\text{-}\underset{\substack{|\\ CH_2\\ |\\ OH}}{CH}\text{-}(CH_2)_x\text{-}COOR \qquad x+y+z = 14,\quad y = 1 \text{ or } 2$$

I



$$CH_3\text{-}(CH_2)_5\text{-}\underset{\substack{|\\ OH}}{CH}\text{-}(CH_2)_y\text{-}\underset{\substack{|\\ CH_2\\ |\\ OH}}{CH}\text{-}(CH_2)_x\text{-}COOR \qquad x+y = 9,\quad y = 1 \text{ or } 2$$

II

EXPERIMENTAL PROCEDURES

Hydroxymethylated Oils

Castor oil, safflower oil, oleic safflower oil, and castor methyl esters (ca. 90% methyl ricinoleate) were hydroformylated at 2000 or 3500 psi H_2+CO with rhodium and triphenylphosphine catalysts (5,6). The hydroxymethylated products were obtained from these derivatives by hydrogenation at 100 C and 1000 psi in the presence of Raney nickel (6). Reaction conditions and analyses of the products are listed in Table I. Additional thin layer chromatographic (TLC) data indicate three diol components in the methyl esters from hydroxymethylated castor oil, the most polar of which has the same R_f as methyl dihydroxymethylstearate. Further characterization of these diols will be reported later (E.N. Frankel, unpublished).

Polyol Esters of Hydroxymethylated Castor Acids (HMHS)

Glycerol hydroxymethylhydroxystearate (G-HMHS): Hydroxymethylated castor methyl esters (Me-HMHS, 103 g, 0.30 moles) and glycerol (220 g, 2.40 moles) were dissolved in 800 ml dioxane with warming. Sodium methoxide catalyst (2.0 g) was added and the mixture refluxed for 20 hr. To remove methanol, refluxing solvent was returned through 80 g of 4A molecular sieve (Matheson Coleman and Bell, Norwood, Ohio) in a Soxhlet thimble. After the catalyst was neutralized with 3 ml conc. HCl, most of the dioxane was removed on a rotary evaporator, and the mixture was diluted with 300 ml ether. Glycerol (160 ml) which separated was removed. The ether solution was washed 4 times with water, dried over $MgSO_4$, and evaporated to yield 105 g G-HMHS (hydroxyl[OH] value 380.5, acid value 7.0). NMR spectra ($-OCH_3$ band at δ 3.64 ppm) showed ca. 95% conversion of methyl ester.

Trimethylolpropane hydroxymethylhydroxystearate (TMP-HMHS): Using a similar procedure, 65 g TMP-HMHS (OH value 332.6, acid value 7.6) was obtained from 69 g Me-HMHS and 132 g trimethylolpropane. NMR spectra ($-OCH_3$ band at δ 3.64 ppm) showed ca. 99% conversion of methyl ester.

Pentaerythritol hydroxymethylhydroxystearate (PE-HMHS): A mixture of 103 g (0.30 moles) Me-HMHS, 61 g (0.45 moles) pentaerythritol, and 2.0 g sodium methoxide was heated under vacuum at 200-220 C for 4 hr. The product was cooled, taken up in ether, washed with 0.5 N HCl, then with water until neutral. The ether solution was dried over $MgSO_4$ and evaporated to yield 87.2 g PE-HMHS (OH value 281, acid value 1).

Preparation and Evaluation of Foams

Rigid urethane foams were prepared by procedures used previously with castor oil (7). Polymethylene polyphenylisocyanate (PAPI) (Upjohn Co., Kalamazoo, Mich.) was reacted with blends of the above hydroxymethlated deriva-

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[1] ARS, USDA.

TABLE I

Preparation and Analyses of Hydroxymethylated Oils

Analyses and reaction conditions	Castor oil	Castor Me esters	Safflower oil	Oleic safflower oil
Hydroformylation[a]				
Catalyst (5%)	Rhodium/$CaCO_3$	Rhodium/$CaCO_3$	Rhodium/C	Rhodium/C
Catalyst concentration, wt %	1	1	1	1
Ph_3P, wt %	0.5	0.5	0.5	0.9
Solvent	Toluene	Toluene	Toluene	None
Temperature, C	110	110	90	110
H_2 + CO 1:1, psig	2,000	2,000	3,500	2,000
Time, hr.	3	3	4-1/2	3
Gas liquid chromatographic analysis[a,b]				
Saturates, %	---	---	12.6	9.5
Monoformyl, %	---	---	20.4	90.5
Diformyl, %	---	---	67.0	---
Hydroxymethylated products[c]				
Gas liquid chromatography[d]				
Saturates, %	2.1	2.1	7.0	8.9
Monohydroxy, %	18.9	13.0	23.9	91.1
Dihydroxy, %	79.0	84.9	69.1	---
Hydroxyl value[e]	321	315	238	185
Acid value	4	4	0	0
Equivalent wt [f]	173	176	236	303

[a] Ref. 5.

[b] On methyl esters, JXR silicone column programed from 180-260 C at 2 C/min, flame ionization detector. Hydroformylated castor esters showed several peaks which were not identified.

[c] Prepared by hydrogenation of hydroformylated products with Raney nickel at 100 C/1000 psig H_2.

[d] On acetate esters.

[e] Calculated values for methyl hydroxymethylstearate = 170.5; methyl dihydroxymethylstearate = 312.5; methyl hydroxymethylhydroxystearate = 325.

[f] Equivalent wt = 56,100/(hydroxyl value + acid value).

TABLE III

Rigid Urethane Foams from Hydroxymethylated Oils and Polyol Esters of Castor Acids

Polyol blend			Polyol blend average equivalent wt	Foam properties						
					Compressive strength^{b}			Humid aging, 70 C, 100% relative humidity		
Percent	Polyol^{a}	Copolyol		Density	parallel	perpendicular	Closed cells	1 day	7 day	14 day
		Percent quadrol		lb/ft^{3}	psi	psi	%	Δ volume %	Δ volume %	Δ volume %
34.5	Castor oil	65.5	100	2.14	42	21	91	5.1	5.1	8.5
43.1	Castor oil	56.9	110	2.17	41	20	93	3.4	8.5	8.5
50.1	Castor oil	49.9	120	2.47	32	17	91	5.1	5.1	8.5
46.6	HM castor oil	53.4	100	2.36	40	20	93	5.1	5.1	5.1
58.2	HM castor oil	41.8	110	2.34	36	19	91	3.4	5.1	8.5
67.7	HM castor oil	32.3	120	2.44	34	17	91	6.8	5.1	5.1
35.6	HM oleic safflower oil	64.4	100	2.17	41	17	91	6.8	---	8.5
44.3	HM oleic safflower oil	55.7	110	2.17	38	20	92	6.8	5.1	5.1
51.6	HM oleic safflower oil	48.4	120	2.19	35	18	92	8.5	1.7	5.1
39.1	HM safflower oil	60.9	100	2.26	44	22	92	3.4	5.1	8.5
48.7	HM safflower oil	51.3	110	2.32	44	18	90	5.1	8.5	6.8
56.8	HM safflower oil	43.2	120	2.21	36	15	93	8.5	5.1	8.5
54.4	G-HMHS	45.6	100	2.03	47	20	91	5.1	10.2	10.2
67.7	G-HMHS	32.3	110	2.04	43	21	91	3.4	5.1	8.5
78.8	G-HMHS	21.2	120	2.13	42	17	92	10.2	8.5	8.5
48.5	TMP-HMHS	51.5	100	2.08	48	19	93	5.1	8.5	11.9
60.4	TMP-HMHS	39.6	110	2.07	42	22	90	3.4	1.7	5.1
70.2	TMP-HMHS	29.8	120	2.04	42	18	91	5.1	8.5	11.9
42.5	PE-HMHS	57.5	100	2.33	49	20	92	5.1	3.4	5.1
53.0	PE-HMHS	47.0	110	2.49	37	20	87	0	-1.7	3.4
61.6	PE-HMHS	38.4	120	2.42	39	17	91	5.1	5.1	8.5
		Percent TIPA								
46.7	Castor oil	53.3	100	2.12	43	19	94	5.1	1.7	5.1
53.6	Castor oil	46.4	110	2.21	38	18	92	1.7	3.4	5.1
59.3	Castor oil	40.7	120	2.16	31	17	92	6.8	3.4	5.1
59.2	HM castor oil	40.2	100	2.25	44	19	91	5.1	3.4	8.5
68.0	HM castor oil	32.0	110	2.22	38	19	93	5.1	8.5	8.5
75.3	HM castor oil	24.7	120	2.47	32	18	93	8.5	5.1	10.2

[a] Abbreviations: HM = hydroxymethylated, HMHS = hydroxymethylhydroxystearate, G = glycerol, TMP = trimethylolpropane, PE = pentaerythritol, Quadrol = N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylenediamine, and TIPA = triisopropanolamine.

[b] Normalized to compressive strength at density of 2.00 lb/ft^{3} (7).

TABLE II

Proportions of Polyols and Polyisocyanate in Foam Formulations

Polyol equivalent wt	Percent polyol blend	Percent polymethylene polyphenylisocyanate
100	41.3	58.7
110	43.6	56.4
120	45.8	54.2

tives with either triisopropanolamine (TIPA) or N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine (Quadrol) (BASF Wyandotte Corp., Wyandotte, Mich.) using a NCO/OH ratio of 1.05. The foam mixtures also included,/100 g polymer: 14.5 g CCl_3F, 1.0 g L-530 silicone oil (Union Carbide Corp., New York, N.Y.) and 0.02-0.10 g dibutyltin dilaurate (Union Carbide Corp.).

The polyol blends, with average equivalent wt of 100, 110, and 120 were reacted with PAPI (equivalent wt. 135) in the proportions listed in Table II to yield ca. 90 g each foam:

All tests were run as described previously (7) on 1 in. high x 1.5 in. diameter pellets. To facilitate comparisons, compressive strengths were normalized, as described previously (8), to those of foams with a density of 2 lb/ft^3.

RESULTS AND DISCUSSION

The hydroxymethyl derivatives of this investigation had much higher hydroxyl values (185-381) than does castor oil (167) but still required the addition of low mol wt polyols to form polyol blends with hydroxyl values of 467-561 that would yield low density, rigid urethane foams with satisfactory properties. Properties of the foams prepared from these hydroxymethyl derivatives are compared in Table III with those of foams prepared from castor oil.

All these foams had high closed cell contents, excellent resistance to shrinkage on humid aging, and satisfactory compressive strengths that were affected more by the average equivalent wt than by the composition of the polyol. Somewhat stronger foams, particularly at the highest polyol equivalent wt, were obtained from glycerol and trimethylolpropane hydroxymethylhydroxystearates. Satisfactory foams were obtained using either Quadrol or TIPA as the copolyol.

At a given compressive strength level, determined by the average polyol equivalent wt, the amount of fatty acid based polyol that can be incorporated increases in the following order: castor oil, HM oleic safflower oil, HM safflower oil, HM castor oil, TMP-HMHS and glycerol-HMHS. The hydroxymethylated oils and derivatives, with their primary hydroxyl groups, were more reactive and generally required less catalyst than did castor oil or other commonly used polyols with secondary hydroxyl groups.

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