Polyurethane Foams from Hydroxymethylated Fatty Diethanolamides

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ABSTRACT

Satisfactory rigid polyurethane foams were prepared from diethanolamides of hydroxymethylated oleate, linseed oil, safflower oil and their methyl esters. These foams were improved when the fatty polyols were blended with a commercial, low molecular weight polyol.

INTRODUCTION

Because of increased demand for rigid urethane foams in new applications, there is a need for more raw materials meeting specific cost and property requirements.

Numerous studies have demonstrated that fatty polyols offer certain advantages in foam formulations (1-10). However one apparent disadvantage of fatty polyols in rigid foam applications is their low hydroxyl number and poor distribution of hydroxyls in the glyceride molecule. The hydroxyl groups in castor oil and other fatty polyols are widely spaced so that when they crosslink with diisocyanate there are insufficient "hard segments" to yield a stable rigid foam.

One approach to increasing the number of hydroxyl groups and improving their distribution is to use polyol fatty diethanolamide derivatives. For example, acceptable foams have been prepared from N,N-*bis*(2-hydroxyethyl)ricinoleamide (1). Hydroxymethylated oils and partial glycerides offer another approach to increasing hydroxyl content and improving the degree of crosslinking necessary for stable rigid foams. We have made foams from hydroxymethylated linseed oils and partial glycerides (11). These foams and others were markedly improved when fatty polyols were blended with a low molecular weight polyol, such as triisopropanolamine or Quadrol (N,N,N',N'-*tetrakis*[2-hydroxypropyl] ethylenediamine).

In a continuing effort to increase hydroxyl distribution and content in fatty polyols, we prepared a series of hydroxymethylated fatty diethanolamides and evaluated them in standard foam formulations. The new polyols are readily synthesized by reaction of diethanolamine with either fats or their methyl esters. Compared to natural fatty polyols, the new ones have up to five primary hydroxyl groups per fatty acid positioned to favor crosslinking with the diisocyanate.

EXPERIMENTAL PROCEDURES

Polyol Synthesis

Linseed oil (Superb Linseed Oil, Archer Daniels Midland), linseed fatty esters, safflower oil fatty esters (G. Fuller, Western Regional Research Lab.) or methyl oleate were hydroformylated at 90 C and 3500 psi $H_2 + CO$ with a mixture of 1% Rh/C (5%) and 0.5% Ph_3P as catalyst (12,13). The hydroformylated products were converted to hydroxymethyl derivatives by hydrogenation at 100 C and 1000 psi H_2 in the presence of 10% Raney nickel (12). A typical procedure to make hydroxymethylated fatty diethanolamides from diethanolamine and hydroxymethyl fatty derivatives is as follows: Diethanolamine (147.2 g [1.4 mol], Fischer Scientific Co.) was placed in a three-necked flask fitted with a stirrer, thermometer, nitrogen inlet, dropping funnel and Dean Stark trap. Sodium methoxide catalyst (1.9 g) was added and the flask heated to 110 C. Hydroxymethylated fatty methyl esters were added (230.0 g, 0.7 mol) dropwise. Liberated methanol was collected in the Dean Stark trap. The mixture was heated for an additional 2 hr. Excess diethanolamine and byproducts were removed by washing an ethereal solution of the crude product with 15% aqueous NaCl solution. Properties of the polyols are summarized in Table I.

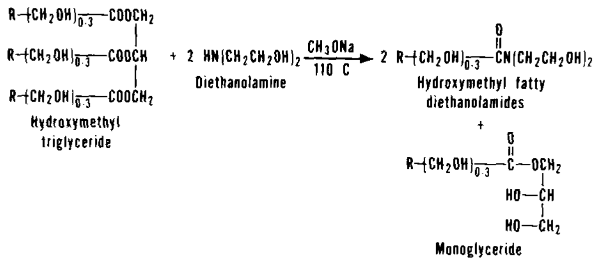
Foam Preparations and Evaluations

All foams were prepared as before (11) by reacting polymethylene polyphenylisocycnate (PAPI) with a polyol or polyol mixture at an NCO/OH ratio of 1.05. The amount of Freon 11 blowing agent added was 14-16 parts per 100 parts of polymer. Test methods included: Density, ASTM D1622-63; compressive strength, ASTM D1621-64; dimensional stability under "humid" and "dry" conditions, ASTM D2126-62T; open cell content, National Aniline Standard Test CF-TM2 (water was substituted for methanol).

RESULTS AND DISCUSSION

Diethanolamide Polyols

Diethanolamine reacts readily with hydroxymethyl fatty esters to form the corresponding diethanolamides (equations 1-3).



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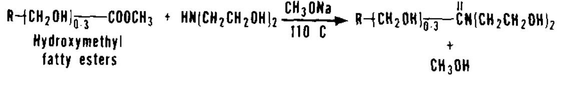

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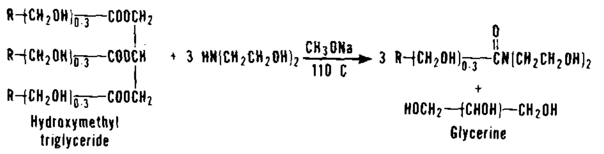

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When 1 mol hydroxymethyl linseed oil was reacted with 2 mol diethanolamine according to equation 1, the polyol product theoretically should have contained 2 mol hydroxymethyl linseed diethanolamide and 1 mol of its monoglyceryl esters (foams 1 and 2, Table I). However the reaction was incomplete and the hydroxymethyl fatty

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TABLE I

Foam Formulations and Properties

	HM-LS-DEA[a]				HM-S-DEA	HM-SF-DEA		Castor oil[b]
Formulations and evaluations	1	2	3	4	5	6	7	8
Analyses								
Hydroxyl no.[c]	383	383	415	415	395	419	419	167
Viscosity[d]	105	105	49	49	10	27.5	27.5	7.5
Color[e]	10	10	12	12	1	12	12	1
Polyol blend								
Equivalent wt	146	110	135	110	110	134	110	110
Hydroxyl no.[c]	383	510	415	510	510	419	510	510
B components,[f] g								
Polyol	65.0	40.3	65.0	44.0	41.6	65.0	44.4	25.8
Quadrol	0.0	19.7	0.0	16.0	18.4	0.0	15.6	34.2
DABCO 33	0.6	0.0	0.6	0.0	0.0	0.6	0.0	0.0
DBTDL	0.1	0.09	0.1	0.06	0.03	0.1	0.03	0.03
DMEA	0.6	0.0	0.6	0.0	0.0	0.6	0.0	0.0
A component, g								
PAPI	61.9	76.4	67.1	76.4	76.4	67.9	76.4	76.2
Properties								
Foaming time, sec								
Stir	20	27	25	23	25	40	22	15
Tack-free	40	38	45	45	40	40	37	29
Rise	45	45	50	45	45	50	42	38
Density, lb/ft^3	2.054	1.937	2.057	2.054	1.850	1.893	1.807	1.890
Compressive strength, psi								
Parallel	20.4	27.7	25.9	33.6	23.8	18.2	28.6	25.4
Perpendicular	15.2	21.4	13.3	23.7	14.7	13.5	13.6	12.1
Open cells, %	4.2	7.5	6.4	5.5	5.3	6.0	3.6	4.0
Volume change, %								
Humid aging, 158 F, 100% relative humidity, days								
1	7.2	5.4	-1.3	3.1	13.7	0.5	7.2	2.4
7	5.1	5.8	-0.2	2.6	10.9	-0.6	4.3	2.8
14	-4.4	6.5	-0.8	2.6	9.9	-2.6	4.0	3.4
21	-5.8	6.8	-0.5	3.2	8.3	-2.4	4.1	3.2
28	-11.2	7.2	-0.8	2.1	3.6	-3.8	4.6	3.0
Dry aging, 212 F, 7 days	-7.6	2.4	-3.0	-1.4	6.1	1.9	13.6	2.1

[a] Abbreviations: HM = hydroxymethylated; LS = linseed; S = stearate; SF = safflower; DEA = diethanolamide. Foams 1-4 made from linseed oil; foams 5-7 made from fatty methyl esters.

[b] Baker Castor Oil Co., Bayonne, N.J. Viscosity in stokes at 25 C as reported by the supplier.

[c] AOCS Official Method CD 13-60.

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

[e] Gardner (14).

[f] Quadrol (N,N,N',N'-*tetrakis*[2-hydroxypropyl]ethylenediamine); DABCO 33 (triethylenediamine); DBTDL (dibutyltin dilaurate); DMEA (dimethylethanolamine); PAPI (polymethylene polyphenylisocyanate). Also included: DC 193 (silicon oil) 1.2 g; Freon 11 (trichloromonofluoromethane) 20.0 g.

diethanolamides contained mono- and diglyceryl esters together with unreacted hydroxymethyl oils. Reaction 2 (foams 5-7) and reaction 3 (foams 3 and 4) were carried out with 2 and 6 mol, respectively, of diethanolamine (100% excess) to yield hydroxymethyl fatty diethanolamides and methanol or glycerine as byproducts. The unreacted diethanolamine and byproducts were removed by water washing. The unsaturated fatty esters were converted to their corresponding diethanolamides with two primary hydroxyl functions, whereas the hydroxymethylated fatty esters yielded diethanolamides with three to five primary hydroxyls available for branching and crosslinking of the polymers.

Foams

The hydroxyl numbers of the diethanolamides are still too low to produce, by themselves, low density foams with acceptable dimensional and strength properties. Therefore, as in the previous study (11), blends of hydroxymethyl fatty diethanolamides and Quadrol with an equivalent weight of 110 were formulated into foams. Control foams were also prepared from the hydroxymethylated diethanolamides without adding Quadrol.

Formulations given in Table I reveal that, at a hydroxyl equivalent weight of 110, more hydroxymethylated diethanolamides can be incorporated into foams than castor oil. Another desirable property of these new polyols is the higher reactivity of their primary hydroxyl groups. Although foams from the polyols were satisfactory without Quadrol (foams 1, 3 and 6), their dimensional stability was rather poor. More shrinkage was observed at higher polyol equivalent weight (foam 1). When the polyols were blended with Quadrol to an equivalent weight of 110 (foams 2, 4 and 7), volume change of the foams was negligible. Foams made from hydroxymethylated safflower and linseed diethanolamides exhibited excellent resistance under high temperature and humidity during storage (foams 1-4, 6-7). However foam made with hydroxymethylstearic diethanolamide and Quadrol (foam 5) expanded slightly more than 10% after 1 day humid aging conditions and then shrank to near its original volume. Generally, compressive strength of the foams increased markedly and their tendency to shrink decreased as the hydroxyl equivalent weight of the polyol decreased.

All foams made from these polyols meet the requirements of commercial products with respect to density, compressive strength and dimensional stability (15).

ACKNOWLEDGMENT

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