Rigid Polyurethane Foams from Diethanolamides of Carboxylated Oils and Fatty Acids

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ABSTRACT

New polyols of high hydroxyl content and reactivity were made from linseed and soybean oils and acids by catalytic carboxylation followed by reaction with diethanolamine. Urethane foams made with these diethanolamides were stronger than those made with castor oil at equivalent polyol wt. Because of their higher hydroxyl content, a larger amount of diethanolamides could be incorporated in foam formulations than is possible with castor oil. The rigid urethane foams prepared with the new polyols meet the requirements of commercial products with respect to density, compressive strength, and dimensional stability.

INTRODUCTION

Castor oil is a useful natural polyol to make rigid urethane foams suitable for thermal insulation and structural supports (1). Another source of fatty polyols is from the reaction sequence: hydroformylation, or oxo reaction, of polyunsaturated fats with a rhodium:triphenylphosphine catalyst followed by catalytic hydrogenation with Raney nickel (2,3). These oxo-derived hydroxymethylated oils have a larger number of hydroxyl groups that are primary and more reactive than the secondary hydroxyl groups of castor oil; consequently, a higher proportion of hydroxymethyl oils than of castor oil can be incorporated into foam formulations (4). Superior foams were made from hydroxymethylated castor oil, safflower oil, oleic safflower oil, and polyol esters of castor acids (5). The hydroxyl content of hydroxymethylated oils was increased further by reacting them with diethanolamine. Satisfactory rigid polyurethane foams were made from the diethanolamides of all these hydroxymethylated fats (6).

Still another source of fatty polyols is available by direct carboxylation of unsaturated fats. Polycarboxy acids have been prepared from vegetable oils by reaction with palladium catalysts, CO, and water (7). The diethanolamides of carboxylated oils and fatty acids were expected to be particularly suitable for rigid urethane foams because of their increased distribution of reactive primary hydroxyl groups. This paper describes the evaluation of carboxylic acid diethanolamides in standard foam formulations and their comparison with castor oil foams.

EXPERIMENTAL PROCEDURES

Carboxylated Oils

Linseed and soybean oils and their fatty acids were hydrocarboxylated with water:carbon monoxide (3200-4000 psi) at 140-150 C with a palladium chloride-triphenylphosphine catalyst (7,8) (Table I). Acid values of products were within 90-95% of the values calculated from gas liquid chromatography (GLC) analyses. This deviation from calculated values is due to ca. 5-10% neutral cyclic ketone included in the GLC peak corresponding to monocarboxy acids (7).

Polyol Synthesis

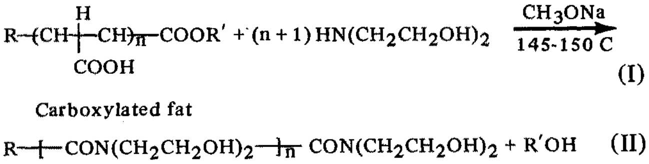
A typical procedure to prepare carboxylated fatty diethanolamides (6) follows: Carboxylated oils or acids were stirred with diethanolamine (100% excess based on carboxyl equivalent) and sodium methoxide (0.5% by wt). The mixture was heated at 145-150 C under N_2 until the theoretical amount of water was collected in a Dean-Stark trap. Reaction times varied from 18 to 48 hr. The cooled reaction mixture, dissolved in a mixture of ethyl acetate and ethanol, was washed with water until neutral. The solution dried with Na_2SO_4 was filtered, and the solvent was stripped off in vacuum. Analyses for hydroxy value of polyols are given in Table I.

Foam Preparation and Evaluations

Foams were prepared by reacting polymethylene polyphenylisocyanate (PAPI) (Upjohn Co., Kalamazoo, MI) with the polyol mixture at an NCO:OH ratio of 1.05. The same procedure and test methods were used previously (4).

RESULTS AND DISCUSSION

Diethanolamine reacts with carboxylated oils and fatty acids to form the corresponding diethanolamides.



$$R\text{—}(\underset{\text{COOH}}{\overset{\text{H}}{\text{CH}}}\text{—CH})_n\text{—COOR}' + (n+1)\,HN(CH_2CH_2OH)_2 \xrightarrow[\text{145-150 C}]{CH_3ONa} \qquad \text{(I)}$$

Carboxylated fat

$$R\text{—}[\text{—}CON(CH_2CH_2OH)_2\text{—}]_n\ CON(CH_2CH_2OH)_2 + R'OH \qquad \text{(II)}$$

R′ = H or triglyceride radical n = 0,1,2,3

TABLE I

Analyses of Carboxylated Products and Their Diethanolamide Derivatives

Starting materials	Carboxylated products: GLC analysis[a] (%): Pal	St	Un	Carboxy acids: Mono[b]	Di	Tri	Acid value	Diethanolamides: Hydroxyl value
Linseed oil	4.9	3.9	0.7	32.6	24.6	33.3	225	373
Linseed acids	5.5	3.3	0.4	25.3	25.6	39.9	368	367
Soybean oil	9.0	3.4	5.6	40.1	37.6	4.3	173	311
Soybean acids	10.6	5.1	7.0	47.6	27.5	2.2	293	309

[a] By gas liquid chromatography (GLC) analysis of methyl esters on JXR column (2). Triglycerides were saponified and methylated (diazomethane); acids were methylated (diazomethane); Pal = palmitate, St = stearate, Un = unsaturates.

[b] Includes 5-10% cyclic ketones (7).

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TABLE II

Preparation and Properties of Foams from Carboxylated Diethanolamides

	Starting Materials											
	Linseed oil			Linseed acid		Soybean oil			Soybean acids			Castor oil[a]
	Foams											
Formulations and evaluations	1	2	3	4	5	6	7	8	9	10	11	12
Polyol blend												
Equivalent wt	150	110	110	110	110	180	110	110	181	110	110	110
Hydroxyl value	373	510	510	510	510	311	510	510	309	510	510	510
B components[b] (g)												
Diethanolamides	60.0	39.3	39.3	38.7	38.7	60.0	34.0	34.0	60.0	33.8	33.8	25.8
Quadrol	0.0	20.7	20.7	21.3	21.3	0.0	26.0	26.0	0.0	26.2	26.2	34.2
A component (g)												
PAPI	55.9	76.4	76.4	76.4	76.4	46.7	76.4	76.4	46.3	76.4	76.4	76.2
Properties												
Foaming time (sec)												
Stir	60	40	60	20	40	70	40	40	60	20	40	15
Tack free	150	80	90	40	80	155	70	80	150	40	85	29
Rise	150	85	95	40	85	160	80	90	150	40	90	38
Density (lb/ft^3)	1.93	1.81	1.84	1.86	1.90	1.70	1.83	1.81	1.71	1.87	1.95	1.89
Compressive strength (psi)												
Parallel	23.9	30.1	26.5	33.0	38.4	17.4	34.8	36.9	19.8	23.7	26.4	25.4
Perpendicular	16.1	15.2	15.0	15.2	14.9	13.0	13.2	15.7	13.0	16.4	26.0	12.1
Closed cell (%)	93.0	93.7	95.6	95.1	95.9	94.2	93.2	95.3	90.4	97.2	90.7	96.0
Volume change (%)												
Humid aging [d] (158 F)												
1 day	5.5	4.8	9.3	6.7	7.7	6.6	4.4	5.3	9.0	4.5	3.9	2.4
7 days	6.2	7.7	8.2	9.0	6.5	-2.8	6.8	1.6	6.3	6.8	5.0	2.8
14 days	6.2	8.8	8.8	9.6	7.0	-6.0	8.6	5.2	3.0	8.2	5.7	3.4
Dry aging (212 F)												
7 days	1.3	9.0	5.8	5.8	4.5	3.0	11.9	12.4	-1.7	5.1	7.2	2.1

[a] Hydroxyl value:167. Provided by NL Industries, Bayonne, NJ.

[b] All formulations included 1.2 g silicone oil and 20.5 g Freon 11 (trichloromonofluoromethane). Foams 1, 6, and 9 without Quadrol included 0.50 g triethylenediamine. Foams 4, 10, and 12 included 0.030 g dibutyltin dilaurate. Quadrol = [N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine].

[c] PAPI = Polymethylene polyphenylisocyanate.

[d] 100% Relative humidity.

The alkanolamides formed readily with either the terminal carboxy acid or the triglyceride ester but much more slowly with the internal branched carboxy acid groups. This low reactivity of the internal branched carboxy acids to esterification is well known (9,10). The long reaction times caused side reactions as evidenced by infrared spectra (IR) (new ester bands at 1740 cm^{-1}) and lower hydroxyl value than expected. These side reactions may be due to interesterification of internal carboxy acid groups of one diethanolamide with the free ethanolamine of another diethanolamide molecule.

Although side reaction problems were encountered in preparing the carboxy acid diethanolamides, these polyols had much higher hydroxyl values (309-373) than castor oil. Blends with Quadrol [N,N,N'N'-tetrakis (2-hydroxypropyl) ethylenediamine] were made to increase the hydroxyl content to an equivalent wt of 110. Foams prepared from these carboxy acid diethanolamides and blends with Quadrol were compared with foams made with an equivalent castor oil-Quadrol blend (Table II).

Control foams (Nos. 1, 6, and 9) were made with diethanolamide polyols without Quadrol and required triethylenediamine catalyst. Foams 4, 10, and 12 that included dibutyltin dilaurate as a catalyst required shorter stir times. Without catalyst, however, stir times were adequate for homogenous stirring and foaming of the mixtures.

All formulations gave foams with acceptable densities (in the range 1.70-1.95) (Table II). All foams from polyol blends with Quadrol had high closed cells, excellent resistance to shrinkage on humid aging, and good compressive strengths. Foams from linseed polyols with Quadrol were the best and showed higher compressive strength than those from equivalent blends of castor oil.

Foams 1, 6, and 9 from diethanolamides without Quadrol were generally satisfactory, but their dimensional stability was poorer than those made from blends with Quadrol. Of these three diethanolamides, one sample from linseed oil gave a surprisingly good foam (No. 1) that had acceptable compressive strength and density; another from soybean acids gave a foam (No. 9) that had good aging stability.

Carboxylated fat diethanolamides have an advantage over castor oil for foam formulations because they can be incorporated in higher amounts. Foams of acceptable properties were even made without the copolyol Quadrol, which is essential with castor oil (1). In general, the urethane foams prepared from diethanolamide derivatives of carboxylated linseed and soybean oils meet requirements for commercial products with respect to density, compressive strength, and dimensional stability (11). Suitable uses include thermal insulation and structural supports.

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