Rigid Urethane Foams from Blown Castor Oils[1]

C. K. LYON, VILMA H. GARRETT, and L. A. GOLDBLATT,[2]
Western Regional Research Laboratory,[3] Albany, California

Abstract

Solvent-blown rigid urethane foams prepared from a low-cost polyol mixture composed of raw castor oil and triisopropanolamine have been described. Foams with higher compressive strengths can be obtained by substituting oxidized (blown) castor oil for the raw castor oil in formulations of this type.

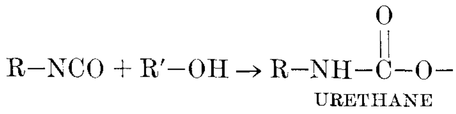
The properties of rigid foams prepared from several commercial blown castor oils are described. The properties of these foams are correlated with the degree of oxidation of the blown oils used, as indicated by their oxygen content, density, viscosity, and refractive index. Removal of acid from blown oils having high acid values has no significant effect on the compressive strength of foams prepared from these oils.

When blown castor oil is used instead of raw castor oil, less isocyanate is required to produce a urethane foam of specified density and compressive strength.

Introduction

The production and use of rigid polyurethane foamed plastics has increased rapidly in the past decade and is expected to increase even more rapidly in the next few years. This rigid foam is used chiefly as an insulating material, in structural panels, and in flotation equipment.

The principal reaction involved in the preparation of rigid urethane foams is that between isocyanates and hydroxy compounds to form urethanes.



$$\text{R–NCO} + \text{R}'\text{–OH} \rightarrow \text{R–NH–}\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}\text{–O–R}'$$

URETHANE

The most commonly used isocyanate is toluene diisocyanate but many polyhydroxy compounds (or polyols), containing three to eight hydroxyl groups per molecule, are used. Castor oil is one of the trihydroxy compounds which may be included in the polyol. The use of a difunctional isocyanate plus a polyfunctional hydroxy compound yields a highly crosslinked polyurethane polymer. This reaction is exothermic, and in solvent-blown foams the heat generated is used to vaporize a dissolved low-boiling solvent, such as trichlorofluoromethane, which expands the plastic to a foam while it is being formed.

In this work, a two step procedure was used. This is known to yield superior rigid foams in many cases. A prepolymer was first prepared from all of the isocyanate plus a portion of the polyol. This prepolymer was then reacted with the remainder of the polyol, in the presence of the blowing agent and other additives, to produce a foamed plastic.

The preparation of solvent-blown rigid urethane foams from low-cost castor oil-triisopropanolamine polyol mixtures has been reported (1). The present paper is concerned with an investigation of the effect on the properties of these foams of substituting blown or oxidized castor oil for raw castor oil.

TABLE I

Castor Oil—Triisopropanolamine Polyol Mixtures

Equiv. weight of polyol mixture	Polyol composition[a]	
	Castor oil (raw or blown)	Triisopropanolamine
	%	%
100	43.1–44.9	56.9–55.1
120	56.0–58.0	44.0–42.0
140	65.0–67.6	35.0–32.4

[a] Range of composition due to variation in equivalent weight of castor oil samples (see Table II).

Test Methods

Blocks 4 x 4 x 11 in. cut from 250 g batches of foam were used for the determination of thermal conductivity. All other tests were run on 1 in. high x 1.5 in. diam pellets cut parallel to the direction of foam rise from 10 g batches of foam.

Density. The procedure of ASTM D 1622-59T was used.

Compressive Strength. The procedure of ASTM D 1621-59T was used except that the cross-sectional area of the test specimens was 1.768 in.^{2} All compressive strengths are reduced, by means of the empirical relationship described previously (2), to those of a foam with a density of 2 lb/ft.^{3}

Humid Aging. Sample volumes were measured before and after aging over water in a desiccator for 14 days at 70C.

Per Cent Closed Cells. The method of Remington and Pariser (3) was used except that displacement volumes were determined with a Beckman Model 930 Air Comparison Pycnometer using the modified 0.5–1.0 atmosphere procedure. This procedure is similar to that reported recently by Rice and Nunez (4).

Thermal Conductivity. The Pittsburgh Corning Thermal Conductivity Probe (5), manufactured by Custom Scientific Instruments Co., was used.

Experimental and Discussion

To prepare the prepolymer, a mixture containing 78% toluene diisocyanate (80% 2,4-isomer; 20% 2,6-

TABLE II

Castor Oils—Raw and Blown

Castor oil[a]	Oxygen content[b]	Density $d^{25/25}$	Viscosity at 25C (Brookfield)	Refractive index n_D^{25}	Acid value[c]	OH value[d]
	%		poise			
Raw	15.2	0.9601	6	1.4775	1	164
Blown No. 1	15.8	0.9668	10	1.4780	4	168
Blown No. 2	16.6	0.9759	17	1.4786	9	136
Blown No. 3	17.2	0.9924	36	1.4811	9	150
Blown No. 4	18.1	0.9956	47	1.4800	16	158
Blown No. 5	18.7	1.0126	660	1.4838	14	140
Blown No. 6	19.4	1.0156	295	1.4832	18	144
Blown No. 7	19.7	1.0162	228	1.4825	21	150
Blown No. 8	19.7	1.0178	202	1.4821	25	143

[a] Blown No. 1—Pale 170 Oil—Baker Castor Oil Co.
Blown No. 2—K Oil—Baker Castor Oil Co.
Blown No. 3—Prepared by bubbling a rapid stream of air through raw castor oil for 4 hr at 175C.
Blown No. 4—Blown Z-2—Pacific Vegetable Oil Co.
Blown No. 5—OX-50 Oil—Spencer Kellogg.
Blown No. 6—15 Oil—Baker Castor Oil Co.
Blown No. 7—Pale 16 Oil—Baker Castor Oil Co.
Blown No. 8—Blown Z-6 HA—Pacific Vegetable Oil Co.

[b] 100 − (%C + %H).

[c] AOCS method.

[d] Acetylation in pyridine, 20 hr/RT (6).

---

[1] Presented at the AOCS meeting in Toronto, Canada, 1962.

[2] Present address: Southern Regional Research Laboratory, New Orleans, La.

[3] A laboratory of the W. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

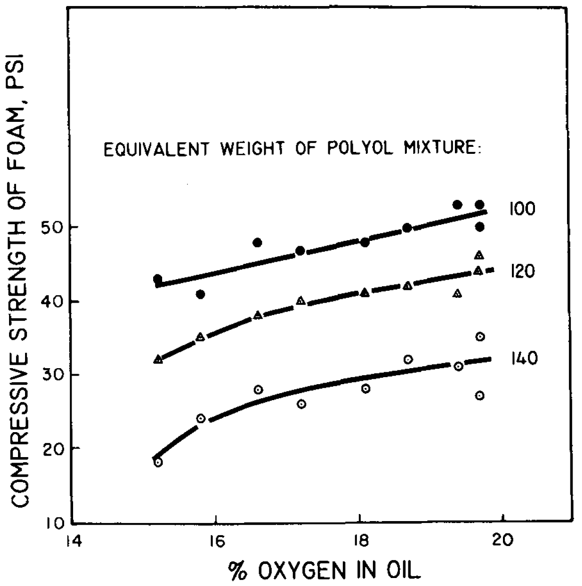


Fig. 1. Effect of oxygen content of castor oil in polyol mixture on compressive strength of foam.

isomer) and 22% Atlas G-2408 (adduct of sorbitol and propylene oxide with OH value of 574) was heated under nitrogen for 1 hr at 75C. This prepolymer had a viscosity at 25C of 8,000–10,000 cps and an isocyanate content of 27.5–28.0%.

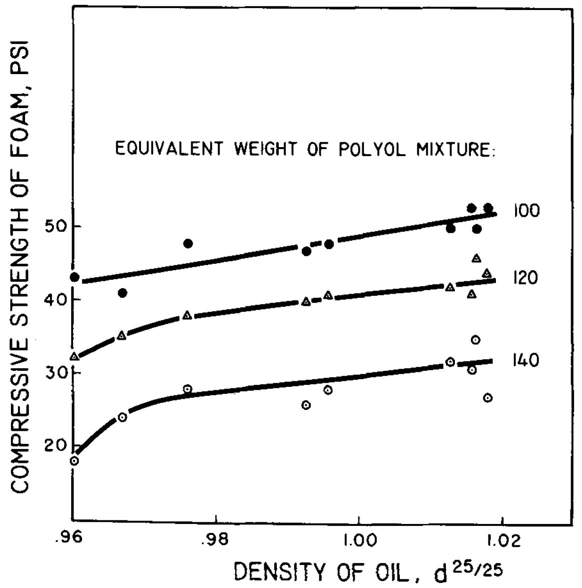


Fig. 2. Effect of density of castor oil in polyol mixture on compressive strength of foam.

TABLE III

Comparison of Foams from Raw and Blown Castor Oil

Polyol equiv. weight	Castor oil in polyol[a]	Foam properties				
		Density	Comp. strength (at dens. = 2.0)	Closed cells	Humid aging (14 days/70C)	Thermal conductivity (after 14 days)[b]
		lb/ft^3	psi	%	△ vol., %	K
100	raw	2.1	43	88	+20	0.16
100	blown No. 7	2.0	50	89	+28	0.16
120	raw	2.1	32	89	+3	......
120	blown No. 7	2.1	46	90	+2	0.17
140	raw	2.7	18	89	0	......
140	blown No. 7	2.4	35	91	+4	0.17

[a] Polyol composed of mixture of castor oil and triisopropanolamine. Properties of castor oils used are listed in Table II.
[b] Initial K values were 0.01–0.02 units lower.

Castor oil and triisopropanolamine were mixed to obtain polyols with equivalent weights of 100, 120 and 140 (Table I). The properties of the castor oil samples used in these polyol mixtures are shown in Table II. The blown castor oils were numbered from 1–8 in the order of their increasing degree of oxidation as measured by their oxygen contents. The densities, viscosities, refractive indices and acid values increase generally with increasing oxygen content. The hydroxyl values are unrelated to oxygen content.

Foams were prepared by adding a polyol solution containing the catalysts to a prepolymer solution containing the blowing agent and surfactant. This mixture was stirred rapidly for about 20 sec and allowed to foam in an open top container. One equivalent of polyol was used for each equivalent of isocyanate in the prepolymer. The concentrations of the additives used are listed below.

	Parts per 100 parts polymer
Catalysts:	
triethylenediamine	0.6
stannous octoate	0.01–0.05
Blowing agent: CCl_3F	16
Surfactant:	
silicone (Union Carbide L-520)	1.0 –1.5

The strength of these foams was found to increase with an increase in the oxygen content of the castor oil used in the polyol (Fig. 1). The first point on the left of each curve is for raw or unblown castor oil. It can be seen that foams from some of the more highly oxidized oils are as strong as foams prepared from a raw castor oil polyol mixture with an equivalent weight 20 units lower. The advantage of preparing foams from a higher equivalent weight polyol is that more of the low cost castor oil is used and less of the expensive isocyanate is required.

The compressive strength of these foams may also be correlated with the density (Fig. 2), viscosity, and refractive index of the castor oil (raw or blown) used in the polyol component, since these properties of the

TABLE IV

Material Composition of Foams[a]

Materials	Equivalent weight of polyol					
	100		120		140	
Castor oil in polyol[b]	Raw	Blown No. 7	Raw	Blown No. 7	Raw	Blown No. 7
	parts by wt	parts by wt	parts by wt	parts by wt	parts by wt	parts by wt
Prepolymer component:						
toluene diisocyanate	46.9	46.9	43.6	43.6	40.6	40.6
G-2408 (Atlas)	13.3	13.3	12.3	12.3	11.4	11.4
CCl_3F	16.0	16.0	16.0	16.0	16.0	16.0
L-520 silicone (Union Carbide)	1.5	1.5	1.5	1.5	1.5	1.5
Polyol component:						
castor oil	17.3	17.4	25.0	25.2	31.9	32.1
triisopropanolamine	22.5	22.4	19.1	18.9	16.1	15.9
triethylenediamine	0.6	0.6	0.6	0.6	0.6	0.6
stannous octoate	0.01	0.01	0.01	0.01	0.05	0.05
Total	118.1	118.1	118.1	118.1	118.1	118.1

[a] Properties of foams listed in Table III.
[b] Properties of castor oils listed in Table II.

TABLE V

Effect of Acid Removal from Oil on the Compressive Strength of Foams

Blown castor oil in polyol[a]		Equivalent weight of polyol[b]		
Oil No.	Acid value	100	120	140
		Compressive strength of foam, psi		
6	18	53	41	31
6 Deacidified[c]	6	46	41	36
7	21	50	46	35
7 Deacidified[c]	4	46	42	33

[a] See Table II.

[b] Polyols composed of mixtures of oils and triisopropanolamine.

[c] Blown castor oil (200 g) in 700 ml 6/1 MeOH/tetrahydrofuran was passed through column of about 200 g Dowex 1 x 8 in. OH^- form. Column was rinsed with about 300 ml of 6/1 MeOH/THF. Solvent was removed from combined eluates on rotary evaporator.

oil generally increase with increasing degree of oxidation.

A detailed comparison of the properties of foams prepared from raw castor oil and a highly oxidized castor oil is shown in Table III. At each equivalent weight level, the compressive strength of the blown oil foam is higher than that of the raw oil foam. Also, the difference in strength of the two types of foam increases as the polyol equivalent weight is increased. The blown-oil and raw-oil foams do not differ significantly in the other properties measured. The overall composition of these foams is given in Table IV.

The increased strength of foams prepared from oxidized castor oil may be due to increased hydrogen bonding between urethane groups and the oxygen-containing groups ($>C=O$, $-OH$) formed during oxidation, or to increased functionality of the oxidized oils. The possibility that the increased strength of these foams was due to the higher free acid content of the blown oils was investigated. These acids would, on reaction with isocyanates, produce a higher content of urea and amide groups, which are known to reinforce urethane polymers (7). Most of the free acid was removed from two samples of blown castor oil by means of a strongly basic anion exchange resin. Foams were then prepared from these deacidified oils and compared with foams prepared from the original oils (Table V). Use of the deacidified oils did not cause any significant change in foam properties. Therefore, the increased strength of these foams is not due just to the higher free acid content of the blown oils.

REFERENCES

1. Lyon, C. K., Vilma H. Garrett, and L. A. Goldblatt, JAOCS, *39*, 69–71 (1962).
2. Lyon, C. K., Vilma H. Garrett, and L. A. Goldblatt, *Ibid.*, *38*, 262–266 (1961).
3. Remington, W. J., and R. Pariser, Rubber World, *138*, 261–264 (1958).
4. Rice, D. M., and L. J. Nunez, SPE Journal, 321–323 (1962).
5. D'Eustachio, D., and R. E. Schreiner, Am. Soc. Heating Ventilating Engrs. Trans., *58*, 331–342 (1952).
6. Fritz, J. S., and G. H. Schenk, Anal. Chem., *31*, 1808–1812 (1959).
7. Saunders, J. H., Rubber Chem. & Technol., *33*, 1259–1292 (1960).

[Received May 10, 1963—Accepted June 13, 1963]

Copolymerization of Methyl Esters of Unsaturated C_{18} Fatty Acids[1]

F. R. MAYO and CONSTANCE W. GOULD, Stanford Research Institute, Menlo Park, California

Abstract

In order to assay the possibilities of making high polymers from linseed oil, the copolymerizations of styrene with the methyl esters of oleic, linoleic, linolenic, and conjugated linolenic acids were studied at 60–130C and copolymerizations of the last three esters with acrylonitrile were studied at 60C. Appropriate free radical initiators were employed in all cases. The esters without conjugated unsaturation show little tendency to enter a copolymer with styrene, but copolymers containing up to 40% by weight of conjugated linoleate can be obtained. Linoleic, linolenic, and conjugated linoleic esters copolymerize readily with acrylonitrile. Products containing up to 45 mole %, 80 wt %, of the conjugated ester can be made. However, methyl eleostearate, with three conjugated double bonds, inhibits the polymerization of both styrene and acrylonitrile. Quantitative comparisons of the behaviors of the esters are made through the copolymerization equation. The probable performance of these and other vinyl monomers in copolymerization with linseed oil is discussed.

Introduction

THE WORK reported here is a portion of that carried out under Contract No. 12-14-100-4505 (71) with the USDA, directed toward the utilization of linseed oil in emulsion paints. Since linseed oil is unsuitable for use directly in emulsion, and since it does not give a high polymer by itself (except on drying with oxygen), an ultimate objective was to copolymerize linseed oil with some vinyl monomer to make a high molecular weight copolymer. In order to determine the relative reactivities of the various unsaturated groupings in linseed oil toward polymerizing radicals, the individual methyl esters of C_{18} unsaturated fatty acids were examined in bulk or solution copolymerization with free radical initiators.

Review of the literature brought out the following points. Almost all the copolymerization studies involving unsaturated fatty esters involved styrene. Since the unconjugated fatty acid residues are unreactive in copolymerization with styrene below 100C, higher temperatures were usually employed. Here the free radical copolymerization is complicated by the non-radical or Diels-Alder dimerization of the fatty acid residues, and literature data cannot be interpreted quantitatively. Only one paper was susceptible to quantitative treatment. Harrison and Tolberg (1) studied the copolymerization of styrene with methyl esters of C_{18} fatty acids. Their quantitative results extend the previous semi-quantitative conclusions of Hewitt and Armitage (2).

Harrison and Tolberg separated each copolymer from monomer by a tested procedure, and analyzed separately for carboxymethyl and benzoate groups by infrared. Their results are summarized in Table 1. As they point out, the rates of polymerization

---

[1] Presented at the Symposium on Recent Advances in Drying Oil Chemistry, Division of Organic Coatings and Plastics Chemistry, Am. Chem. Soc. meeting in Washington, 1962.