Urethane Polymers From Hydroxylated Fish Oil

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Abstract

Alewife fish oil was hydroxylated by performic, peracetic and pertungstic acid methods. Products were compared with respect to yield, free acid, hydroxyl number, saponification value and peroxide value. Fish oils oxidized with performic acid resulted in high yields (83% to 95%), low acid values (0.12 to 0.19), high hydroxy (142 to 245) and saponification (247 to 271) numbers, and relatively low peroxide values (72 to 266). Performic acid hydroxylated alewife and menhaden oils were used to prepare urethane foams. These foams exhibited characteristic low compressive strengths at 10% deflection (6.4 to 9.5 psi), low density (1.45 to 1.65 pcf), high porosity (0.7 to 1.7% closed cells) and high water absorption compared to a conventional polyether urethane foam. Performic acid hydroxylated alewife oil was further refined, using cation and anion exchange resins, for use in the preparation of urethane elastomers. These polymers generally exhibited higher tensile and Graves tear strengths than a comparable castor oil elastomer used as a control. Though dielectric strengths were similar for both fish oil and castor oil elastomers, tensile elongation at break point was greater for the castor oil elastomers. When the isocyanate index of the fish oil elastomers was increased from 105 to 156, the Graves tear strength exhibited the greatest change.

Introduction

The utilization of fatty fish to produce fish meal and animal food provides large quantities of fish oil as the principal by-product. In a period from January to December of 1969, about 156 million pounds of fish oil were produced in the United States (1). Since about 90% of highly unsaturated (2,3) fish oil was derived from menhaden and about 1.3% derived from alewife, samples were obtained to investigate the usage of hydroxylated fish oils as polyols in the formation of urethane polymers.

The search for low cost polyols has covered a wide range of natural and synthetic products. Recently, for example, the use of a dried whey-dimethyl sulfoxide mixture as the polyol has been reported by the authors (4). The preparation of polyols from animal fats has been developed largely by Saggese, Scholnick and co-workers (5–7).

In this paper we report the results of using three hydroxylation procedures on alewife oil and one on menhaden oil to form polyhydroxy compounds. The results of using fish oil polyols along with conventional polymerization procedures to produce urethane foams and urethane elastomers are also presented. Several physical properties of fish oil-urethane foams are reported and compared to a conventional polyether foam. In addition several physical properties of fish oil-urethane elastomers are presented and compared to a castor oil elastomer.

Materials and Methods

The following chemicals were furnished by the Freeman Chemical Corp. of Port Washington, Wis.: Dow-Corning 7 compound, antifoam A, propoxylated sorbitol (hydroxyl number 490); 80% 2, 4–, 20% 2, 6– tolylene diisocyanate (TDI); Dabco 33 LV, a 33.3% solution of triethylenediamine in dipropyleneglycol manufactured by Houdry Process and Chemical Co.; L5410, a rigid foam surfactant; and castor oil. Polymethylene polyphenylisocyanate (PAPI) was a gift of the Polymer Chemical Division of the Upjohn Co., the alewife oil was obtained from the Schilling Fish Co. of Green Bay, Wis., and the menhaden oil was a gift of Archer, Daniels, Midland Co., Minneapolis. Ion exchange resins, AG50W-X4 (200–400 mesh, H^+ form) and Dowex 21K (50–100 mesh, Cl^- form), were obtained from Bio-Rad Lab., whereas 70% hydrogen peroxide was purchased from Food Machinery Corp.

Hydroxylation of Fish Oils

Performic Acid Procedure. The procedure of Swern et al. (8), with slight modifications, was used. Two hundred g of fish oil, 200 ml of hydrogen peroxide (30%), and 360 ml of formic acid (90%) were added at room temperature to a 2 liter flask placed on a combination heater-stirrer. After about 30 min, the reaction became exothermic and was controlled with an ice water bath to maintain a temperature of about 40 C. This temperature was maintained for about 4 hr with the aid of external heat during the latter stages of reaction.

To isolate the product, the above mixture was poured into 3 liters of cold water and the oil product extracted with about 500 ml of diethyl ether using a separatory funnel. The aqueous layer was discarded along with five subsequent washes of the oil-ether fraction. Saturated sodium bicarbonate solution was added to neutralize any acid still present, and residual traces of water were removed by adding anhydrous sodium sulfate. If the oil product was to be used in producing urethane foams, the volatile ether layer was removed using a rotating vacuum apparatus. However, if the oil was to be used in the preparation of urethane elastomers, it was further refined by the use of cation and anion exchange resins.

The cation exchange resin, AG 50W-X4 (200–400 mesh, H^+ form) was dried with anhydrous methanol and washed with diethyl ether several times before use. The oil-ether layer was added to 30 g of the resin and the mixture stirred. Next the oil-ether layer was treated with 30 g of an anion exchange resin, Dowex 21 K (50–100 mesh, Cl^- form) which had been previously treated with 1 N NaOH to produce the OH^- form, dried with anhydrous methanol, and washed several times with diethyl ether before use. Further drying of the oil-ether layer was then accomplished using anhydrous sodium sulfate. A rotary vacuum evaporator was employed in the removal of the ether layer.

In all cases the hydroxy-formoxy product was isolated, and no attempt was made to remove the formoxy residues. In a practical sense the additional reaction step to remove formoxy groups was considered undesirable since reasonable good foams and elastomers were obtained with the hydroxy-formoxy oils. Future work should include finding mild methods to remove the formoxy residues without hydrolyzing triglyceride esters.

TABLE I

One Shot Foam Formulations and Foaming Characteristics

Formulation number	1	2	3
Propoxylated sorbitol (OH-490)	20		
Hydroxylated alewife oil (OH-245)		20	
Hydroxylated menhaden oil (OH-323)			20
Silicone L-5410	0.2	0.2	0.2
Dabco 33 LV	0.2	0.03	0.03
Polymethylene polyphenylisocyanate (PAPI)	24.6		
Tolylene diisocyanate: 80% 2,4 isomer: 20% 2,6 isomer (TDI)		12.5	16.1
Water		0.5	0.5
Fluorotrichloromethane (Freon-11)	7.6		
Isocyanate index	105	102	109
Foaming Characteristics			
Stirring time, sec	60+	50	50
Rise time, sec	150–175	35–40	40–45
Tack-free time, sec	150–175	35–40	40–45

Peracetic Acid Procedure. The method of Findley et al. (9) was used to epoxidize alewife fish oil. Hydroxylation of the epoxidized product was accomplished by using the procedure of Scholnick et al. (7).

Pertungstic Acid Procedure. The method of Luong et al. (10) was employed in this hydroxylation procedure. Preconditioning time, with stirring, was 5 hr at room temperature using 2 g of tungstic acid and 50 ml of formic acid (70%). The pertungstic acid mixture was heated to 55 C and 50 g of fish oil was added. Reaction time was approximately 20 hr with stirring at this temperature. The hydroxylated product was isolated by the same method used in the performic acid procedure.

Properties of Hydroxylated Fish Oils

Free Acid (mg KOH/g). The AOCS Official Method Cd 3a-63, (11) was used for determination.

Saponification Values. The method of Vinson et al. (12) was employed.

Peroxide Values. The AOCS Official Method Cd 8–53 (13) was used.

Hydroxyl Numbers. The procedure presented in "The Analysis of Fats and Oils" (14) was used.

Yield (Per cent). The yield (per cent) was (g product/g fish oil originally used) × 100.

Urethane Foams

Preparation. Foam preparations were based on 20 parts of polyol as presented in Table I. Formulation 1 is for a conventional fluorocarbon blown foam using propoxylated sorbitol (OH 490) as the polyol and PAPI as the polyisocyanate. Formulations 2 and 3 are for water-blown foams containing hydroxylated alewife oil (OH 245) and hydroxylated menhaden oil (OH 323), respectively, as the polyols and TDI as the isocyanate. In all cases the one-shot method of preparation was followed which allowed the ingredients to be mixed and foamed in 12 oz waxed paper cups. The required amount of polyisocyanate was added at room temperature to the polyol containing the catalyst, blowing agent and surfactant. Stirring and rise time depended on the type of catalyst(s) and polyisocyanate used.

TABLE II

Physical Property Test Procedures Used to Evaluate Urethane Polymers

Physical property	Procedure	Modification
Foams		
Density	ASTM D 1622–63 (16)	None
Compressive strength	ASTM D 1621–64 (16)	None
Percent closed cells	National Aniline Standard Test CF-TM2	Water used in place of methanol; sample, ⅝ in. diam.
Water absorption	ASTM D 2127–62T (16)	Sample smaller, 2.0 × 2.0 × 1.0 in.
Elastomers		
Graves tear	ASTM D 624–54, Die C (17)	Crosshead speed = 2 in./min
Tensile and elongation	ASTM D 412–64T, Die C (17)	Crosshead speed = 2 in./min
Dielectric strength	ASTM D 149, Short time Test (17)	None

TABLE III

Urethane Elastomer Formulations

Formulation (parts by weight)	A	B	E	C
Castor oil (OH-164)				40.0
Hydroxylated alewife oil (OH-193)	40.0	40.0	40.0	
Tolylene diisocyanate: 80% 2,4 isomer, 20% 2,6 isomer (TDI)	18.8	18.8	12.7	10.8
Dabco 33/LV	0.06	0.06	0.09	0.03
Antifoam A surfactant	0.05	0.05	0.05	0.05
Isocyanate index	156	156	105	105

The isocyanate (NCO) index [(weight of polyisocyanate/equivalent weight of polyisocyanate divided by the weight of the polyol/combining weight of the polyol) × 100], which is usually set at 105, was used to determine the correct ratio of isocyanate to hydroxyl groups. Typical values of NCO indices, adjusted for the reactivity of water, are also presented in Table I for each formulation. The fish oil formulations were analogous to those used by Ehrlich and Patton (15) for castor oil foams.

Testing. Test procedures used to evaluate fish oil and conventional foams are given in Table II. Several standard tests presented by the American Society for Testing and Materials (ASTM) were used (16).

Urethane Elastomers

Preparation. Urethane elastomers were prepared principally from performic acid hydroxylated alewife oil and from castor oil as the control. These formulations are presented in Table III.

The catalyst (Dabco 33LV) was mixed into the oils along with the surfactant (antifoam A) and the mixture heated to 60 C. It was then placed in a desiccator and a vacuum pump was employed to remove entrapped gases. The correct amount of 2,4-; 2,6-tolylene diisocyanate (TDI) was added to the mixture, which was again mixed thoroughly. The mixture was placed in the vacuum chamber for approximately 2 to 3 min. It was subsequently poured into a mold, thinly coated with Dow-Corning 7 compound and allowed to harden to obtain an elastomer with a uniform thickness of about ⅛ in. Tack free time at room temperature was about 3 hr for fish oil elastomers and about 5 hr for castor oil elastomers.

Testing. Test procedures used to evaluate fish oil and castor oil elastomers are also presented in Table II. Standard tests presented by ASTM were employed (17).

Results and Discussion

Several properties of hydroxylated alewife oil, using three peracid oxidation methods, are presented in Table IV. Yields of hydroxylated oil were low for the peracetic acid method, possibly because this involves two steps. The free acid contents of the hydroxylated oils were relatively low, indicating the rigorous washing procedures used. Hydroxyl numbers of hydroxylated alewife oil, using performic and

TABLE IV

Properties of Hydroxylated Alewife Oil

Modification	Yield, %	Free acid (mg KOH/g)	Hydroxyl number	Saponification value	Peroxide value
Hydroxylated					
Performic acid	83–95	0.124–0.187	142–245	247–271	72–266
Peracetic acid	70–76	0.113–0.134	210–227	152–161	105–356
Pertungstic acid	84–91	0.060–0.065	157–158	194–198	1,192–1,493
Unaltered					
Crude alewife oil		0.97	5.7	182	13
Refined castor oil			164	180	

TABLE V

Physical Properties of a Conventional Polyether Foam and a Castor Oil Elastomer vs. Those of Hydroxylated Fish Oil Foams and Elastomers

Test	Formulation[a]			
Urethane foams	1[b]	2		3
Density (pcf)	2.1–2.3	1.45–1.65		1.45–1.65
Compressive strength (psi) parallel at 10% deflection	23.6	6.35		9.5
Closed cells % (porosity)	88.6	0.7		1.7
Water absorption, g/1,000 sq cm	17.3	50.7		56.8
Urethane elastomers	A	B	E	C[c]
Dielectric strength (v/mil)	246.5	240.0		232.5
Graves tear (pli)	26.3	19.1	251.5	29.3
Tensile strength (psi)	4038	3756	2046	255
Tensile elongation % at break point	29.2	30.0	90.8	122.5

[a] Formulation numbers 1, 2 and 3 correspond to the foam preparations presented in Table II whereas formulation letters A, B, E and C correspond to the elastomer preparations presented in Table III.

[b] Conventional polyether urethane foam.

[c] Castor oil elastomer.

peracetic oxidation methods, were generally higher than that of castor oil, while the pertungstic acid method generally yielded oils with hydroxyl values similar to castor oil. The high saponification values for performic acid oxidized alewife oil presumably reflects the presence of formate esters (8), whereas the low saponification values for peracetic acid oxidized oil may represent degradation of the oil. Peroxide values were relatively low for the performic acid oxidized oils. On the other hand peroxide values were very high for pertungstic acid oxidized oils. Because of the high consistent yields, high hydroxyl numbers and low peroxide values obtained with the performic acid system, this method was principally used in other hydroxylations using either alewife or menhaden oils.

The results of testing several of the physical properties of fish oil urethane foams are given in Table V. Since the conventional foam was prepared with PAPI as the polyisocyanate compared to TDI as the polyisocyanate for the fish oil foams, the properties of the conventional foam are included only as a general reference to verify our test procedures.

Densities of about 1.45 to 1.65 pcf were easily obtained in the fish oil foams although higher densities could be produced by varying the amount of blowing agent and type of catalyst used. Catalysts which are known to accelerate the water-isocyanate reaction tended to yield lower density foams. Another property of the fish oil foams was a highly open-celled structure. In addition the fish oil foams exhibited a low compressive strength. When TDI was the isocyanate, compressive strengths (10% deflection) were found to be in the range of 4.3 to 9.5 psi.

These low values would probably be expected because of the decreased number of urethane bonds formed in foams made with this type of low hydroxylated polyol. When hydroxylated menhaden oil (OH 323), with a higher hydroxyl value than alewife oil (OH 245) was used, foams with slightly higher compressive strengths were produced. High water absorption was another characteristic of fish oil foams, obviously due to the high percentage of open cells.

Uniform textures were generally obtained in fish oil foams which possessed textures comparable to those generally obtained in conventional foams.

Hydroxylated fish oils with their low hydroxyl numbers could easily be added in combination with conventional polyols with higher hydroxyl numbers (OH 390 to 750) to form rigid foams with specific properties which would be governed by their intended use.

Difficulties were initially encountered in making fish oil elastomers as polymerization and hardening occurred too rapidly often entrapping undesirable bubbles. Treatment of the oil first with a suitable cation exchange resin to remove any metal ions present, especially Na^+, and then with a suitable anion exchange resin in the OH^- form, to remove any H^+ present, overcame these difficulties. The oil also had to be thoroughly dried with anhydrous sodium sulfate to remove any potential gas-forming water present, before acceptable elastomers could be produced.

The isocyanate index of fish oil urethane elastomer formulations was varied to determine the effect on four important physical properties of the elastomer products formed. These results are presented in Table V. Castor oil elastomers, produced from a polyol with a hydroxyl value of 164, were used as a control for comparing physical properties to those of fish oil elastomers, made from a polyol with a hydroxyl value of 193. From Table V it is evident that there are notable differences in physical properties among these elastomers. Since fish oil elastomer E (FOE-E) has the same NCO index (105) as the castor oil elastomer C (COE-C), these two products were used for comparing properties. The tensile strength (psi) of FOE-E was found to be about eight times greater than that of COE-C, thus indicating a stronger polymer. Graves tear strength in pounds per linear inch (pli) was about 8.7 times greater for FOE-E than for COE-C. In addition to possessing both greater tensile and Graves tear strengths, FOE-E possessed significant elasticity as demonstrated by a tensile elongation at break point of 90.8%, which was 0.74 times that of COE-C. The dielectric strength (volts/mil) of FOE-E was not determined but would be expected to be close to that of COE-C (232.5 volts/mil).

An increase in the NCO index of fish oil elastomers A (FOE-A) and B (FOE-B) to 156, almost doubled the tensile strength, but at the same time the Graves tear (pli) decreased to nearly 1/10. Percent tensile elongation of FOE-A and FOE-B was about ⅓ that of FOE-E. The variability between the values reported for FOE-A and FOE-B probably arises from differences in the composition of the final hydroxylated oils which were prepared separately. Although the hydroxyl numbers were the same, slight differences in hydroxylated oil structures could result in differently cross-linked elastomers to yield physical property variations.

In general the fish oil elastomers were harder, less elastic and more resistant to tearing than castor oil elastomers with comparable NCO indices.

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