Reactions of Aldehyde Oils and Methyl Azelaaldehydate with Polyols[1]

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Abstract

In exploratory tests, mono-, di-, and trialdehyde oils and methyl azelaaldehydate (MAZ), preferably in the form of their acetals, reacted with various polyols with few exceptions to produce potentially useful derivatives. The polyols included pentaerythritol, methyl glucoside, glucose, sorbitol and poly(vinyl alcohol)(PVA). Preliminary evaluation of some of the derivatives was carried out in several applications. Among the more promising were: films derived from MAZ and glucose or PVA; melt adhesives for nonpolar substrates from trialdehyde oil and methyl glucoside; and molding compounds derived from MAZ and PVA.

Introduction

Among the various aldehydic compounds that may be produced by ozonization of soybean oil or its esters are monoaldehyde oil (MAO), dialdehyde oil (DAO), trialdehyde oil (TAO, completely ozonized soybean oil) and methyl azelaaldehydate (MAZ) (1–3). We have reported infrared and nuclear magnetic resonance spectra for aldehyde oils, as well as reactions of DAO with diamines (5). These reactions were noteworthy because of the rapidity of reaction at room temperature. The products were infusible, insoluble factices, properties indicating polymers that are cross-linked but of a low degree of polymerization.

Acetal formation from MAZ with various monohydric alcohols and pentaerythritol has been reported (4). We wished to study the acetals that might be prepared from commercially available polyols. Accordingly, exploratory studies on the reactions of aldehyde oils were extended to the formation of acetals with D-glucose, sorbitol, sucrose, methyl glucoside, amylose and poly(vinyl alcohol)(PVA), as well as pentaerythritol.

Experimental

MAZ reactions were explored with methyl glucoside, sorbitol, amylose, glucose and PVA. With methyl glucoside, the dimethyl acetal of methyl azelaaldehydate (MAZDA) gave a smoother and faster reaction than did MAZ. Accordingly, this derivative was used in most of the reactions. MAZDA (46.4 g) and methyl glucoside (38.8 g) in 140 ml xylene were heated to 144C for 2 hr in the presence of $KHSO_4$ (0.2 g). After evaporation of solvent, a waxy solid (67.2 g) melting at 95–120C was obtained.

In experiments with other polyols, the reaction was allowed to proceed at room temperature for extended periods (60–100 hr) to avoid by-product reactions of the polyols under acidic conditions at higher temperatures. Under these conditions and in ethanol solution, only sorbitol appeared to react to any extent. With $KHSO_4$ as catalyst, a viscous liquid was obtained; with H_2SO_4, a white solid, melting 128–130C. With dioxane solvent and H_2SO_4 catalyst, a viscous liquid was obtained that was evaluated as a film-former. In dioxane solvent with *p*-toluene sulfonic acid catalyst, glucose also gave a viscous liquid that was evaluated as a film.

Both Elvanol 72–60 (100% hydrolyzed) and Elvanol 72–51 (98% hydrolyzed) grades of PVA reacted readily with MAZ in chloroform solution in the presence of hydrogen chloride. After standing 6–16 hr at room temperature, products were obtained that gave films of varying appearance when cast on glass plates. Equal weights of MAZ (25 g) and PVA (25 g of Elvanol 72–60) gave a glossy, somewhat irregular and elastic film nearly transparent in thin areas. MAZ (12.5 g) and PVA (25 g) produced a smooth, tan, translucent and somewhat elastic film. MAZ (10 g) and PVA (50 g) gave a smooth, cream-colored, nearly opaque film that tore easily.

Although a number of variations in solvent, catalyst and temperature were explored, a satisfactory reaction with amylose and MAZ or MAZDA did not take place. Attempts to transesterify MAZDA with PVA, sorbitol and dextrose in the presence of alkaline catalysts also gave no appreciable reaction.

MAO reactions with pentaerythritol, PVA, sucrose and methyl glucoside were attempted. An amber, viscous monopentaerythritol acetal was formed from pentaerythritol (0.02 mole) and MAO (0.04 mole) by refluxing in xylene for 1.5 hr with continuous removal of water. Attempts to form a dipentaerythritol acetal resulted in the monopentaerythritol acetal only. PVA (1 part Elvanol 71–24) and MAO (10 parts)(2:1 molar ratio) in the presence of HCl catalyst gave a rubbery solid that could be compressed to a soft mass. The reaction of PVA (1 part Elvanol 71–24) and MAO (2 parts)(10:1 molar ratio) yielded a light-brown powder that could not be compressed in the laboratory press. These three products were not sufficiently soluble in organic solvents to cast films.

MAO (0.085 mole) and methyl glucoside (0.085 mole) were heated at reflux in xylene with $KHSO_4$ catalyst until most of the solid had gone into solution (12 hr). The product was similar in appearance, viscosity and odor to the starting oil although the aldehyde content of the MAO was reduced to 20% of its original value, as determined by the hydroxylamine hydrochloride method for carbonyl. Little reaction was apparent between MAO and sucrose at 90C after 8 hr.

DAO reactions with pentaerythritol, sorbitol, methyl glucoside and PVA were attempted. Pentaerythritol (7.48 g) and DAO (32.3 g) gave an amber, elastic, but weak, rubbery material after 1.5 hr reflux in xylene in the presence of $KHSO_4$ with continuous removal of water. For illustrative purposes, a similar reaction with the methyl acetal of DAO having an idealized structure is given in Fig. 1. Methanol, instead of water, is the volatile reaction product when the methyl acetal is used. Sorbitol

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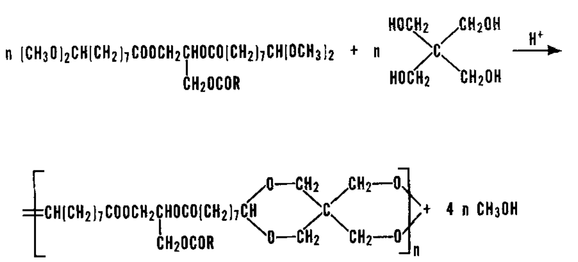

FIG. 1. Reaction of the methyl acetal of dialdehyde oil with pentaerythritol.

(18.2 g) and DAO (90.0 g), after reflux in xylene with $KHSO_4$ for 20 hr, did not react completely. After removal of unaltered sorbitol and xylene, washing and removal of solvent, a viscous amber liquid that cured to a weak rubbery mass at 215C was obtained. Reaction of DAO and sorbitol without a solvent but with $KHSO_4$ at 130–134C for 16 hr produced a dark-brown factice insoluble in most organic solvents. Equal weights (25 g) of PVA (Elvanol 72–60) and DAO in chloroform were treated with HCl at room temperature with agitation for 24 hr. A tan solid amounting to about 130% of the starting PVA was recovered. Solubility of the product was not sufficiently improved over that of PVA to allow preparation of films.

Methyl glucoside did not react when refluxed with DAO in xylene for 16 hr with $KHSO_4$ catalyst. Since methyl glucoside reacted readily with the other aldehydic compounds, this failure to react with DAO must be considered an anomaly.

TAO reactions with sorbitol, methyl glucoside, glucose and PVA were investigated. The TAO contained only 2.66 aldehyde groups per glyceride molecule because of the saturated fatty acids present in the original oil. TAO was used in the form of the methyl acetal (TAOMA) because of the advantages described under reactions of MAZ. Sorbitol (12.1 g) and TAOMA (41.2 g) were heated in xylene with $KHSO_4$. At 90C the sorbitol softened and then melted. At 125C a small amount of liquid distilled off. At 135C the material foamed vigorously. The reaction product was a dark, heterogeneous, semisolid mass. Another attempt with sorbitol was made by heating the reactants in toluene with $KHSO_4$ at 95–100C for 9 hr. No reaction occurred.

Glucose (8.3 g) and TAOMA (13.7 g) were heated in dioxane with *p*-toluenesulfonic acid on a steam bath 18 hr. About 75% of the starting glucose was recovered by filtration. Removal of solvent left a viscous, nearly solid, product that did not form a smooth melt on heating.

PVA (20 g of Elvanol 72–60) and TAOMA (20 g) were stirred in ethanol with HCl at room temperature for 16 hr and then at 70C for 5 hr. The product was a light-tan powder weighing 25% more than the original PVA and insoluble in the organic solvents tested.

Methyl glucoside (25.2 g, 2.66 moles per mole TAOMA) and TAOMA (41.2 g, still containing the NH_4Cl catalyst used in its preparation) were heated in xylene at 130–135C. Methanol distilled off, and after distillation ceased, the temperature was slowly raised to the reflux temperature of xylene (143C). The total heating time was 8 hr. The reaction mixture was filtered hot to remove unreacted methyl glucoside. The filtrate separated into a dark, viscous, lower layer and a much greater volume of clear, reddish, upper layer. The lower layer was stripped of xylene under vacuum. The residue was a clear brown, very viscous material that melted on heating and could be drawn into a long thin thread. This material was tacky when soft and exhibited definite adhesive characteristics. A similar, but resilient, product was formed from 1.33 moles of methyl glucoside per mole of TAOMA. Based on this ratio of reactants, the reaction was apparently complete in 2 hr at 120C with no unreacted methyl glucoside apparent, in contrast to the reaction with greater amounts. Both of these reaction products were evaluated as adhesives.

TABLE I

Chemical Resistance of Films from Methyl Azelaaldehydate Derivatives

Derivative	Cure time at 205C, min	Pencil hardness	Appearance of film after 15 min exposure to		
			3% NaOH	5% H_2SO_4	Boiling H_2O
Sorbitol	30	<2B	Softened	Unchanged	Blushed and softened
	45	2B	Softened	Unchanged	Blushed and softened
Glucose	15	2H	Unchanged	Unchanged	Unchanged
	30	2H	Unchanged	Unchanged	Unchanged

Evaluation Tests

Film Characterization

The sorbitol and glucose derivatives of MAZ were applied in undiluted form to clean glass plates by using a Baker blade at a 4-mil setting. The films were baked in a forced-air oven at 205C. The MAZDA-glucose derivative appeared to have satisfactory film-forming properties except for color, which was quite dark (Table I). Attempts to remove the acetalization catalyst from the derivative by ion-exchange treatment or by washing with water and lower curing temperatures did not improve the color.

Films were also prepared from the PVA and MAZ derivatives and further characterized. The resistance of these films to various liquids is shown in Table II. Strips of film about ¼ in. × 1½ in. were immersed in the various liquids for 24 hr. Complete solubilization was not observed for any film in any solvent. Some swelling was apparent and possible leaching of one of the components was evidenced by disintegration of the films in acetone and butyl acetate.

To determine the water absorption of these films, weighed portions were immersed in distilled water for 2½ hr, blotted, and reweighed. The following results were obtained for various weight ratios of MAZ:PVA:

Weight ratio	Water absorption, %
1:1	44
1:2	86
1:5	91
1:10	55

The water absorption of the films under these conditions followed no particular pattern. Generally, the weight after complete drying was slightly less than the original weight. In contrast to the behavior of these derivatives, film prepared from a 10% solution of unaltered Elvanol 72–60 became a gelatinous mass after only 30 min immersion in water.

A more severe water-absorption test was also carried out. Samples were soaked for 54 hr, removed, blotted and weighed. The films were air dried at 74F and 50% relative humidity and weighed periodically (Table III). Rather unexpectedly, the film with the highest MAZ modification absorbed 4 to

12 times as much water as the films less modified. The film with the highest PVA content, and consequently the lowest MAZ content, showed the lowest water absorption. Recovery of the films depended mainly on the quantity of water absorbed. After 24 hr, all films weighed less than the original weight.

Molding Compound Characterizations

Molding conditions were the same for all samples. A piston-type button mold was used in a heated Preco press at 160C for 15 min under 1,000 lb/sq in.

When PVA was used alone, the final button was nonuniform with a transparent, hard, brittle area and the rest soft and powdery. Modification of the PVA with about 20% MAZDA had little apparent effect on the molded material except for slight discoloration. Approximately 20% modification of the PVA with TAOMA gave a molded button that was opaque but of uniform consistency with slight flexibility. This material had a weight gain of 75.5% after immersion in boiling water for 1 hr. Under the same conditions, unmodified molded PVA had a weight loss of 24.2%. The molded product from PVA modified with approximately 50% MAZDA was translucent, extremely flexible and elastic. This material had a weight gain of 2.6% after immersion in boiling water 1 hr.

Adhesives Characterizations

Preliminary evaluation of the adhesive properties of the methyl glucoside derivative of TAO was encouraging, and studies of a more quantitative nature were undertaken with various substrates including aluminum foil, polyethylene film, kraft paper and wood.

When the product containing a 2.66:1 molar ratio of methyl glucoside to TAO was tested, slow application of stress caused failure within the adhesive layer itself. Under sudden loading, however, failure took place at the interface between the adhesive and one member of the couple and was more pronounced for nonporous substrates. After 1 day paper-to-paper and paper-to-aluminum bonds had the least strength. Greatest bond strengths were observed where polyethylene was one member of the couple. After 28 days the strength of the paper-to-paper bond became zero, apparently because of excessive absorption of the adhesive by the paper. Although the adhesive was absorbed to some extent by the paper in all trials, the strengths of paper-to-aluminum and paper-to-polyethylene bonds were about the same at the end of 1 and 28 days. Samples containing 50% of rosin gave bond strengths similar to those of derivatives alone after 1 day. After 28 days, however, the bond strength had increased two- to fourfold. Little or no absorption of the adhesive by the paper was observed. Since evaluation was only preliminary, considerable development of formulation and application techniques would be necessary to evaluate the adhesive properties of this derivative completely.

Better yields of a derivative with somewhat more tacky and elastic properties were obtained when 1.33 moles of methyl glucoside per mole of TAOMA were used in the preparation. This derivative was evaluated as an adhesive (Table IV). The material was melted and applied with a No. 20 wire-wound rod to 6 in. × 6 in. samples of various heated substrates. A second sheet was applied and sealed by passing a heat-seal iron at 160C over the least heat-sensitive of the two substrates. One set of samples was prepared by applying the adhesive as a melt to one member and then pressing the second sheet over the cool adhesive without further heating. Sample strips 0.5 in. × 6 in., were evaluated by the Suter tester when both members were flexible.

TABLE II
Resistance[a] of Methyl Azelaaldehydate-Polyvinyl Alcohol Films to Various Organic Solvents

Solvent	Weight ratio of MAZ: poly(vinyl alcohol)					
	Elvanol 72–51		Elvanol 72–60			
	1:1	1:2	1:1	1:2	1:5	1:10
Acetone	I	I	D	D	D	D
Chloroform	I	I	S	S	S	S
Ethyl acetate	I	I	....	....	....	....
Ethyl alcohol	S/W	S/W	S	S	S	S
Benzene	....	....	S	S	S	S
Dimethyl formamide	S	S	D	S	S	S
Hexane	I	I	....	....	....	....
Water	S/W	S/W	....	....	....	....
3% Aqueous NaOH	S/W	S/W	S/W	S/W	S/W	S/W
Pyridine	S	S	....	....	....	....
Isopropanol	....	....	S/W	S/D	S/W	S/W
Butyl acetate	....	....	S	D	D	D

[a] I = Insoluble, unaffected by liquid.
D = Film disintegrated but little solubility observed.
S = Swelling of film.
S/W = Swelling of film and whitening.

When one member was rigid, such as glass or wood, the adhesive was evaluated qualitatively by stripping the flexible member and inspecting the area of separation. Again, under the condition of the test, cohesive failure of the adhesive occurred rapidly except when the substrate failed. Sometimes sudden loading caused failure in the bond between the adhesive and one of the substrates. This type of failure was especially common if one member was polyethylene. When relatively slow tension was applied, the adhesive was found on both members after separation. If, however, the couple was suddenly pulled apart, the polyethylene film would always be free of adhesive.

Comparative tests with commercial materials were not made for several reasons. In these exploratory tests, optimum formulations were not developed. Furthermore, the variety of substrates tested would require a large number of different controls, resulting in complex and perhaps misleading comparisons.

Discussion

The aldehydic compounds, MAZ, MAO, DAO, and TAO, all reacted with the polyols pentaerythyritol, glucose, sorbitol, and PVA. Methyl glucoside reacted with MAZ and TAO, but apparently no reaction occurred with DAO. The reactions were best carried out by transacetalization of the methyl acetals of the aldehydes (see Fig. 1 for an example). MAZDA failed to react with amylose, and MAO failed to react with sucrose. The aldehyde-polyol products were not fully characterized since the studies were exploratory only. Because certain products appeared to have some promise in various applications, a limited number of preliminary evaluation tests were carried out.

Films

Several of the carbohydrate derivatives of MAZDA and TAOMA were evaluated as films. The MAZDA-sorbitol derivative, MAZDA-glucose derivative and

TABLE III
Water Sensitivity of MAZ-Polyvinyl Alcohol Films

Film	Weight ratio of MAZ: poly(vinyl alcohol) (Elvanol 72–60)			
	1:1	1:2	1:5	1:10
Increase in weight, %	385	79	60	25
Time for recovery to original weight, hr	24	2	1	1

TABLE IV
Adhesive Evaluation of Methyl Glucoside-Trialdehyde Oil Derivative (1.33:1 Molar Ratio)

Derivative applied to:	Second sheet	Bond strength g/in.		Remarks[a]
		24 hr	28 days	
By sealing with hot (160C) iron				
Kraft paper	Kraft paper	240, 260	490, 390	
Kraft paper	Aluminum foil[b]	600, 560	560, 600	
Kraft paper	Polyethylene film[c]	650, 690	650, 720	Cohesive failure
Kraft paper	Cellophane film[d]	520, 490	590, 600	
Kraft paper	Calendered paper[e]	340, 400	....	Calendered paper tore
Calendered paper	Polyethylene film	420, 430	600, 580	
Calendered paper	Cellophane film	510, 470	780, 720	
Calendered paper	Aluminum foil	290, 220	....	Calendered paper tore
Aluminum foil	Aluminum foil	1040, 1080	1240, 1120	
Aluminum foil	Polyethylene film	570, 610	1080, 1080	
Aluminum foil	Cellophane film	230, 290	700, 720	
Calendered paper	Wood[f]	....	....	Separation occurred in paper
Calendered paper	Glass	....	....	Separation occurred in paper
Glass	Aluminum foil	....	....	Fairly strong, even adhesion
Glass	Polyethylene film	....	....	Fairly strong, even adhesion
Cellophane film	Cellophane film	....	....	Heat distorted sample and rendered it nonuniform
Polyethylene film	Polyethylene film	....	....	Qualitatively good adhesion
By sealing with cold iron				
Kraft paper	Aluminum foil	760, 800	1260, 1320	
Kraft paper	Polyethylene film	480, 490	650, 680	Paper tore on duplicate test
Calendered paper	Polyethylene film	460, 460	890, ...	
Calendered paper	Cellophane film	450, 470	670, 700	
Calendered paper	Aluminum foil	....	580, 580	Paper tore at these values
Aluminum foil	Aluminum foil	730, 800	700, ...	Second sample not uniform
Aluminum foil	Polyethylene film	670, 690	890, 850	

[a] Failure occurred in the adhesive unless otherwise noted.
[b] Pure aluminum foil.
[c] VisQueen.
[d] MSAD 80.
[e] Kromekote, 60-lb.
[f] Tongue depressors.

the TAOMA-methyl glucoside derivative cured to various degrees at elevated temperatures. A preliminary evaluation of four derivatives was made to determine if any showed potential in film applications.

Only the MAZDA-glucose derivative appeared worthy of further evaluation as a film (Table I). It gave the hardest films with good resistance to boiling water, acid and alkali. Either curing temperature or curing time, or both, for the MAZDA-glucose derivative could probably be reduced as the properties of the film were not enhanced by the increase in curing time from 15 to 30 min. This derivative was also baked at lower temperatures for various times. When the films were cured sufficiently to produce a fairly hard film, however, they darkened markedly. The reason for discoloration is not clear. Curing in the absence of air might prevent discolorization, but this method seemed impractical and was not attempted.

The MAZ-PVA derivative, slurried in chloroform, without heating, cast, and air-dried at room temperature, formed films which could be stripped from glass panels after air drying. The products varied from a semitransparent, glossy film, obtained from the derivative with highest MAZ modification, to a flat, opaque, weak film, obtained from the derivative with lowest modification. The opaque films did not appear to be homogeneous but were granular. All of the films felt dry, and there was no bleeding to indicate the presence of unreacted oil. The films were strong enough to handle easily but could be torn fairly easily. Film strength was roughly proportional to the concentration of MAZ in the reaction mixture. Possibly the strength of the film might be increased if more homogeneous structures were obtained. There was little resemblance of the modified films to an unmodified PVA film in clarity and strength.

Adhesives

The tacky nature of the TAO derivative of methyl glucoside indicated that this material might have potential as an adhesive. Its high viscosity indicated that it could be conveniently applied as a melt. Accordingly, a series of tests was carried out with various substrates including aluminum foil, polyethylene film, paper and wood.

With the product containing a 2.66:1 molar ratio of methyl glucoside to TAO, the failure in all cases was in the adhesive itself. The product containing a 1.33:1 molar ratio of methyl glucoside to TAO gave better results. The pairs of substrates between which the latter derivative was evaluated and the bond strengths where obtainable are shown in Table IV. In general, the highest bond strengths came from nonporous substrates. In some instances the calendered paper tore and bond strength values were not obtained. Samples that were cold sealed had bond strengths of the same order as comparable heat-sealed couples.

The bond strengths of the adhesive on the various substrates were determined after 24 hr and after 28 days. The bond strengths for all combinations had increased during this period. This increase, in general, was somewhat greater when nonporous materials were used for both members of the couple. There was no noticeable absorption of this derivative into kraft paper as had been observed with the derivative prepared by reacting 2.66 moles of methyl glucoside per mole of TAO acetal.

Miscellaneous Evaluations

PVA modified with 50% MAZDA gave a molded product having some interesting properties. The molded disc was translucent, extremely flexible and elastic and was relatively insensitive to boiling water.

The MAO-methyl glucoside derivative had some activity as an emulsifying agent, since a smooth emulsion was formed between mineral oil and water. The emulsion was stable for only about 15 min, however. The TAO-methyl glucoside product was tested as a carbon-black dispersing agent, but the result was not promising.

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