tering differential thermal analysis curves is described. In addition, examples of melting curves of water and of some fats are given.

Acknowledgment

The authors are greatly indebted to R. Keuning for his valuable advice and the assembling of the electronic parts of the apparatus and to J. W. E. Coenen for carrying out the X-ray analysis.

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[Received August 12, 1957]

Reactions of Unsaturated Fatty Alcohols. V. Preparation and Properties of Some Copolymers of Unsaturated Fatty Vinyl Ethers with Lower Alkyl Vinyl Ethers[1]

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IN PREVIOUS PUBLICATIONS (6, 7) we have described the preparation, polymerization, and polymer film properties of soybean and linseed vinyl ethers. The fatty vinyl ethers were prepared from the corresponding alcohols, using acetylene and an alkaline catalyst at atmospheric pressure. Polymerization of the vinyl ethers was accomplished by using the Lewis-acid type of catalysts and a flash technique at temperatures down to —30°C. in solvents. Polymers of highest molecular weight were obtained at —30°C. in methylene chloride, using boron trifluoride-etherate catalyst.

Baked films of these polymers containing metallic driers showed promise as protective-coating materials although improvement of their properties was indicated in two areas: (a) retarding oxidative degradation of the films, and (b) preventing the wrinkling and what appears to be "gas-checking," as manifested by tung oil, or dried films more than 2 mils thick. Oxidative degradation of fatty vinyl ether polymer films, which was especially pronounced when cobalt drier was used, led to the formation of free acids and esters that resulted in poor alkali resistance. Stability to alkali was improved by suitable formulation, for example, by adding antioxidants or by using driers other than cobalt. Properly prepared films resisted 5% alkali for over 24 hrs.

It was believed that modification of fatty vinyl ethers by copolymerization with other vinyl ether monomers would improve alkali resistance and other properties of films from the polymers. This paper describes the preparation and properties of copolymers of unsaturated fatty vinyl ethers with several lower alkyl vinyl ethers and reports the results from a study of the effects of structure on the oxidative stability and wrinkling of copolymer films.

Preparation and Properties of Copolymers

Starting Materials. Soybean vinyl ether was prepared from a commercial sample of the fatty alcohol (Unadol 40, Archer-Daniels-Midland Company[2]), using acetylene at atmospheric pressure (7). The product analyzed as follows: vinyl ether, 94.5%; conjugated diene, 32.2%; conjugated triene, 1.3%; soybean alcohol, 3.8%.

Ethyl, butyl, isobutyl, 2-ethylhexyl, and 2-chloroethyl vinyl ethers were obtained from commercial sources and used as received. 2-Methoxyethyl vinyl ether was distilled before use to improve the color.

Nopol vinyl ether was prepared from nopol (obtained from Dow Chemical Company) by a modification of a transvinylation technique (8) as follows: 83 g. (0.5 mole) of nopol, 500 g. (5 moles) of n-butyl vinyl ether, and 5.1 g. (0.016 mole) of mercuric acetate were mixed in a round-bottom flask and refluxed for 10 hrs. Analysis for vinyl ether content by an iodometric method (7) showed that the mixture contained 80.4% Nopol vinyl ether. Potassium carbonate, 4.4 g. (0.032 mole), was added to neutralize the catalyst, and the butyl vinyl ether was distilled off to yield a dark residue. Distillation of the residue gave 64 g. of a water-white distillate (88.4% vinyl ether), which was purified further by stirring with sodium ribbon for 4 hrs. at room temperature. The final product was 97.5% vinyl ether.

Anal. Calcd.: C, 81.2; H, 10.48
Found: C, 80.6; H, 10.47

Polymerization Procedure. A typical copolymerization was carried out in the following manner. A mixture of lower alkyl vinyl ether and soybean vinyl ether (10 to 15 g. total charge) was dissolved in 50 ml.

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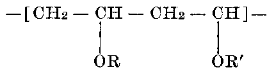
[1] Presented at the fall meeting, American Oil Chemists' Society, Cincinnati, O., September 30–October 2, 1957.

[2] Since the Department of Agriculture does not recommend the products of one company over those of another, the names are furnished for information only.

of methylene chloride and cooled to −30°C. in a solid carbon dioxide-ethanol bath. The polymerization was initiated with boron trifluoride-etherate (4 to 5 drops of 7% BF_3 in ethyl ether). The temperature rose rapidly during the polymerization. The rate of temperature rise appeared to be directly related to the amount of lower alkyl vinyl ether in the copolymer. After completion of the reaction (about 30 seconds) the catalyst was neutralized with ammonium hydroxide and washed with water until neutral, then the solvent was stripped off to yield yellow to water-white viscous liquids. Number average molecular weights of the copolymers were determined cyroscopically in cyclohexane solution (3), and the results are shown in Table I. Since gelation occurred during copolymerization of ethyl and soybean vinyl ethers in methylene chloride at −30°C., chloroform was used as the solvent.

TABLE I

Soybean Vinyl Ether and Lower Alkyl Vinyl Ethers Copolymerized at −30°C. in CH_2Cl_2



$$-[CH_2-\underset{\displaystyle OR}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OR'}{\underset{|}{CH}}]-$$

R = Soybean

R′	Mole percentage of R′		Mol. wt.	Degree polymerization[b]
	Reactants	Products[a]		
Ethyl	75	76.7	1755[c]	13.8
	50	53.2	1480[c]	8.1
	25	31.1	1545[c]	6.5
Butyl	75	76.2	2320	15.6
	50	46.3	2620	13.3
	25	24.1	2550	10.4
Isobutyl	75	74.9	2940	19.8
	50	53.6	2980	15.2
	25	24.6	3160	12.9
2-Chloroethyl	75	74.7	2970	19.4
	50	47.6	2720	13.6
	25	26.2	2360	9.6
2-Methoxyethyl	75	74.9	2810	18.8
	50	50.6	2170	11.0
	25	26.9	2620	10.7
2-Ethylhexyl	75	75.7	4450	23.4
	50	58.5	3300	14.7
	25	36.5	2675	10.3

[a] Determination of infrared analysis (5).

[b] Degree polymerization = $\dfrac{\text{mol. wt.}}{\text{av. mol. wt. of vinyl monomer unit}}$

[c] Polymerized in chloroform at −15°C.

Polymerization was unsuccessful with nopol vinyl ether alone or when copolymerized with soybean vinyl ether under the conditions described. These polymerizations required a large amount of boron trifluoride etherate to initiate the reaction, which was followed by a very low temperature rise. Examination of the product from the nopol vinyl ether polymerization showed considerable unreacted vinyl groups. Apparently the catalyst is consumed in promoting isomerization reactions of the nopol vinyl ether since terpenes with the α-pinene-type structure easily undergo a Wagner-Meerwein rearrangement in the presence of weak acids (4).

Table I lists composition data obtained on alkyl soybean vinyl ether copolymers. The products were examined in the infrared and found to have about the same composition on a molar basis as the initial reaction mixture. The quantitative infrared method used in the composition work depends on a comparison of C—O—C ether absorption in the copolymer at 9.1 microns with pure samples of the two homopolymers involved (5). Table I also gives the degree of polymerization of the copolymers. In each series as the amount of soybean vinyl ether in the copolymer was increased, the length of the polymer chain became shorter. This result indicates that impurities in a soybean vinyl ether may act as a chain terminating agent during the copolymerization.

Table II shows the changes in diene and triene conjugation in the unsaturated fatty vinyl ether when copolymerized with several lower alkyl vinyl ether monomers. Previous work with the unsaturated vinyl ether homopolymers showed that some reduction in diene conjugation was observed when these materials were polymerized. Soybean and linseed polymers have about 80% and 85%, respectively, of the diene conjugation originally present in the vinyl ethers (6). The data listed in Table II show that the reduction in diene conjugation in going from monomers to polymers was much less with the copolymers than with the homopolymers. Isobutyl-soybean copolymers contained 99% of the original diene conjugation while the butyl-linseed and 2-chloroethyl-linseed copolymers contained 93.5%. This result indicates that the side chain double bonds in soybean copolymers are less involved in the polymerization reaction than they are in linseed copolymers.

TABLE II

Changes in Unsaturation of Soybean and Linseed Vinyl Ethers During Copolymerization with Lower Alkyl Vinyl Ethers

Copolymer	Percentage diene			Percentage triene		
	Calc.	Found	Change	Calc.	Found	Change
Isobutyl-soybean (3:1)[a].......	17.9[b]	17.9	0.2	0[b]	0	0
n Butyl-linseed (3:1)[a].........	12.1[c]	11.3	0.8	1.5[c]	1.0	0.5
2 Chloroethyl-linseed (3:1)[a].	11.8[c]	11.0	0.8	1.5[c]	0.9	0.6

[a] Molar composition of copolymer.

[b] Calculated from the soybean vinyl ether monomer (diene, 36.3%; triene, 0%), assuming no loss in unsaturation during copolymerization.

[c] Calculated from the linseed vinyl ether monomer (diene, 29.6% triene 3%), assuming no loss in unsaturation during copolymerization.

Preparation and Properties of the Copolymer Vinyl Ether Films. In studying the oxidative stability and alkali resistance of copolymer films, conditions for preparing films were selected that were known from previous work (6) to produce extensive degradation of homopolymer films. Thus, under the conditions chosen, films from soybean vinyl ether homopolymer were dissolved by 5% alkali in 3 min. The purpose of selecting such vigorous conditions was to magnify differences that might be found among copolymers and thus permit structural effects to be discerned more clearly. No attempt was made to determine the maximum stability to alkali that might be achieved under other conditions of film formation.

Alkali Resistance and Hardness. Copolymer films were prepared on standard microscope slides from a solution of 1 g. of the copolymer in 3 g. of toluene containing cobalt naphthenate (0.1% cobalt by weight of the polymer). A few drops of this solution were drawn as uniformly as possible into a film by using a doctor blade. The microscope slides were baked at 150°C. for 1 hr. in an electric oven, and films of approximately 0.5 mil thick were evaluated for alkali resistance by immersion in 5% aqueous sodium hydroxide for 24 hrs. Film hardness was determined by using the Wilkinson pencil hardness method (1). The baked films prepared in this study were clear and free of wrinkles. The results are given in Table III.

TABLE III

Hardness, Alkali, and Solvent Resistance of Soybean Vinyl Ether Copolymer Films where R′ Represents a Lower Alkyl Vinyl Ether [a]

R′	Mole percentage R′ in copolymer	Film [b] hardness	Resistance to 5% NaOH [c]		Swelling in $CHCl_3$
			Swelling	Dissolve	
			min.	*hrs.*	*min.*
Ethyl	75	3+	60	4–6	8
	50	4+	60	8–12	17
	25	4+	120	6–8	8
Butyl	75	2+	15	2–3	15
	50	3	7	0.3	7
	25	3	14	1–2	15
Isobutyl	75	2	30	5–7[d]	5
	50	2+	30	12–18[d]	5
	25	4	240	>45[d]	4
2-Chloroethyl	100	3+	......[e]	>72	4
	75	4	90	>72[d]	4
	50	4	90	>72[d]	8
	25	5	90	>72[d]	60
2-Methoxyethyl	75	3	5	4[d]	5
	50	3	4	4[d]	5
	25	4+	3	18–24	5
2-Ethylhexyl	75	Tacky	......	3[d]	3
	50	2	......	0.5[d]	4
	25	2+	......	0.5[d]	5
Soybean	100	5	......	0.05	>20 hrs.
Soybean [f]	100	3–4	150	>20	>20 hrs.

[a] Baked 1 hr. at 150°C.; contain 0.1% cobalt drier.
[b] Hardness of lead required to scratch film.
[c] Immersed 24 hrs.
[d] Darkened on contact with alkali.
[e] Did not swell during 24-hr. immersion.
[f] Film prepared without cobalt drier.

Baked films prepared from 2-chloroethyl-soybean copolymer were the most resistant to aqueous alkali of all the copolymers tested. In contrast to other lower alkyl vinyl ether homopolymers, 2-chloroethyl vinyl ether homopolymer formed a medium-hard film with excellent alkali resistance. The soybean vinyl ether copolymers listed in Table III may be classified in order of decreasing alkali resistance as follows: 2-Chloroethyl, isobutyl, ethyl, 2-methoxyethyl, 2-ethylhexyl, and n-butyl. It should be emphasized however that differences in alkali resistance among the last two copolymer series are slight. Since soybean vinyl ether polymer films had poor alkali resistance when prepared with cobalt, it might be expected that the copolymers richest in soybean vinyl ether would have the poorest alkali resistance. Table III shows that in most copolymer series this result was not obtained. Considering all the copolymer series, there seems to be no correlation between the amount of soybean vinyl ether in a copolymer and the amount of alkali resistance obtained.

A comparison of the alkali resistance of copolymer films with that of soybean homopolymer film shows that very significant increases in stability are achieved by copolymerization. Thus, although some copolymer films were destroyed by alkali in 3 hrs. or less, others resisted 5% alkali for periods up to 24 hrs. In contrast, the homopolymer film was dissolved in 3 min. Previous work showed that by proper formulation fatty vinyl ether films can be prepared that will resist 5% alkali more than 400 times as long as films containing cobalt drier. Further investigations are in progress to determine the formulation effects on copolymer films.

2-Chloroethyl-soybean copolymer films were the hardest of the copolymers studied, followed in order of decreasing hardness by ethyl, 2-methoxyethyl, butyl, isobutyl, and 2-ethylhexyl. In general, the lower alkyl-soybean vinyl ether in 1:3 molar composition produces the hardest film in that series, a result consistent with the fact that soybean vinyl ether polymer formed a very hard film.

Solvent Resistance. Films for this study were baked on microscope slides as described. Baked lower alkyl-soybean vinyl ether copolymers containing cobalt drier were resistant to a wide variety of solvents, including 95% ethanol, butanol, diethyl ether, hexane, acetone, mineral oil, and kerosene. The films were immersed for 20 hrs. Chloroform caused swelling of all the copolymer films as shown in Table III. In tests where a significant difference in swelling time was noted, the copolymers containing 1 mole of alkyl vinyl ether to 3 moles of soybean vinyl ether were affected least. The 2-chloroethyl-soybean copolymer series demonstrates this trend particularly well. Soybean vinyl ether homopolymer was unaffected by chloroform after 20 hrs. of immersion; however this polymer did show some swelling in benzene. All copolymers except the 2-methoxyethyl-soybean series were unaffected by benzene after 20 hrs.; the 2-methoxyethyl copolymer swelled slightly.

Degradation of Vinyl Ether Copolymers

Alkali resistance of the copolymers was found to be superior to the unsaturated vinyl ether homopolymers (Table III). Previous data obtained from infrared spectroscopy and chemical analyses showed that alkali solubility of the homopolymer films was associated with degradation of the ether linkage producing esters, acids, and carbonyl compounds (6). Films of the copolymers containing cobalt drier were cast on silver chloride plates and baked for 1 hr. at 150°C. The plates were examined in the infrared, and the results were compared with the spectra obtained on the homopolymers. In all spectra the appearance of new bands or changes in old bands resulting from baking the copolymers were similar to those observed in baked soybean or linseed vinyl ether homopolymer films; *e.g.*, hydroxyl absorption near 3,330 $cm.^{-1}$, carbonyl absorption at 1,720 $cm.^{-1}$ and C—O absorption of the ester linkage at 1,180 cm^{-1} appeared in the spectra while the C—O—C ether band at 1,100 $cm.^{-1}$ became weaker. However in a given copolymer series the intensity of the spectra bands relative to each other was significant, particularly with reference to the 1,100 $cm.^{-1}$ and 1,180 $cm.^{-1}$ bands.

Table IV lists infrared data on baked films of 2-chloroethyl-soybean copolymer series, n-butyl-soybean copolymer series, and soybean vinyl ether homopolymer. Examination of these data reveals that the poly-2-chloroethyl film has a very strong C—O—C ether

TABLE IV

Comparison of Infrared Spectra of Vinyl Ether Polymer Films [a]

Vinyl ether polymer	Molar composition	Pertinent bands in $cm.^{-1}$			
		3330	1720	1180	1100
2-Chloroethyl-soybean	1:3	W [b]	S	VS	M
	1:1	W	S	VS	MS
	3:1	W	S	S	VS
2-Chloroethyl	......	W	M	VW	VS
n-Butyl-soybean	1:3	M	VS	VS	M
	1:1	M	S	VS	MS
	3:1	M	S	S	S
n-Butyl	......	W	M	M	VS
Soybean	......	S	VS	VS	W

[a] Baked 1 hr. at 150°C. on AgCl plates.
[b] VS, very strong; S, strong; MS, medium strong; M, medium; W, weak; VW, very weak.

band at 1,110 cm.$^{-1}$ and medium to very weak bands at 3,330 cm.$^{-1}$, 1,720 cm.$^{-1}$, and 1,180 cm.$^{-1}$ while the 2-chloroethyl-soybean copolymers show a progressively weaker band at 1,110 cm.$^{-1}$ and a progressively stronger band at 1,180 cm.$^{-1}$ as the amount of soybean vinyl ether was increased. Since the bands at 1,720 cm.$^{-1}$ and 1,180 cm.$^{-1}$ are associated with carbonyl and ester groups, respectively, baked copolymer films richer in soybean vinyl ether appeared to contain more of these degradation products.

Infrared data on the n-butyl-soybean copolymer series indicate the same trend as the 2-chloroethyl series in regard to degradation although the degradation appears more extensive in this series. A comparison of infrared data in Table IV with the alkali solubility studies in Table III shows that there is a relationship between oxidative degradation as shown by infrared spectra and alkali solubility of the copolymer films. However the infrared spectra apparently failed to give information on one important point, namely, the free acid content of the baked films.

Baked films of soybean vinyl ether polymer containing cobalt drier dissolved completely in 5% aqueous sodium hydroxide in 3 to 5 min., and the 2-ethylhexyl-soybean copolymer films dissolved in less than 30 min. Rapid solution of these films could not be caused entirely by hydrolysis of ester groups because polyvinyl palmitate and soybean polyacrylate films immersed in 5% aqueous alkali did not dissolve within 30 min. Soybean and stearyl vinyl ether polymers after degradation by oxygen at 150°C. for 4 hrs. (6) were found to contain up to 31.4% of the acid corresponding to the alkyl chain in the vinyl ether. More recently analyses of degradation products obtained from the oxidation of isopropyl lauryl ether demonstrated the formation of considerable quantities of lauric acid and smaller amounts of lower acids from C_1 to C_{11} (2).

Summary

Soybean vinyl ethers derived from soybean alcohols were copolymerized with lower alkyl vinyl ethers, *e.g.*, ethyl, butyl, isobutyl, 2-chloroethyl, 2-methoxyethyl, and 2-ethylhexyl, in methylene chloride at −30°C., using boron trifluoride etherate catalyst. Molecular weights ranging from 2,000 to 4,000 were obtained on these copolymers by cryoscopic measurements in cyclohexane. An analytical method, using infrared spectroscopy, was employed to determine the composition of the copolymers.

The properties of each alkyl-soybean vinyl ether copolymer were studied at three molar compositions, *e.g.*, 3:1, 1:1, and 1:3. The products were water-white to amber viscous liquids and were soluble in aromatic, chlorinated, and gasoline type of solvents.

Copolymers films were prepared under conditions that were shown to produce extensive degradation of some homopolymer films in order to magnify small differences in properties. These films were hard, wrinkle-free, and resistant to most common solvents, also were 20 to 500 times more resistant to 5% aqueous alkali than soybean vinyl ether polymer prepared under the same conditions.

Copolymer films were baked on silver chloride plates and examined in the infrared. Oxidative degradation of the C—O—C ether linkage was observed in all copolymer films; however the 2-chloroethyl-soybean copolymer series was least susceptible to this degradation.

Acknowledgment

The authors wish to express their appreciation to C. A. Glass for infrared analyses, to Miss Jean Mallan for the ultraviolet analyses, and to Mrs. Clara McGrew for the microanalysis.

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[Received December 3, 1957]

Application of Near Infrared Spectrophotometry to the Study of the Autoxidation Products of Fats[1, 2]

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RECENT IMPROVEMENTS in the quartz spectrophotometer, extending its range to approximately 3,000 $m\mu$, have produced an instrument having greater resolution, in certain parts of the near infrared, than is possible with instruments equipped with NaCl, LiF, of CaF_2 optics (6). Published work on the near infrared spectra of pure compounds (4, 5) suggested that this technique might be useful in analyzing the mixture of oxygen-containing compounds formed in autoxidized fats.

The so-called near infrared portion of the spectrum, from about 700–3,500 $m\mu$, is the region in which are concentrated the fundamental hydrogen stretching absorption bands and many overtone bands of fundamental absorptions farther out in the infrared. A narrow segment of this near infrared region, from 2,700 to 3,000 $m\mu$, is of particular interest to those studying the products of fat oxidation. The primary absorption bands of the O—H stretch of alcohols, hydroperoxides, and acids are found between 2,750 and 2,830 $m\mu$. There is also a strong first overtone band of the C=O stretching vibration of esters, aldehydes, and ketones absorbing from 2,880 to 2,920 $m\mu$. These bands lie so close together that in mixtures they are difficult to resolve and usually appear as one band. However spectral studies of autoxidized methyl linoleate (2) and methyl esters of peanut oil fatty acids (7) have indicated that alcohol and hydroperoxide absorb at sufficiently

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[1] Presented at the 31st Fall Meeting of the American Oil Chemists' Society, Cincinnati, O., Sept.30–Oct. 2, 1957.

[2] American Meat Institute Foundation Journal Paper Number 156.