Comparative Evaluation of Polymers of Heat-Bodied Conjugated and Non-Conjugated Linseed and Soybean Oils

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IN recent years a number of methods for the isomerization of vegetable oils have been developed (4, 13, 14, 21), and some studies have been conducted to determine the performance characteristics of isomerized oils (6, 18). However, comparative evaluations of the properties of the polymerized oils or their polymers prepared from conjugated and non-conjugated oils have never been made.

This investigation was undertaken to compare some of the properties of the polymers of heat-bodied conjugated and non-conjugated linseed and soybean oils. Such an evaluation of oils, polymerized to the same viscosity, should be of value for utilization purposes and might provide evidence for or against the generally accepted Scheiber Theory of polymerization (1, 2, 15). This theory postulates that the polymerization of non-conjugated fat acid esters proceeds first by rearrangement to conjugated isomers followed by polymerization of the conjugated esters.

Due to the complexity of the products formed by polymerization of triglycerides it has not been possible to demonstrate conclusively the mechanism of the polymerization reaction by isolation of a product whose structure can be determined by chemical methods. Although Petit (12) isolated a small amount of product containing a six-carbon atom ring from a polymerized linseed oil, it is possible that the compound was only one of a great many present. One criterion which might be used is the performance of the materials in question; for example, the resistance of oil films to water and dilute alkali might be compared. If the Scheiber Theory is correct, films of the polymers from conjugated and non-conjugated oils heat-bodied to the same viscosity should have similar properties. If they do not, doubt as to the correctness of Scheiber's Theory is indicated.

It has been pointed out that the advantages of isomerized oils for polymerization are increased rates of bodying, low decomposition losses, and the formation of products with excellent color and low acid number (6). The use of polymerization catalysts such as diphenyl disulfide (11), polynuclear quinones (17), aromatic hydrocarbons (16), etc., offers the possibility of obtaining the same advantages if the performance characteristics of the polymers are similar.

TABLE I.

Constants of Alkali-Refined Linseed and Soybean Oils Prior to Heat-Bodying.

Kind of oil	Iodine value	Refractive index at 25°C.	Acid value	Viscosity 25°C.	Color	Conjugation, per cent
Alkali-refined linseed[a]	178.0	1.4780	.23	A	5	......
Conjugated linseed	....	1.4871	.54	E	5	32.5[b]
Alkali-refined soybean	131.9	1.4724	.12	A	3	......
Conjugated soybean	....	1.4780	.38	C	2-3	26.8[c]

[a] Starting materials used for the preparation of the isomerized oils, and the preparation of the heat-bodied oils with diphenyl disulfide as polymerization catalyst.

[b] 5.0 per cent triene conjugation, 27.5 per cent diene conjugation.

[c] 2.4 per cent triene conjugation, 24.4 per cent diene conjugation.

Experimental

Alkali-refined linseed and soybean oils were used as starting materials. The isomerized oils were prepared by means of a nickel-carbon catalyst (13). The analytical constants of the various oils prior to heat-bodying are listed in Table I.

Twelve hundred-gram samples of the oils were heat-bodied at 306° ± 2° C. in a 2-liter, three-necked flask fitted with a mechanical stirrer, thermometer, iron-constantin thermocouple and inlet and outlet tubes for carbon dioxide. The flask was heated at a uniform rate by means of a Gas-Col mantle; after reaching 306° C. the temperature was controlled within ± 2° C. by a Wheelco capacitrol instrument. The oils were heated until they had reached a viscosity of approximately Z at 25° C. (Gardner Scale). As a polymerization catalyst 0.5% diphenyl disulfide (Eastman C. P. grade) was chosen as a representative example of one class of material. The constants of the polymerized oils are given in Table II. The slight viscosity differences of the various oils which arise from the extreme difficulty in heat-bodying oil to a prescribed viscosity are not considered significant.

The polymers of each bodied oil were separated from the non-polymeric fraction according to the procedure of Kolthoff (9). Approximately 1200 ml.

TABLE II.

Constants of Alkali-Refined Linseed and Soybean Oils After Heat-Bodying at 304-308°C.

Oils	Viscosity at 25°C.	Time heated at 304-308°C. (hours)	Iodine value	Refractive index at 25°C.	Acid value	Color	Conjugation per cent[a]	Percentage polymer
Alkali-refined linseed	Z_1	5.5	111.9	1.4871	12.8	4	1.5	66.5
Alkali-refined linseed + 0.5% diphenyl disulfide	Z^+	4 5	96.0	1.4887	8.7	6	2.1	69.4
Conjugated linseed	Z_2	1.0	93.1	1.4888	5.0	4	7.0	68.5
Alkali-refined soybean	Z_1^-	15.0	83.5	1.4817	30.4	6	2.1	64.5
Alkali-refined soybean + 0.5% diphenyl disulfide	Z_1	4.5	79.8	1.4820	13.8	5	3.6	75.7
Conjugated soybean	Z	5.5	79.2	1.4810	11.1	4	4.2	76.6

[a] After polymerization of the oils, the conjugation remaining was practically all diene. These values for per cent conjugation must be accepted with reservation because general absorption of cyclic structures known to be present in bodied oils greatly increases the experimental error in determining small amounts of conjugation.

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TABLE III.

Constants of the Polymers From Heat-Bodied Linseed and Soybean Oils.

Polymer	Viscosity	Iodine value	Refractive index at 25°C.	Acid value	Color	Conjugation, per cent[a]	Set-to-touch time (hours)
Alkali-refined linseed	Z_5	99.6	1.4892	5.7	5	1.5	1¾
Alkali-refined linseed + 0.5% diphenyl disulfide	Z_4	97.2	1.4910	6.3	6	4.6	>8
Conjugated linseed	Z_5^+	98.0	1.4891	2.4	5	6.9	1¼
Alkali-refined soybean	Z_4^+	78.3	1.4850	16.5	7	3.8	7
Alkali-refined soybean + 0.5% diphenyl disulfide	Z_4	77.7	1.4839	7.0	6	3.8	>8
Conjugated soybean	Z_3^+	75.9	1.4840	5.6	4-5	5.3	3¼

[a] Diene conjugation. These values for per cent conjugation must be accepted with reservation because general absorption of cyclic structures known to be present in bodied oils greatly increases the experimental error in determining small amounts of conjugation.

of acetone was added to 200 grams of polymerized oil in a two-liter flask and the mixture heated with stirring on a steam bath until complete miscibility had been effected. The solution was transferred to a separatory funnel and allowed to cool to room temperature. Two distinct layers were formed. The lower layer was drawn off into a tared flask and the acetone removed by heating on a steam bath under reduced pressure with a stream of carbon dioxide bubbling through the oil for three hours. After the flask was cooled, it was reweighed and the percentage of polymer determined. The characteristics of the polymeric fractions are shown in Table III.

In this work conjugation was determined with a Beckman quartz spectrophotometer using purified Skellsolve F as the solvent. An $E^{1\%}_{1\,\text{cm.}}$ of 1150 at 2320 Å was taken as 100% diene conjugation and an $E^{1\%}_{1\,\text{cm.}}$ of 1850 at 2705 Å as 100% triene (8).

Acid numbers were determined by titration using 0.1 N alcoholic potassium hydroxide solution. Viscosities were measured at 25° C. by comparison with Gardner bubble viscometers. Colors were obtained by matching Gardner color standards. Iodine values were determined by the rapid Wijs method (7).

The polymeric materials were prepared for evaluation by reducing to a J viscosity with mineral spirits and naphthenate driers were added. In all cases 0.3% lead and 0.03% manganese was added (per cent metal based on non-volatile material).

The following testing procedures were used:

Drying Time. The drying rates of the polymeric materials were determined by the finger method. Films (0.003" wet thickness) were cast on glass panels by means of a doctor blade and the time for the film to set-to-touch noted. The results are given in Table III.

Cold Water Resistance. Films of the polymers were flow-coated on standard tin panels and the coated panels were allowed to drain and dry in a vertical position. For testing, the end of the panel which was uppermost during the drying was immersed in distilled water. Triplicate sets of panels were used and each panel was examined visually every 24 hours for whitening and cloud formation. The results are shown in Table IV.

Hot Water Resistance. Three sets of panels were prepared as for the cold water tests. They were immersed in boiling distilled water for 15 minutes and then removed and examined (see Table IV).

Alkali Resistance. Test tubes were dipped in the samples of polymeric material, then removed, inverted and allowed to drain dry. The tubes were suspended in a 0.1 N sodium hydroxide solution and examined periodically. The results of these tests are summarized in Table V.

All the films prepared for the resistance tests were allowed to air-dry for three weeks in constant temperature, constant humidity room at 75 ± 3° F. and 60 ± 5% relative humidity.

Discussion

This study confirms the results, obtained by Bradley and Richardson (3) and Mitchell and Kraybill (10), that small amounts of conjugation are formed during heat-bodying of non-conjugated linseed oil. Furthermore, we have found this to be true for soy-

TABLE IV.

Resistance of Polymer Films to Water.

A. Cold Water.

Polymer	24 Hours		48 Hours		96 Hours	
	Condition	Recovery, min.	Condition	Recovery, min.	Condition	Recovery, min.
Alkali-refined linseed	Light cloud	12	Light cloud	18	Very slight white	35
Alkali-refined linseed + 0.5% diphenyl disulfide	Heavy white	25	Very heavy white	35	Very heavy white	47
Conjugated linseed	Light cloud	12	Light cloud	16	Very slight white	30
Alkali-refined soybean	Moderate white	20	Heavy white	22	Heavy white	40
Alkali-refined soybean + 0.5% diphenyl disulfide	Heavy white	25	Very heavy white	38	Very heavy white	48
Conjugated soybean	Moderate cloud	14	Slight white	15	Moderate white	29

B. Boiling Water—15-minute exposure

Polymer	Condition	Recovery, min.
Alkali-refined linseed	Moderate white	6
Alkali-refined linseed + 0.5% diphenyl disulfide	Very heavy white	27
Conjugated linseed	Slight white	4
Alkali-refined soybean	Heavy white	20
Alkali-refined soybean + 0.5% diphenyl disulfide	Heavy white	18
Conjugated soybean	Moderate white	20

TABLE V.

Resistance of Polymer Films to Dilute Alkali.

Polymer	5 minutes	10 minutes	15 minutes	25 minutes	30 minutes	40 minutes	1¼ hours
Alkali-refined linseed	Beginning to wrinkle—yellowed	80% wrinkled	100% wrinkled and loosened	100% off			
Alkali-refined linseed + 0.5% diphenyl disulfide	Puckered—yellowed	Film dissolving	Completely dissolved				
Conjugated linseed	Beginning to wrinkle—slight yellow	60% wrinkled	100% wrinkled	100% off			
Alkali-refined soybean	Beginning to wrinkle	100% wrinkled	Loosened	100% off			
Alkali-refined soybean + 0.5% diphenyl disulfide	Beginning to wrinkle—slight yellow	Softening	Beginning to wrinkle	100% wrinkled	100% off		
Conjugated soybean	OK	Very-slight white	White	White-softening		Beginning to wrinkle	100% off

bean oil. These results lend evidence for Schreiber's Theory of polymerization.

However, the results shown in Tables IV and V indicate that polymers from heat-bodied, conjugated linseed and soybean oils are superior to polymers from the non-conjugated oils, bodied without a catalyst or with diphenyl disulfide as a polymerization catalyst, in resistance to water or dilute alkali. This fact is important because it cannot be readily accounted for on the basis of Scheiber's theory of polymerization. Therefore, doubt as to the correctness of this theory is indicated.

It should be noted that the acid number of the polymer from the heat-bodied soybean oil is considerably higher than those of the other two polymers in the same series. This is a factor to be considered because the poor resistance of materials with high acid number of alkaline solutions is well known. However, the acid number of the soybean polymer obtained from the bodied oil using the diphenyl disulfide catalyst is about the same as the acid number of the polymer from bodied conjugated soybean oil, yet the latter is far superior in performance.

As far as we have been able to determine, no explanation for the activity of polymerization catalysts in general has ever been given. However, Terrill (19) and Cannegieter (5) proposed that certain of these materials act to isomerize catalytically some of the polyunsaturated fat acid radicals to conjugated configurations prior to polymerization and do not have a catalytic effect on the actual polymerization mechanism. This viewpoint was experimentally substantiated for the catalytic activity of sulfur dioxide by the work of Waterman and co-workers (20, 22, 23). These investigators found that sulfur dioxide can be used as a polymerization catalyst for linseed and soybean oils under certain conditions and as a conjugation catalyst under other conditions.

It is interesting to note that Waterman and Van Vlodrop state that linseed oil polymerized with sulfur dioxide is of better quality than the oil polymerized without the catalyst (20).

On the other hand, according to our evaluation tests the polymers produced using 0.5% diphenyl disulfide as a polymerization catalyst were inferior in performance to the polymers obtained from heat-bodied conjugated oils. This apparently indicates that the polyunsaturated fat acid radicals were not isomerized to conjugated configurations prior to their polymerization when using this catalyst.

Therefore, it appears that in the heat-bodying of vegetable oils, polymerization takes place through more than one mechanism, depending on the kind of material, conjugated or non-conjugated, and on the type of catalyst, if one is present.

Summary

Films from polymers of heat-bodied, catalytically conjugated linseed and soybean oils have been shown to be superior, in their resistance to water and dilute alkali solution, to films from polymers of non-conjugated oils that were heat-bodied alone and with 0.5% diphenyl disulfide as a polymerization catalyst. These results are not accounted for on the basis of the Scheiber theory of polymerization.

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