Studies of Thermal Polymerization of Vegetable Oils with a Differential Scanning Calorimeter

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ABSTRACT: Vegetable oils are often thermally polymerized to provide a vehicle for printing inks and paints. The formations of isomerization, and the intra- and intermolecular bonds involved in the thermal process are crucial in designing a product with the appropriate characteristics. It was found, with a differential scanning calorimeter, that the thermal polymerization of various vegetable oils could be activated at lower temperatures under a dry-air purge and/or in the presence of metallic catalysts. The Diels-Alder reaction and the formation of intermolecular bonds in alkali-refined soybean oil under a dry-air purge could be activated at 99 and 161°C in the presence of metallic catalysts, compared with 231 and over 300°C in the absence of metallic catalysts, respectively. The energies needed to activate the Diels-Alder reaction and to form intermolecular bonds were calculated, and is in good agreement with available data. The hardness test of baked vegetable-oil systems was also implemented to qualitatively determine the degree of cross-linking.
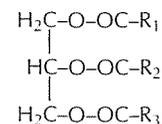   Paper no. J9037 in *JAOCS 76*, 1211–1216 (October 1999).

KEY WORDS: Activation energy, cross-link, DSC, vegetable oils.

Because of increasingly stringent environmental requirements, vehicles for printing inks and paints with lower, or even zero, volatile organic compound (VOC) content are desirable. Soybean- and linseed oil-based vehicles have been successfully used in both lithographic and letterpress news inks (1,2) and paints (3–9). They are used in film formation, have better compatibility with pigments, and are environmentally friendly.

Soybean oil, which is the second cheapest among vegetable oils (10), is a semidrying oil (11,12) because of its lower double-bond density. Semi-drying oils cannot dry at room temperature if their functional groups are not modified. As a result, the use of soybean oil in both the printing ink and paint industries is significantly limited. Although linseed oil falls into the category of drying oils, it is generally modified in order to shorten its drying time (3).

Vegetable oils are primarily composed of a triglyceride with the following structure:

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$$H_2C-O-OC-R_1$$
$$HC-O-OC-R_2$$
$$H_2C-O-OC-R_3$$

where R_1, R_2, and R_3 are the same or different hydrocarbon residues of fatty acids. The weight percentages of various fatty acid compositions in soybean and linseed oils are listed in Table 1 (13).

A triglyceride has three functional groups, whose activities are determined by the number of double bonds measured as the iodine number, and their positions on them. When these trifunctional groups are incorporated, the polymer will be either branched or cross-linked (14). During drying, the functional groups of triglycerides experience both intramolecular and intermolecular linkages *via* oxygen uptake (3) and the Diels-Alder reaction, if heat is provided. An intramolecular linkage can occur not only inside a monomer (a triglyceride), but also inside a dimer (a molecule linked by two triglycerides), trimer, and so on. It can occur either *via* the Diels-Alder reaction or the opening of double bonds inside a molecule *via* oxygen uptake from air. The intramolecularly linked molecules have fewer double bonds, and a weaker ability to cross-link. Their remaining functional groups may react with other triglycerides, reduce the ability of a system to cross-link, and thus result in poor mechanical properties.

How to make use of vegetable oils depends on how well they are understood. In order to explore the market for vegetable oils in both printing inks and paints, it is important to find optimal approaches to synthesizing fatty acid and/or soybean oil derivatives, and to understanding the thermal process. In this paper, the cross-linking mechanisms of soybean and linseed oils, the effects of metallic catalysts on oxygen uptake during thermal processing [as measured with the differential scanning calorimeter (DSC)], the estimation of

TABLE 1
Acid Composition of Vegetable Oils (%)[a]

Oil	9,12,15-Linolenic	9,12-Linoleic	Oleic	Saturated
Soybean	5–9	52–55	22–28	14
Linseed	48–54	14–19	20–24	10

[a]See Reference 13.

threshold energies to activate thermal polymerization, and the hardness of the baked-oil films after application are reported.

EXPERIMENTAL PROCEDURES

Sample preparations. Alkali-refined soybean oil was obtained from Golden Chef (Chandler, AZ). Heat-bodied soybean oil was prepared by heating the alkaline-refined soybean oil at $305 \pm 3°C$ under a nitrogen purge for 5 h. Its apparent viscosity was M as determined with a Gardner Bubble Viscometer (ASTM D-1545-63; Paul Gardner Co., Inc., Pompano Beach, FL) and its color index was 1 as measured by a Gardner Color scale (ASTM D 1544-63). Soy fatty acids (Industrene 225) with iodine values of 135–150 were obtained from Witco Corp. (Memphis, TN). Metallic catalysts were obtained from Mooney Chemical (Cleveland, OH). The calcium, cobalt, and zirconium catalysts contained 10, 12, and 12% metal content by weight, respectively. The suggested amounts (15) in paints—2% calcium, 0.5% cobalt, and 0.5% zirconium metallic catalysts by weight—were added to the samples to be tested. The compositions of these samples are listed in Table 2.

The samples were applied onto 3 × 5 in. cold roll steel (CRS) Q-Panels (Q-Panel Lab Products, Cleveland, OH) using a film applicator (Paul N. Gardner Company, Inc.) with 2-mL wet thickness. Then they were baked in an oven for 30 min at various temperatures. The hardness of a film was determined by pencil hardness test (ASTM D3363) at more than 10 different spots 1 h after baking. The hardness of pencil leads are ranked from softest to hardest as follows: 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 1H, 2H, 3H, 4H, 5H, 6H. In this test, pencil leads of increasing hardness values are forced against a coated surface in a precisely defined manner until one lead mars the surface. The hardness is expressed as the grade of the next softest pencil. The differences in the hardness among replications of the same lead were within one grade (15).

DSC experiments were carried out using a 2910 TA instrument (TA Instrument, Inc., New Castle, DE). Samples were purged under either dry air or dry nitrogen at a ramping rate of 5.00°C/min. At least three replicates were made for each sample. The difference in temperatures were within 1°C.

RESULTS AND DISCUSSION

Hardness. Since aromatic segments do not exist in triglyceride systems, the hardness of the coating films only depends on their degree of cross-linking (3,16–22). A highly cross-linked system is a high molecular-weight system. However, a higher molecular-weight system does not necessarily imply a highly cross-linked system. Molecular weight determined from gel permeation chromatography and viscosity measurements can only be called "apparent molecular weight." No information on the degree of cross-linking can be obtained from these measurements. Currently, measurements of film hardness and Young's modulus are the two methods used to determine the degree of cross-linking (15). In this experiment, hardness measurements were used to qualitatively determine the degree of cross-linking for the purpose of simplicity. In Table 3, the baked-film hardness of alkali-refined soybean oil, heat-bodied soybean oil, and linseed oil with the addition of metallic catalysts is listed.

In general, the hardness of commercial thermal-cured paints should not be lower than 4H, and that of ambient-cured paints should fall in the range of 2B to 2H, depending on the application. It was observed that the films of soybean oil (code A), heat-bodied soybean oil (code B), and linseed oil (code I) baked at 120 and 140°C were soft and tacky. It could be that the functional groups of triglycerides baked below 140°C are not sufficiently reactive. A large number of linkages were not cross-linked, which resulted in poor hardness. Although the films baked at 160 and 180°C could dry, they were not hard enough to be a thermal-cured paint. At higher temperatures, the functional groups of triglycerides were reactive enough to cross-link. That explains why the hardness of the films baked at 200°C was excellent. The conjugated double bonds of the heat-bodied soybean oil were significantly reduced in the thermal pre-polymerization *via* isomerization (the Diels-Alder reaction). As a result, the heat-bodied soybean oil had a reduced ability to react with oxygen and showed a lower degree of cross-linking and pencil hardness.

One possible explanation, from the above analysis of film hardness, is that baked vegetable oils with the addition of metallic catalysts experience two competitive linkages in the thermal processes, depending on curing temperature. At lower temperatures (140°C and below), although isomeriza-

TABLE 2
Preparation of Samples

Code	Composition	Addition of catalysts[a]
A	Soybean oil	Yes
B[b]	Heat-bodied soybean oil	Yes
I	Linseed oil	Yes
J	Soybean oil	None
K	Linseed oil	None
L	Linoleic acid	None
M	Linolenic acid	None
N	Soy fatty acid	None

[a]Yes, metallic catalysts were added; none, no metallic catalysts were added.
[b]Prepared under a nitrogen purge.

TABLE 3
The Hardness of Films[a]

Code	120°C	140°C	160°C	180°C	200°C
A	<6B	<6B	F	F	4H
B	<6B	<6B	<6B	HB	2H
I	<6B	<6B	F	F	5H

[a]Hardness was determined using the pencil hardness test (ASTM D3363). More than 10 measurements were carried out in the testing. The differences in hardness among replications of the same lead were all within the same hardness grade. Leads are ranked from softest to hardest as follows: 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 1H, 2H, 3H, 4H, 5H, 6H. Films were tested 1 h after application. The temperature fluctuation in baking was within 3°C.

tion does occur, the degree of cross-linking is very low, and the film has very poor mechanical properties. At higher temperatures (200°C and above), cross-linking is dominant, and the films have excellent mechanical properties.

DSC. Figure 1 shows DSC curves of alkali-refined soybean oil (code A, see Table 1), heat-bodied soybean oil (code B), and linseed oil (code I) with the addition of metallic catalysts under a dry-air purge. Each of the three curves contained a peak in the range of 150 to 170°C. Only in the curves of alkali-refined soybean oil and linseed oil were there shoulders at 81.26 and 99.09°C, respectively. Based on the above analysis of hardness, these peaks could be thought of as an indication of cross-linking, and the shoulders as an indication of the Diels-Alder reaction. The heat-bodied soybean oil did not have such a shoulder because its double bonds had been significantly reduced in the process of thermal prepolymeriza-'ion. Linseed oil showed a stronger exothermic signal than ;oybean oil because it had a higher double-bond density. It ilso had a stronger ability to take up oxygen, to cross-link, ind to give off more energy than soybean oil during heating.

Figure 2 shows DSC curves of alkali-refined soybean oil code J) and linseed oil (code K) without the addition of netallic catalysts, and under a dry-air purge. There was an :xothermic peak at 272.77°C and a shoulder at 199.04°C for he linseed oil, and a shoulder at 230.55°C for the soybean)il. Again, the peak indicated cross-linking, while the shoulder indicated the Diels-Alder reaction. Both the peak and ;houlders shifted to higher temperatures without the addition)f metallic catalysts.

Figure 3 is a comparison of DSC curves of linseed oils vith (code I) and without (code K) the addition of metallic :atalysts, and under a dry-air purge. Both peaks and shoulders were shifted to lower temperatures with the addition of netallic catalysts.

Figure 4 shows DSC curves of linoleic (code L) and inolenic (code M) acids without the addition of metallic catlysts, and under a dry-air purge. Linoleic acid had a peak at
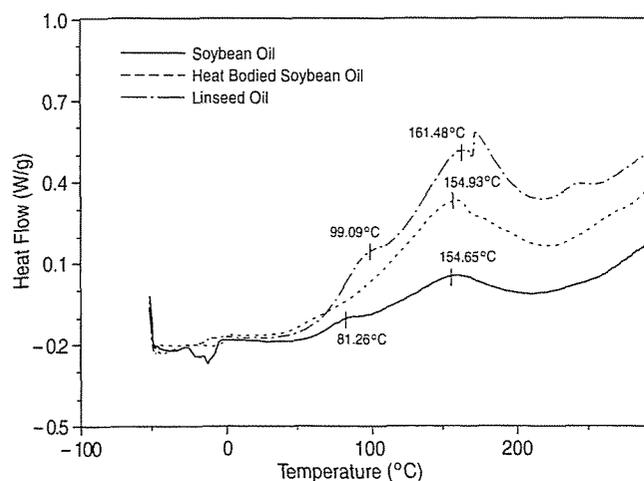
FIG. 2. DSC spectra of vegetable oils in the absence of metallic catalysts and under a dry-air purge. See Figure 1 for abbreviation.

250.49°C and a shoulder at 149.23°C. Similar to the above figures, the shoulder is thought to be the result of the Diels-Alder reaction. In the DSC curve of linolenic acid the shoulder became a large peak at 117.80°C because of the much higher double-bond density of linolenic acid. The peak at 231.51°C was smaller because of the reduction of double bonds in the Diels-Alder reaction at the lower temperature (117.80°C).

Figure 5 shows the DSC curves of soybean oil (code A), heat-bodied soybean oil (code B), and linseed oil (code I) with the addition of metallic catalysts, and soybean oil (code K) without the addition of metallic catalysts and under a nitrogen purge. There were no peaks or shoulders above room temperature. A valley appeared in each curve only because thermal polymerization was an endothermic process. This valley indicated that there is no optimal temperature below 300°C in the process of thermal polymerization under a nitrogen purge.

FIG. 1. Differential scanning calorimeter (DSC) spectra of vegetable oil n the presence of metallic catalysts, described in the Experimental Procedures section, and under a dry-air purge.
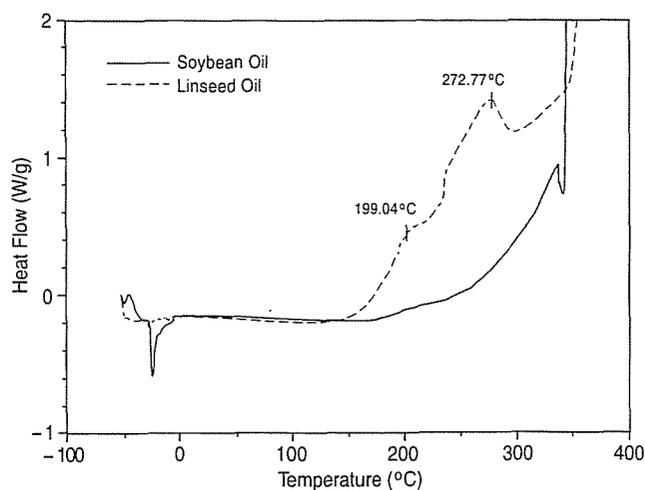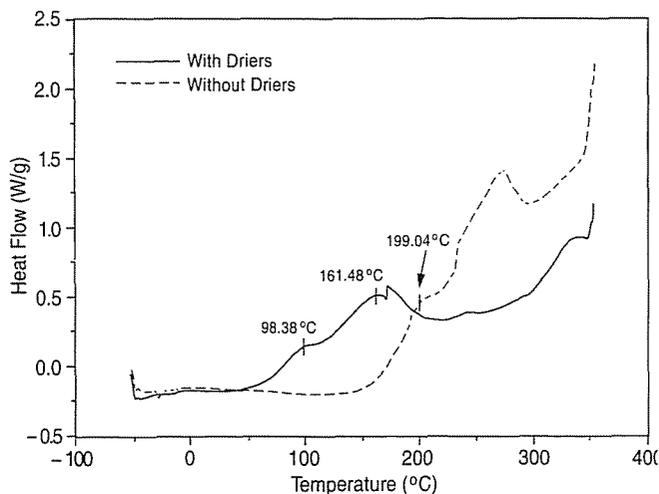
FIG. 3. DSC spectra of linseed oil in the absence of metallic catalysts and under a dry-air purge. See Figure 1 for abbreviation.
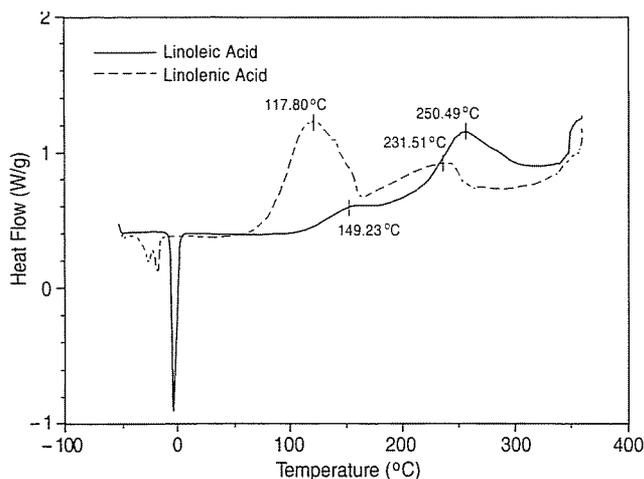
FIG. 4. DSC spectra of linoleic acid and linolenic acid in the absence of metallic catalysts and under a dry-air purge. See Figure 1 for abbreviation.

FIG. 6. DSC spectra of soy fatty acids in the absence of metallic catalysts, described in the Experimental Procedures section, and under a dry-nitrogen purge. See Figure 1 for abbreviation.

Figure 6 shows the DSC curve of soy fatty acids (code N) without the addition of metallic catalysts, and under a nitrogen purge. Thermal polymerization started above 300°C. It is the lowest temperature for the thermal polymerization of soya fatty acids (Fig. 5).

The results derived from the DSC curves of some vegetable oils under a dry-air purge are summarized in Table 4.

From the above results, several conclusions can be tentatively drawn. (i) Under a nitrogen purge, thermal polymerization of soybean and linseed oils below 300°C is not efficient, even with the addition of metallic catalysts (Fig. 5). (ii) There is more than one reaction involved in the process of thermal polymerization. Intermolecular linkage formation competes with other reactions. Isomerization starts at a lower temperature and depletes double bonds, resulting in poor mechanical properties when compared with thermal polymerization at higher temperatures. (iii) Without the addition of metallic catalyst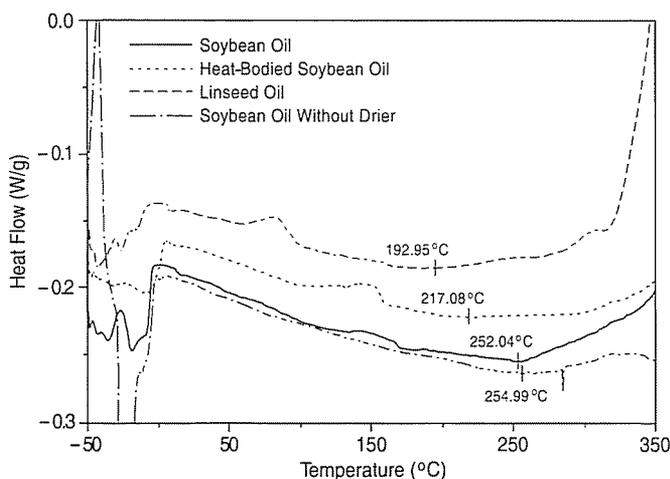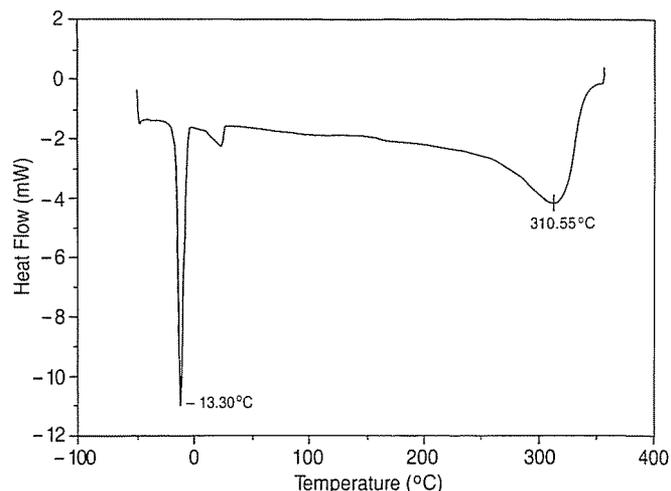s and under a dry-air purge, soybean oil and linseed oil start to thermally polymerize when the temperature is above 230 and 200°C, respectively. This observation is consistent with the suggested temperature (240°C) of thermal isomerization for triglycerides (23). In order to minimize the rate of heat bodying, the temperature should not be over 240°C. (iv) Without the addition of metallic catalysts, and under a dry-air purge, linseed oil and soybean oil start to cross-link when the temperature is above 270°C and 300°C, respectively. (v) The temperatures that initiate the Diels-Alder reaction and cross-linking can be lower under a dry-air purge than they are under a nitrogen purge. A higher degree of cross-linking between triglycerides can be obtained in the presence of oxygen. This is consistent with the current theory about the mechanism of drying (11,12). (vi) Under a dry-air purge, the temperatures needed to initiate the Diels-Alder reaction and cross-linking can be reduced with the addition of metallic catalysts. The Diels-Alder reaction of soybean and linseed oils starts below 100°C, and cross-linking starts at approximately 160°C.

Threshold energy. If RT is defined as threshold energy, where R is the gas constant and T is the absolute temperature, then the threshold energies of vegetable oils purged with dry air can be calculated from Table 4, and are listed in Table 5.

As seen in Table 5, the threshold energies are greater without the addition of metallic catalysts. In the absence of metallic catalysts, the threshold energy of the Diels-Alder reaction for soybean oil is higher by a factor of 1.353 (4186/3093 = 1.353), and 1.332 (3924/2945 = 1.332) for the linseed oil, compared to those in the presence of metallic catalysts. If the same factor is assumed, then the threshold energy of cross-linking for the soybean oil in the absence of metallic catalysts (code J) can be estimated as follows:

$$3612 \times 1.353 = 4887 \text{ J/mol} \qquad [1]$$

This is in a good agreement with the value (>4763 J/mol) in Table 5. The lowest temperature required to activate cross-linking in soybean oil is

FIG. 5. DSC spectra of vegetable oils in the presence of metallic catalysts and under a dry-nitrogen purge. See Figure 1 for abbreviation.

TABLE 4
The Diels-Alder Reaction and Cross-linking of Vegetable Oils in Air[a]

Code	Content	Drier[b]	Diels-Alder reaction	Cross-linking
A	Soybean oil	Yes	Yes (99.09°C)	Yes (161.48°C)
B	Heat bodied oil	Yes	Not available	Yes (154.93°C)
I	Linseed oil	Yes	Yes (81.26%C)	Yes (154.65°C)
J	Soybean oil	None	Yes (230.55°C)	Yes (>300°C)
K	Linseed oil	None	Yes (199.04°C)	Yes (272.77°C)
L	Linoleic acid	None	Yes (149.23°C)	Yes (250.49°C)
M	Linolenic acid	None	Yes (112.80°C)	Yes (231.51°C)

[a]The deviations of recorded temperatures were within 2°C.
[b]Yes, metallic catalysts were added; none, no metallic catalysts were added.

TABLE 5
The Threshold Energies of Vegetable Oils in Air

Code	Content	Drier[a]	Diels-Alder reaction (J/mol)	Cross-linking (J/mol)
A	Soybean oil	Yes	3093 ± 17	3612 ± 17
B	Heat bodied oil	Yes	Not available	3557 ± 17
I	Linseed oil	Yes	2945 ± 17	3555 ± 17
J	Soybean oil	None	4186 ± 17	>4763
K	Linseed oil	None	3924 ± 17	4536 ± 17
L	Linoleic acid	None	3510 ± 17	4351 ± 17
M	Linolenic acid	None	3207 ± 17	4194 ± 17

[a]Yes, metallic catalysts were added; none, no metallic catalysts were added.

$$4887/8.31 - 273.13 = 315°C \qquad [2]$$

This result is consistent with that obtained from DSC, where the temperature is above 300°C.

DSC is a powerful tool when used to study the thermal polymerization of vegetable oils. From the analyses based on the DSC experiment and pencil hardness, considerable information, such as the lowest temperatures needed to activate the Diels-Alder reaction and cross-linking, can be obtained. In the thermal polymerization process, the intermolecular linkages compete with the Diels-Alder reaction and intramolecular linkages of triglycerides. The Diels-Alder reaction and cross-linking can only occur above the threshold temperatures. The Diels-Alder reaction of triglycerides starts when the temperature is above a certain point (about 140°C), depending on what gas is purged, and which and how much metallic catalyst is added. However, the cross-linking of triglycerides starts at a higher temperature (200°C or above). Below this temperature, the degree of cross-linking is low, and the hardness is poor.

ACKNOWLEDGMENT

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