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.


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:

$$\text{H}_2\text{C}–\text{O}–\text{OC–R}_1$$

$$\text{H}_2\text{C}–\text{O}–\text{OC–R}_2$$

$$\text{H}_2\text{C}–\text{O}–\text{OC–R}_3$$

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>
<thead>
<tr>
<th>Oil</th>
<th>9,12,15-Linolenic</th>
<th>9,12-Linoleic</th>
<th>Oleic</th>
<th>Saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean</td>
<td>5–9</td>
<td>52–55</td>
<td>22–28</td>
<td>14</td>
</tr>
<tr>
<td>Linseed</td>
<td>48–54</td>
<td>14–19</td>
<td>20–24</td>
<td>10</td>
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*See Reference 13.
threshold energies to activate thermal polymerization, and the hardness of the baked-oil films after application are reported.

**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-
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 prepolymerization. Linseed oil showed a stronger exothermic signal than soybean oil because it had a higher double-bond density. It also had a stronger ability to take up oxygen, to cross-link, and 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 metallic catalysts, and under a dry-air purge. There was an exothermic peak at 272.77°C and a shoulder at 199.04°C for the linseed oil, and a shoulder at 230.55°C for the soybean oil. Again, the peak indicated cross-linking, while the shoulder indicated the Diels-Alder reaction. Both the peak and shoulders shifted to higher temperatures without the addition of metallic catalysts.

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

Figure 4 shows DSC curves of linoleic (code L) and linolenic (code M) acids without the addition of metallic catalysts, and under a dry-air purge. Linoleic acid had a peak at 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.
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 catalysts 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:

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

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
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.

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REFERENCES


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