Free Radical Maleation of Soybean Oil *via* a Single-Step Process

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ABSTRACT: In this study a new value-added product was developed from soybean oil for use as a chemical feedstock. The investigation and optimization of this work resulted in a fast and simple process to maleate soybean oil. An anhydride functionality was introduced into soybean oil through a free radical-initiated maleation. Two initiators were evaluated, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane peroxide and di-*tert*-butyl peroxide. The effects of reaction time, initiator concentration, maleic anhydride concentration, and reaction temperature were investigated. The maleated soybean oil was characterized using acid value, iodine value, and FTIR spectroscopy. The acid value was directly related to the initial concentration of maleic anhydride, whereas the concentration and type of initiator had little effect on the acid value. The peroxide-initiated functionalization of soybean oil with maleic anhydride in a closed vessel at elevated pressure and temperature was found to proceed by a Diels–Alder mechanism.

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KEY WORDS: Free radical initiation, maleation, maleic anhydride, process, soybean oil.

As the demand for petroleum exceeds production, alternative feedstocks must be found. Agriculturally based chemicals are one of the most attractive alternatives because they are environmentally friendly chemical feedstocks and offer a sustainable source of development. In previous work, we have reported on the rationale, design, and engineering of biobased materials (1,2). One potential agricultural feedstock is soybean oil (SO), which is a mixture of TG containing long-chain FA. Typically, SO contains 4.3–4.6 double bonds per mole depending on the origin of the seed. The presence of unsaturation allows for chemical modifications through specific reactions with these double bonds and the introduction of reactive carbonyl functional groups.

There is a great deal of literature on the functionalization of vegetable oils using maleic anhydride (MA) to enhance their reactivity. Morrel and Samuels (3) studied the reaction between MA and conjugated oil systems using oils from china wood and oiticica containing FA with conjugated double bonds. The reaction was found to follow a typical Diels–Alder addition. Root (4) investigated the functionalization of SO with MA and described the use of benzoyl peroxide in the maleation reaction. He concluded that the use of benzoyl peroxide as a catalyst was advantageous, as it allowed the reaction to proceed at a lower reaction temperature of 110°C as compared with 160–190°C when benzoyl peroxide was not used. Root hypothesized that the presence of a peroxide leads to electron delocalization, resulting in conjugation of the double bonds within the unsaturated FA in the SO to form a conjugated system, as shown in Figure 1. However, the mechanism of MA addition to SO and the products of this reaction are still ill defined and are the subject of a great deal of debate in the literature. Clocker (5) postulated a cyclobutane structure for oleic acid adducts. Bickford and coworkers (6) studied the reaction between MA and methyl oleate and suggested that MA was added at the 8th or 11th carbon atom. The results of Teeter *et al.* (7) and Kappelmeier *et al.* (8) also support a succinic-type structure on the basis of model compound studies using methyl linoleate and methyl linolenate. Accordingly, the reactions with di-unsaturated, nonconjugated double bonds proceeded by the "-ene" reaction mechanism and the succinic-type addition occurred at the 8th, 11th, and 14th carbon atoms, with a major addition product at the 11th carbon. Based on these results, Kappelmeier *et al.* (8) postulated that conjugation might occur simultaneously with an attack at the methylene carbon by which a second mole of MA can be added by a Diels–Alder addition. Somewhat similarly, Plimmer and Robinson (9) suggested that a second mole of MA could be added to the cyclohexene ring. Nagakura and Yoshitomi (10), however, suggested that the presence of free radicals leads to copolymerization of MA with the TG and based their conclusion on the increase in viscosity of the reaction product. More recently SO maleation was done by Eren and coworkers (11). In this study, they reported that radical-initiated maleation is more difficult to characterize than thermally or Lewis acid-catalyzed maleation adducts of SO; thus, these products were not considered further. The application of maleated SO was also patented recently for use as a binder in paints (12). It is apparent that although maleation of SO was reported previously, most of the work was focused on the mechanism of this reaction and almost no attention was given to process optimization of this free radical-initiated reaction. Therefore, the goal of this work was to assess the process and determine the usefulness of this reaction. The study uniquely focused on maleation within a closed system under elevated temperatures and pressures. The closed system synthesis prevents premature sublimination of the MA, which was a recurring problem in the past and caused lower yields.

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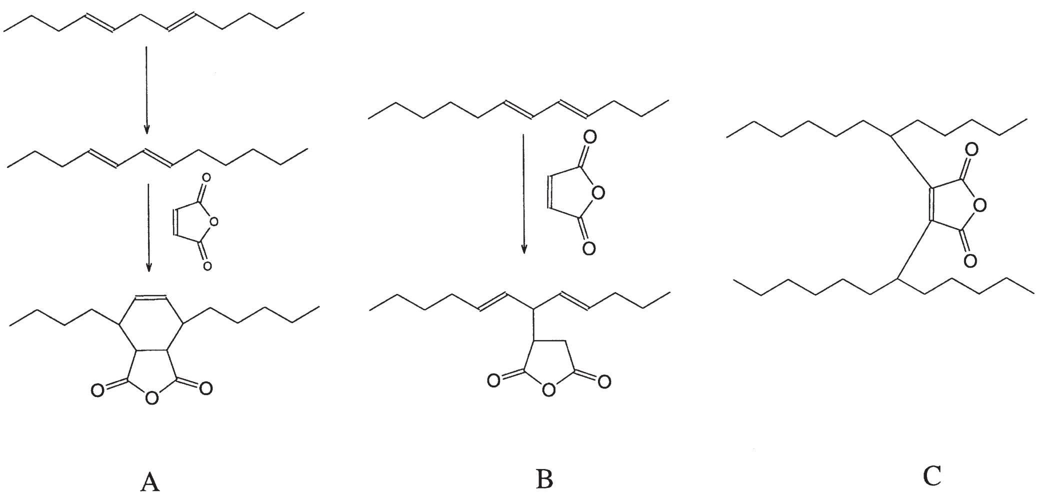

FIG. 1. Possible addition of maleic anhydride to nonconjugated double bonds. (A) Diels–Alder adduct; (B) radical addition; (C) cross-linking.

EXPERIMENTAL PROCEDURES

Materials. Unhydrogenated SO was purchased from Spectrum Chemicals (Gardena, CA). MA, octanol, isopropanol, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane peroxide (L101), and di-*tert*-butyl peroxide were purchased from Sigma-Aldrich (Milwaukee, WI).

Equipment. FTIR analyses were run on a PerkinElmer model 1000 spectrometer with a NaCl window. Viscosity measurements were done using a model EX100 Brookfield viscometer at 25°C.

Method. Reactions were carried out by charging a 2-L Parr reactor equipped with a motorized stirrer, thermocouple, and heating element with MA, SO, and the initiator. The initial reaction time was taken at the time the reactor temperature reached a preset temperature. At the end of each reaction, the reactor was connected to a vacuum pump for 30 min, and any volatile products were collected in a solvent trap immersed in an isopropanol dry-ice bath. Acid value was determined according to ASTM D1980 (13), and iodine value was measured by ASTM D1959 (14).

RESULTS AND DISCUSSION

The effects of reaction time, initiator concentration, and MA concentration were studied in detail using two different initiators, L101 and di-*tert*-butyl peroxide. The degree of maleation was determined using acid value, and the products were further characterized using FTIR spectroscopy and iodine value. The MA functionality was calculated as the moles of MA per mole of SO, as determined by the acid value (mg of KOH/g of sample). Similarly, the number of double bonds was calculated from the iodine value (cg of I_2/g of sample).

The maleation of SO in a closed system under high temperature and pressure in the presence of peroxide proceeded relatively fast. In all cases, the reaction proceeded to completion within *ca.* 30 min independent of the MA concentration in the reaction mixture (MA/SO molar ratios of 0.2, 0.6, and 1.1) as shown in Figure 2. Similarly, no significant differences were observed when the reaction temperature was adjusted to 100, 120, or 150°C. Under these conditions, MA was completely consumed within 30 min, as shown in Figure 2. It is also interesting to note that the type of peroxide had little effect on the progress of the reaction and that essentially the same reaction rates were observed for both the L101 and di-*tert*-butyl initiators. However, the presence of the initiator in the reaction mixture greatly influenced the progress of the reaction (Fig. 3) and led to an MA functionality of 1.0, compared with an MA functionality of 0.25, when no peroxide initiator was used. Yet doubling of the initiator concentration from 0.005 to 0.01 wt% had no effect on the MA functionality, which was statistically similar. Furthermore, when the reaction was run with no peroxide, the resulting iodine value indicated the presence of about 4.5 mol of double bonds per TG, meaning no net change occurred in the number of double bonds after the addition of MA. This same number of double bonds suggests that reactions at lower temperatures favor the -ene addition over the Diels–Alder addition.

It is apparent from Figures 2 and 3 that even in the presence of a peroxide and large excess of MA (up to a molar ratio of MA/SO = 4), the maximum MA functionality never exceeded *ca.* 1. Experimentally, we observed that when excess MA was used (e.g., reactions containing MA/SO molar ratios of 2:1, 3:1, and 4:1), unreacted MA remained in the reaction mixture and was then accumulated and collected in the solvent trap during the workup procedure. Attempts to run the reaction for longer times (up to 240 min) did not lead to higher acid values, and no further increase in maleation was observed. The iodine value of the products with MA functionality around 1.0 was always correlated with SO having about 3.5 double bonds. This net reduction of one double bond from the unmodified SO suggests

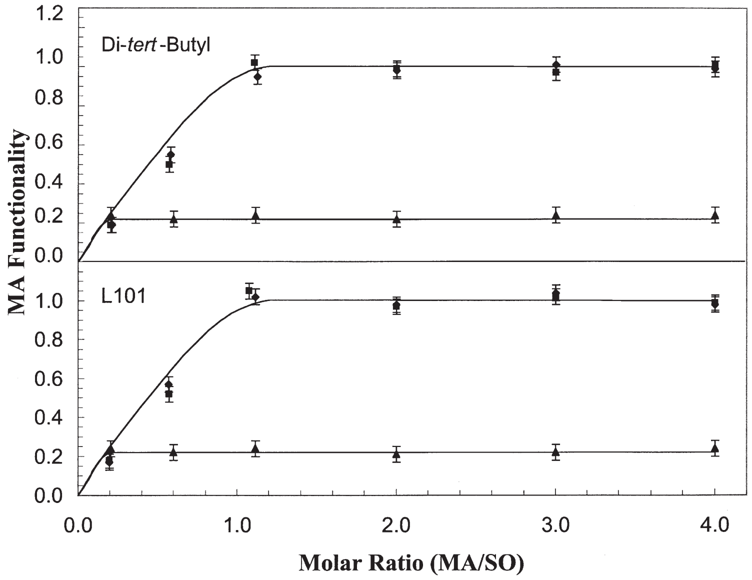

FIG. 2. Effect of reaction time on maleic anhydride (MA) functionality at 150°C using different MA/soybean oil (SO) ratios: ▲, 0.2; ■, 0.6; and ◆, 1.1. Di-*tert*-butyl = di-*tert*-butyl peroxide; L101 = 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane peroxide.

that 1 mol of MA was added to SO by a Diels–Alder addition (Fig. 1). Although further maleation is theoretically possible, it was found experimentally that only 1 mol of MA had reacted, as determined by the acid number. Although the reason for this upper limit addition of MA is not clear at this time, one possible explanation could be that steric hindrance effects impeded further reaction of the MA.

The maleation of SO is accompanied by a noticeable increase in the viscosity from 50 cP of neat SO to 3,500 cP for the maleated SO (Fig. 4). The increased viscosity is most likely due to an increase in hydrogen bonding as MA is grafted into the TG structure. It is not due to opening of the anhydride ring and copolymerization through reaction of the carboxylic groups as was suggested previously, since esterification of the maleated SO with 1-octanol yielded a product with an acid value of 0.1 and a viscosity of only 200 cP (10).

The degree of maleation was not affected by the reaction temperature (Fig. 5), and similar acid values were obtained when the initial temperature was set between 100 and 150°C. However, the temperature profile of the reaction was affected

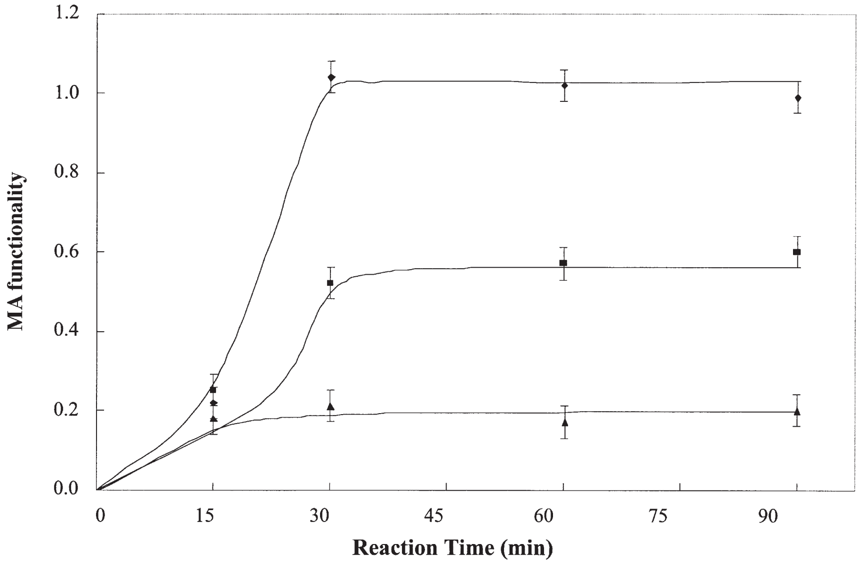

FIG. 3. Effect of peroxide concentration on MA functionality after 60 min at 150°C: ▲, no initiator; ■, 0.005 wt%; ◆, 0.01 wt%. For abbreviations see Figure 2.

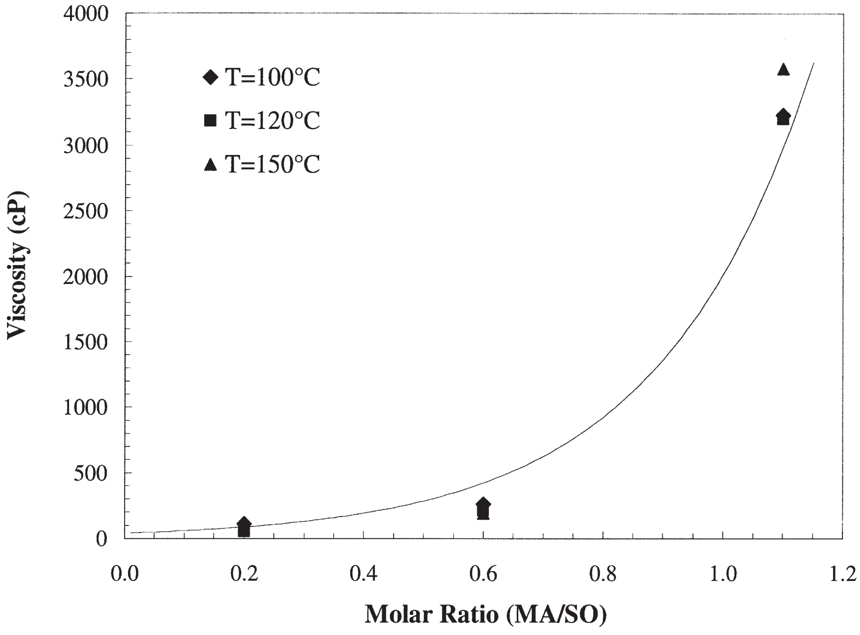

FIG. 4. Change in viscosity with increases in MA concentration. For abbreviations see Figure 2.

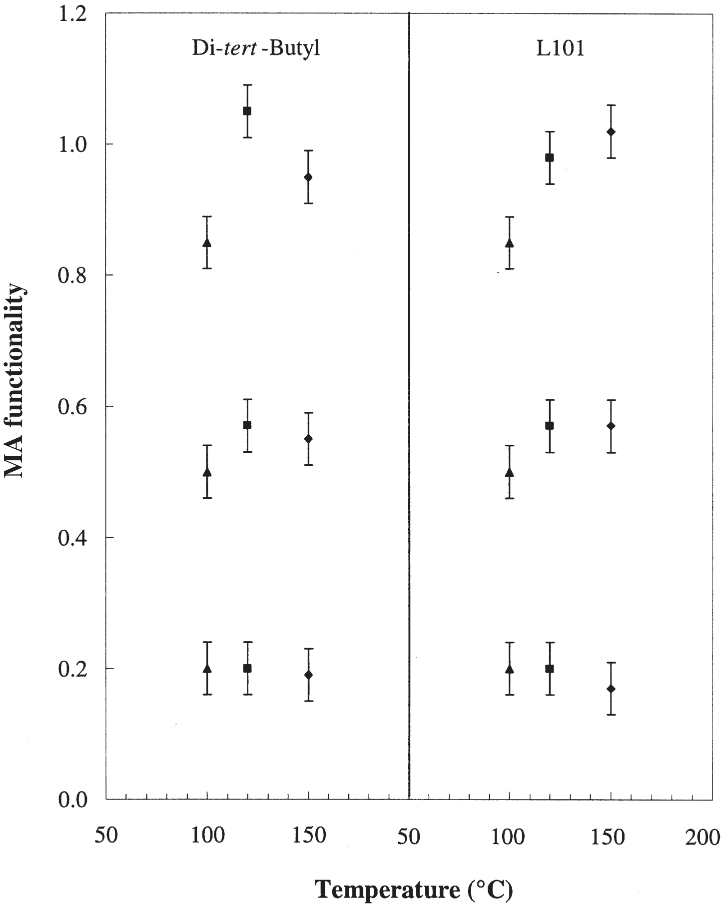

FIG. 5. Effect of reaction temperature on the maleation of SO: ▲, 100°C; ■, 120°C; ◆, 150°C. For abbreviations see Figure 2.

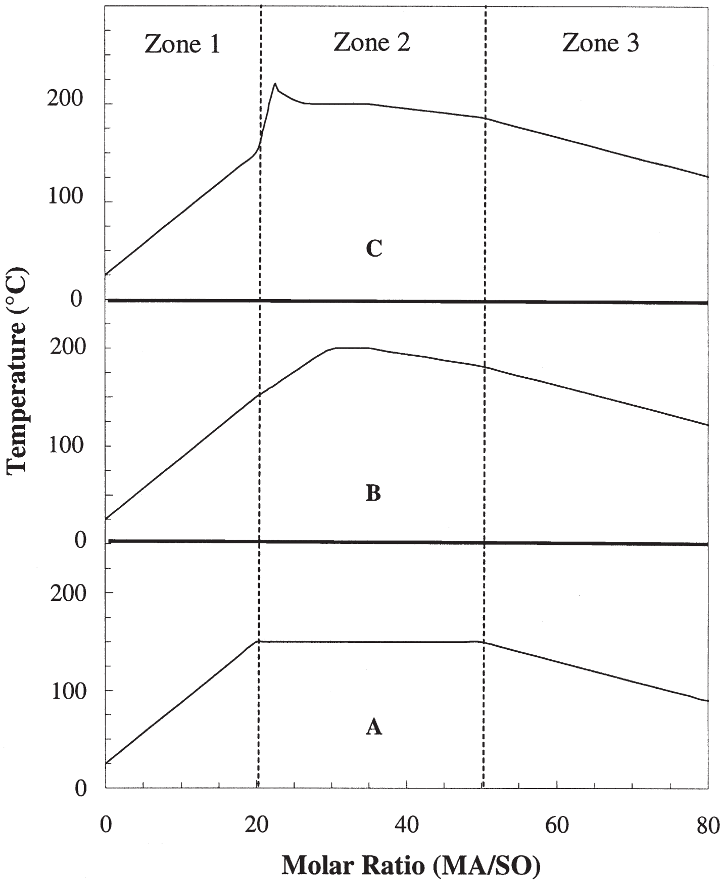

FIG. 6. Temperature profile during maleation. For abbreviations see Figure 2.

by the peroxide concentration, as shown in Figure 6. Three distinct zones were clearly observed in the course of these reactions: Zone 1 represents the time it took to heat the reactor to the preset reaction temperature (e.g., 150°C in Fig. 6), Zone 2 is the time interval (usually 30 min) in which the reaction was allowed to proceed after it reached the preset temperature, and Zone 3 is the time period in which heating was stopped and vacuum was applied to remove any unreacted MA. The typical temperature profile of reactions with no initiator is shown in Figure 6A, where the reaction proceeded to a set point of 150°C, which was sustained for 30 min until heating was terminated and vacuum was applied, resulting in slow cooling. Zone 1 is the same for all the different reactions and is determined by the applied heating. However, the temperature profile in Zone 2 was different when peroxide was included in the reaction mixture (Figs. 6B, 6C). Here, the temperature continued to rise at the end of Zone 1, and although it was set to 150°C, it reached 200°C. This overheating beyond the preset temperature was particularly noticeable in the reactions with 0.01 wt% peroxide and was accompanied by an increase in the reactor pressure (25 psi). Although this exotherm may be partially attributed to the decomposition of the peroxide, we believe it is most likely due to the maleation reaction itself.

The maleated SO was further characterized by FTIR spectroscopy (Fig. 7) and exhibited peaks at *ca.* 1775 and 1850 cm^{-1}, which were not present in SO. These absorption peaks are related to the symmetric and asymmetric stretching of C=O in the MA (15,16). Furthermore, no absorption peaks related to –OH stretching due to the opening of the anhydride were observed, clearly indicating that the anhydride ring remained intact.

Maleation of SO in a closed system at elevated temperatures and pressures is advantageous over open-system processes. The maleated SO product we obtained was pale yellow, in contrast with other studies in which a red-orange liquid was obtained (11). Apparently, the use of high pressure in a closed system is more advantageous and prevents premature decomposition and degradation of the SO. This closed system is also advantageous because it allows for a fast and simple one-step process. Unlike previous studies that required reaction times of up to 7 h for the maleation, with the MA being added to SO in aliquots (17), our reaction was completed within 30 min. Optimal process conditions for maleated SO in a closed-system synthesis appear to be a 30-min reaction time at 150°C in the presence of 0.005 wt% peroxide. The use of a pressurized closed system prevents loss of MA by sublimination during the reaction. We also found that the concentration of MA in the reaction mixture had the most pronounced effect on the extent of the reaction, whereas the acid values were independent of the

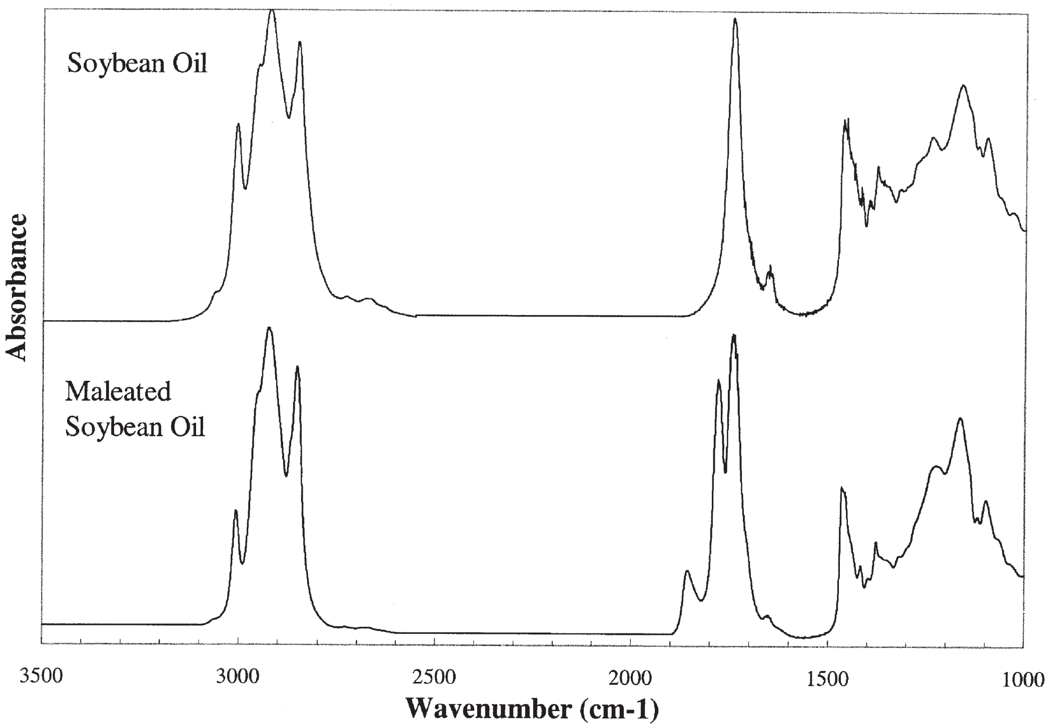

FIG. 7. FTIR of SO and maleated SO. For abbreviations see Figure 2.

concentration and type of peroxide used. However, even when excess MA was present, the MA functionality did not increase above *ca.* 1.0 mol. The data appear to indicate that the maleation reaction in the absence of a peroxide proceeds primarily through "-ene chemistry," whereby a Diels–Alder addition is favored when a peroxide is present. Thus, conjugation of the double bonds in the linoleic and linolenic FA residues is expected to occur only in the presence of a catalyst and at high temperatures.

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