Thermosetting Polymers from Cationic Copolymerization of Tung Oil: Synthesis and Characterization

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ABSTRACT: The cationic copolymerization of tung oil with the divinylbenzene comonomer initiated by boron trifluoride diethyl etherate produces promising plastics. The gel times are largely dependent on the relative composition and the reaction conditions and vary from a few seconds to 1 h. Controlled reactions producing homogeneous materials can be obtained by (1) lowering the reaction temperature or (2) decreasing the initiator concentration to less than 1 wt % or (3) adding a certain amount of a less reactive oil, such as soybean oil, low saturation soybean oil (LoSatSoy), or conjugated LoSatSoy to the reaction. The resulting polymers are rigid and dark brown in color. The weight % of the starting materials converted to the crosslinked polymer is ~85–98% as determined by Soxhlet extraction with methylene chloride. The structure of the bulk product is that of a crosslinked polymer network plasticized by a small amount of low molecular weight oil. The chemical composition of the bulk polymers varies with the original composition of the tung oil system. Dynamic mechanical analysis shows that the resulting products are typical thermosetting polymers with densely crosslinked structures. The modulus of the plastics is approximately 2.0×10^9 Pa at room temperature. One broad glass transition is observed at approximately 100°C. Thermogravimetric analysis shows that the tung oil polymers are thermally stable below 200°C with a 10% weight loss in air around 430°C. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1044–1056, 2000

Key words: tung oil; soybean oil; LoSatSoy; cationic copolymerization; thermosets

INTRODUCTION

Tung oil is readily available as a major product from the seeds of the tung tree.[1] It is practically colorless in its natural state, but the commercial product is generally a yellow color and possesses an earthy odor. Tung oil is an excellent drying oil of vegetable origin used principally in the preparation of paints, varnishes, and related materials.[2–4] Its principal constituent is a glyceride of elaeostearic acid, a conjugated triene. This highly unsaturated, conjugated system is largely respon-

sible for the rapid polymerization and outstanding drying properties of this oil.[2]

The high degree of unsaturation of tung oil has prompted researchers to examine it as a potential monomer for free-radical polymerization or copolymerization into useful bulk polymers. Tung oil has been copolymerized with styrene initiated by benzoyl peroxide to make heat-stable, self-extinguishing, essentially nonshrinking, low-density foams.[5] The monomer reactivity ratios of tung oil and styrene in free-radical copolymerization have been reported.[6] Theoretically, the polymerization of tung oil cannot only be initiated free radically, but also cationically due to the extensive conjugation present.[7,8] However, all literature reports to date have been concerned solely with the production of coatings and bulk polymers by free-radical

polymerization or copolymerization of tung oil.[5,6] We report the first cationic polymerization of tung oil.

This work describes the conversion of tung oil to useful solid plastics by cationic copolymerization with the divinylbenzene comonomer. Boron trifluoride diethyl etherate is used as the initiator. Other less reactive vegetable oils, such as soybean oil and low saturation soybean oil (LoSatSoy), are used to regulate the tung oil reaction rates. This article reports the synthesis and characterization of the resulting tung oil polymers. The possible advantages of these tung oil polymers include the low cost of their preparation from renewable natural resources (i.e., oils) and their presumed ability to biodegrade in an environmentally benign manner after service.

EXPERIMENTAL

Materials

The tung oil used in this study is a commercial product of Alnor Oil Co., Inc. (Valley Stream, NY). It has a yellow color and a specific gravity of 0.933–0.938 at 25°C. Food-grade Wesson soybean oil and HyVee LoSatSoy oil are commercially available in supermarkets and were used without further purification. Norway fish oil ethyl ester was obtained from Pronova Biocare (EPAX 5500 EE, Bergen, Norway). The conjugated LoSatSoy oil was prepared by the rhodium-catalyzed isomerization of the regular LoSatSoy oil in our laboratory.[9] The degree of conjugation is calculated to be up to 95%. The divinylbenzene comonomer was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. The distilled-grade boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) (Aldrich) used to initiate the cationic copolymerization was used as received.

Cationic Copolymerization

The desired amount of the divinylbenzene comonomer was added to the tung oil or mixtures of tung oil and a second natural oil. The mixture was vigorously stirred, followed by the addition of an appropriate amount of the fish-oil-modified initiator. The fish-oil-modified initiator was prepared by mixing the Norway fish oil with boron trifluoride diethyl etherate. The modified initiator was usually required to produce homogeneous polymers.[10] The reaction mixture was then

heated for a given length of time at appropriate temperatures. The nomenclature adopted in this article for the samples is as follows: TUN, SOY, LSS, and CLS represent tung oil, soybean oil, LoSatSoy oil, and conjugated LoSatSoy oil; DVB is the divinylbenzene comonomer; NFO is the Norway fish oil; and BFE is the initiator boron trifluoride diethyl etherate. For example, TUN25–SOY25–DVB35–(NFO10–BFE5) corresponds to a polymer sample prepared from a mixture of tung oil (25 wt %), soybean oil (25 wt %), and divinylbenzene (35 wt %), plus a modified initiating system consisting of 10 wt % of Norway fish oil and 5 wt % of boron trifluoride diethyl etherate.

Soxhlet Extraction by Methylene Chloride

A 2-g sample of the bulk polymer was extracted with 100 mL of refluxing methylene chloride using a Soxhlet extractor in air for 24 h. After extraction, the resulting solution was concentrated by rotary evaporation and subsequent vacuum drying. The soluble substances were isolated for further characterization. The insoluble solid was dried under a vacuum for several hours before weighing.

Characterizations

Dynamic mechanical data were obtained using a Perkin–Elmer dynamic mechanical analyzer Pyris DMA-7e in a three-point bending mode. The rectangular specimens were prepared by placing the reactants within an appropriate mold. Thin-sheet specimens of 1 mm in thickness and 2.5 mm in depth were used, and the span-to-depth ratio was maintained at approximately 5. The measurements were performed at a heating rate of 3°C/min and a frequency of 1 Hz.

A Perkin–Elmer Pyris-7 thermogravimeter was used to measure the weight loss of the polymeric materials. The samples were heated in air from room temperature to 650°C at a heating rate of 20°C/min. The temperature was calibrated by using indium as a standard. All ^{1}H-NMR spectra were recorded in CDCl$_3$ using a Varian Unity spectrometer at 300 MHz.

RESULTS AND DISCUSSION

Structures of Tung Oil, Soybean Oil, and LoSatSoy Oil

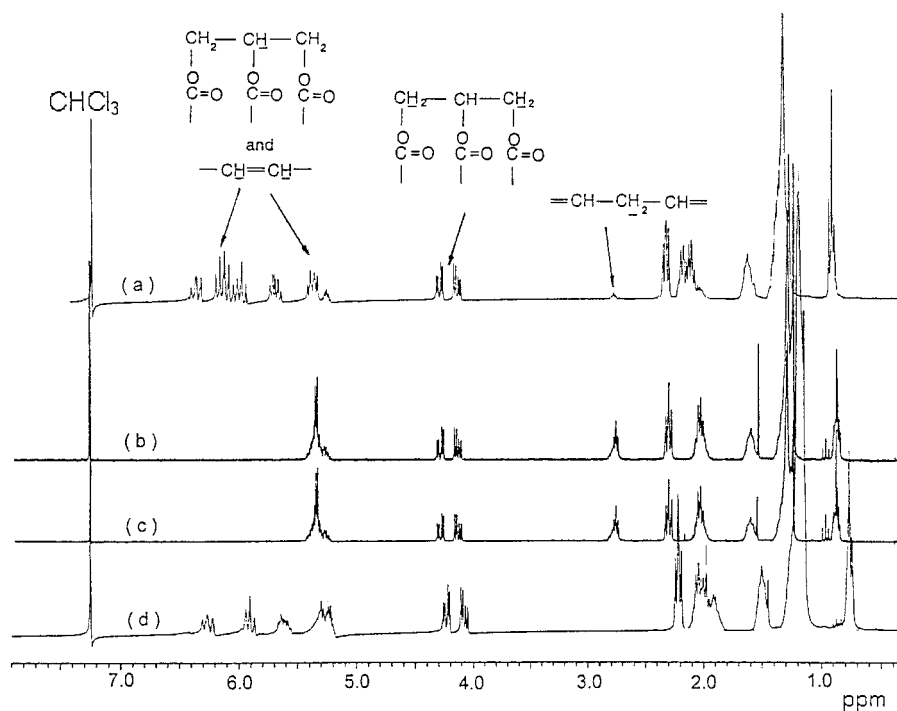Figure 1(a) shows the ^{1}H-NMR spectrum of tung oil. The peaks at 4.1–4.4 ppm correspond to the

Figure 1   ^{1}H-NMR spectra of (a) tung oil, (b) soybean oil, (c) LoSatSoy oil, and (d) conjugated LoSatSoy oil.

protons in the —CH$_2$— groups of the glyceride unit, which indicates that the tung oil used in this study has a triglyceride structure. The vinylic hydrogens are detected in the region 5.2–6.6 ppm. Most of the carbon–carbon double bonds in tung oil are conjugated as evidenced by the presence of only minor peaks at 2.7–2.8 ppm corresponding to the protons in the —CH$_2$— groups between two nonconjugated carbon–carbon double bonds. Based on ^{1}H-NMR spectroscopy, tung oil is calculated to have approximately 7.5 carbon–carbon double bonds per glyceride unit. It has been reported [1,2] that tung oil is a triglyceride composed chiefly of alpha elaeostearic acid (84%), with about 4% of saturated acids, 8% of oleic acid, and 4% of linoleic acid. Thus, in tung oil, most of the carbon–carbon double bonds exist in the form of a conjugated triene.

Figure 1 also shows the ^{1}H-NMR spectra of (b) soybean oil, (c) LoSatSoy oil, and (d) conjugated LoSatSoy oil. The triglyceride of soybean oil has approximately 4.5 carbon–carbon double bonds per molecule according to the spectrum. The three side chains are composed mainly of ~20–30% oleic acid (ester), ~50–80% linoleic acid (ester), and ~5–10% linolenic acid (ester). The structure of LoSatSoy oil is similar to that of the soybean

oil, but with relatively more carbon–carbon double bonds (approximately 5.1 per molecule) present in the triglyceride side chains. In these two natural oils, the protons of the —CH$_2$— groups between the two nonconjugated carbon–carbon double bonds appear at 2.7–2.8 ppm. It follows that most carbon–carbon double bonds in these oils are not conjugated. The spectrum of the conjugated LoSatSoy oil shows that the average number of carbon–carbon double bonds is not affected upon conjugation. The disappearance in the spectra of the peaks at 2.7–2.8 ppm in the conjugated LoSatSoy implies a high degree of conjugation (estimated at 98%).

Cationic Copolymerization

The excellent drying properties of tung oil are a direct result of the reactive conjugated carbon–carbon double bonds which readily undergo free radically initiated homopolymerization by absorbed oxygen.[2–4] Tung oil has also been copolymerized with a styrene comonomer initiated by benzoyl peroxide to form useful bulk polymers.[5,6] Due to the conjugated carbon–carbon double bonds present in tung oil, this oil is expected to undergo facile cationic polymerization as well.[7,8]
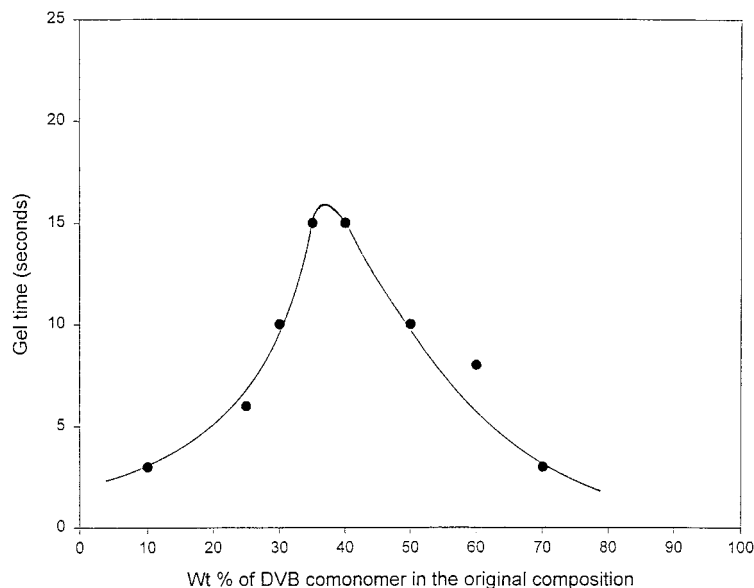
Figure 2 Dependence of gel time on the weight percent of the DVB comonomer in the original composition of the tung oil/DVB systems initiated by fish-oil-modified initiator (NFO10/BFE5) at 0°C.

Indeed, it is very sensitive to the cationic initiator boron trifluoride diethyl etherate used in this study. Tung oil forms an irregular polymeric solid within a few seconds after the initiator is added at room temperature. Lowering the temperature would be expected to decrease the reaction rate, but the tung oil becomes very viscous and even freezes and polymerization is dramatically suppressed. In contrast, DVB has a much lower molecular weight, but a higher density of carbon–carbon double bonds. It is known to be suitable for cationic polymerization.[7,8] Accordingly, addition of the DVB comonomer to the tung oil significantly decreases the viscosity of the system, and copolymerization occurs at lower temperatures.

Figure 2 shows the dependence of the gel time of the copolymerization of tung oil and the DVB comonomer at 0°C on the weight % of the comonomer in the original composition. A modified initiating system, which combines 10 wt % fish oil and 5 wt % $BF_3 \cdot OEt_2$, was used to give rise to homogeneous reactions, as well as resulting homogeneous polymers.[10] The results in Figure 2 show that the gel time first increases when increasing the comonomer concentration in the original composition. It reaches a maximum at a comonomer concentration of approximately 35–40 weight % and then the gel time decreases. In other words, the copolymerization reaction rates are high in both tung oil-dominant and DVB-dominant sys-

tems. The lowest reaction rate is obtained in the middle. It is clear that even at 0°C the reaction is very fast. The time to achieve the gel point is less than 15 s. Figure 3 shows the dependence of the gel time of the copolymerization of tung oil and
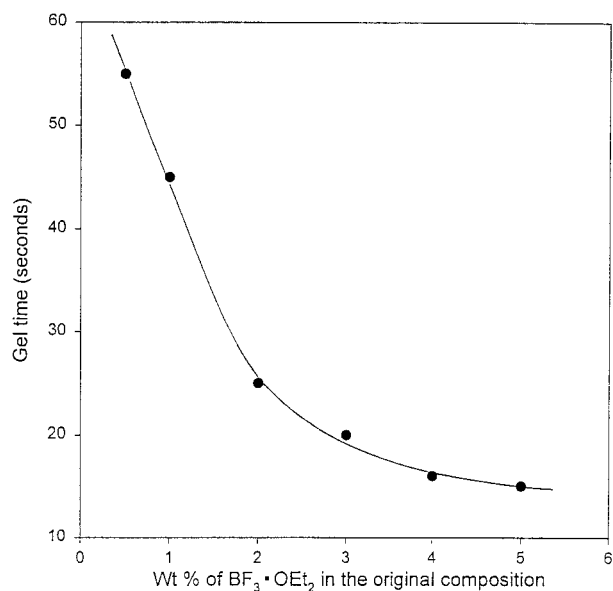

Figure 3 Dependence of gel time on $BF_3 \cdot OEt_2$ concentration in the original composition of the tung oil/35%DVB systems at 0°C. The initiator was modified by 10 wt % fish oil.
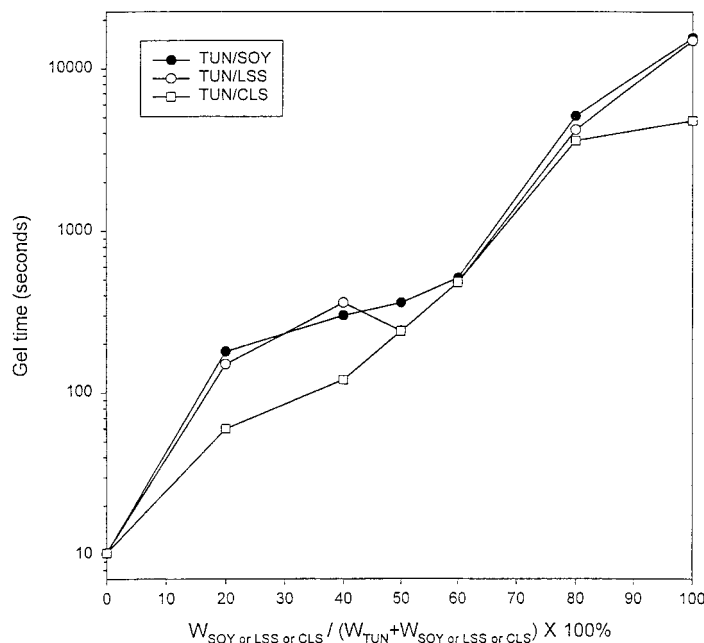
Figure 4   Effect of adding a second oil (SOY, LSS, or CLS) on the gel time of the copolymerization of tung oil. Thirty-five weight percent of the DVB comonomer is used in the original composition and the initiating system is NFO10–BFE5 at 0°C.

the DVB comonomer on the $BF_3 \cdot OEt_2$ concentration in the original composition. The reaction rate does not change much with a $BF_3 \cdot OEt_2$ content of 2–5% by weight. Below 2% $BF_3 \cdot OEt_2$, the reaction rate significantly decreases. The gel time can be extended to more than 50 s. It follows that lowering the initiator concentration is an effective way to decrease the reaction rate.

To further decrease the copolymerization reaction rate, less reactive oils, such as regular soybean oil, LoSatSoy oil, or conjugated LoSatSoy oil, were added to the tung oil. Figure 4 shows the effect on the gel time of the copolymerization of adding a second natural oil to the original composition. The reaction rate is found to decrease regularly by the addition of the second oil. When the second oil constitutes more than 60 wt % of the total weight of tung oil and the second oil, the reaction rate is exponentially decreased (note that the *y*-axis is in log scale). The effects of the regular soybean oil and LoSatSoy oil on the reaction rates are more pronounced than are those of the conjugated LoSatSoy oil, which is easily rationalized by the structures and differences in the reactivities of the second oils.[10] The native soybean oil and LoSatSoy oil have relatively low reactivity, while the reactivity can be significantly improved by conjugating the carbon–carbon double bonds in the side chains of the triglyceride

natural oils. That is the reason why the effect of conjugated LoSatSoy oil on the reaction rates of the tung oil mixtures is less pronounced than on those of the regular natural oils. In general, soybean oil, LoSatSoy oil, and conjugated LoSatSoy oil are much less reactive than tung oil. Thus, adding a certain amount of these oils decreases the reaction rate of the tung oil polymerizations, so as to be more easily controlled.

Figure 5 shows the gel times for 50/50 (w/w) mixtures of tung oil and soybean oil, LoSatSoy oil, or conjugated LoSatSoy oil as a function of the wt % of the DVB comonomer in the original composition. Compared with those of pure tung oil systems (5–15 s) in Figure 2, the gel times of the mixtures of tung oil and a second oil increases up to 100-fold (100–500 s in Fig. 5). A feature that is noteworthy is the appearance of a maximum gel time as a function of the comonomer concentrations in the pure tung oil system (Fig. 2), as well as in the tung oil mixtures (Fig. 5). This phenomenon has also been observed in the cationic copolymerization of the other systems.[11] The maximum gel time of the tung oil mixtures in Figure 5 appears at approximately the same position, that is, 30 wt % of the comonomer, while the maximum gel time appears at 35 wt % of the comonomer in the original composition of the pure tung oil systems as shown in Figure 2.
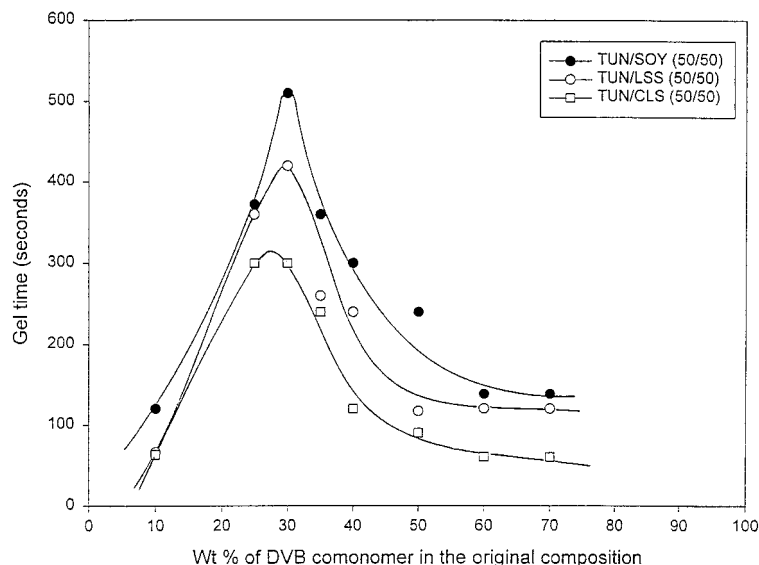
Figure 5 Dependence of gel time on the weight % of the DVB comonomer in the original composition of the (50/50 w/w) tung oil/second natural oil (SOY, LSS, or CLS) systems initiated by fish-oil-modified initiator (NFO10/BFE5) at 0°C.

Table I gives the relative compositions of the samples with the lowest reaction rates (the highest gel times) in Figures 2 and 5. The table shows that although the weight ratio or molar ratio of the oils to the DVB comonomer is different in the original compositions the ratio of the number of carbon–carbon double bonds in the oil to the number in the DVB are close to 1. So, the maximum gel time may be rationalized by the competition between the carbon–carbon double bonds in the oils and in the DVB comonomer. It is known that both tung oil and DVB are very reactive toward cationic polymerization. Thus, the gel time is very short when the initiator is added to pure tung oil or to pure DVB, but when a small amount of the DVB comonomer is mixed with the tung oil, the gel time is increased as a result of the competition between the reactive species. The maximum gel time corresponds to the point where the number of carbon–carbon double bonds in the oils is equivalent to the number of carbon–carbon double bonds in the DVB comonomer. The competition between the oils and the DVB comonomer is the highest at this ratio, and the reaction rate approaches a minimum. When the DVB comonomer concentration is increased further, the amount of carbon–carbon double bonds in the DVB comonomer exceeds the number of carbon–carbon double bonds in the oils, and the competition between the different species decreases. The rate of the resulting reactions thus increases.

The above phenomenon may be understood by examining the probability of formation of a sluggish cation during crossover in the chain propagation of the binary copolymerization.[11] Of the four elementary propagation steps possible in the binary copolymerization, the carbocation from one of the two crossover steps, either $\sim\sim M_1M_2^+$ or $\sim\sim M_2M_1^+$ (M_1 is presumably DVB and M_2 is probably the oil), is apparently relatively unreactive.

Table I   Relative Composition of the Samples with the Lowest Reaction Rate in Figures 2 and 5

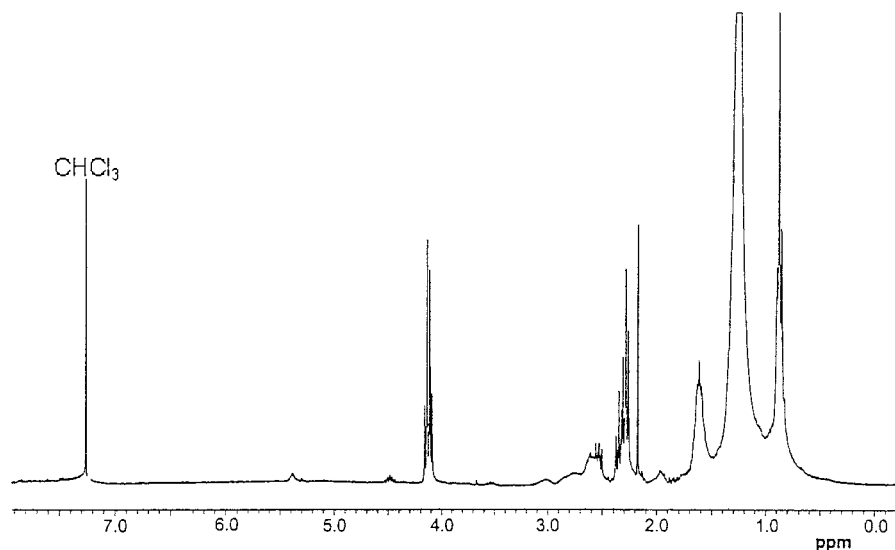| Sample	Wt Ratio, $W_{oil}{:}W_{DVB}$	Molar Ratio, $N_{oil}{:}N_{DVB}$	Molar Ratio, $(C{=}C)_{oil}{:}(C{=}C)_{DVB}$
TUN50–DVB35–(NFO10–BFE5)	1.70:1	1:3.99	1:1.06
TUN27.5–SOY27.5–DVB30–(NFO10–BFE5)	2.17:1	1:3.13	1:1.04
TUN27.5–LSS27.5–DVB30–(NFO10–BFE5)	2.17:1	1:3.13	1.01:1
TUN27.5–CLS27.5–DVB30–(NFO10–BFE5)	2.17:1	1:3.13	1.01:1

Figure 6 ¹H-NMR spectrum of the soluble oily substances extracted from the tung oil bulk polymer TUN50–DVB35–(NFO10–BFE5).

If the ratio of M_1 to M_2 is approximately 1 (i.e., a 1:1 stoichiometry of C=C bonds), the probability of formation of the relatively unreactive cation is the highest. As a result, the gel time of the copolymerization increases. When the concentration of either comonomer is reduced, homopolymerization is favored. Thus, the copolymerization rate increases due to the decreased probability of formation of the unreactive cation.

Characterization of the Polymers

The products resulting from these polymerizations are generally hard, rigid plastics with a dark brown color. The bulk polymer is composed of crosslinked polymer molecules and a small amount of the unreacted free oil.[10] After Soxhlet extraction by methylene chloride, more than 90 wt % of the insoluble substances from the tung oil bulk polymers are retained. These highly crosslinked substances are not soluble or even swellable in common solvents, such as THF and CH_2Cl_2. The oily substances extracted from the bulk polymer are composed mainly of unreacted free oil and initiator residual fragments. Figure 6 gives the ¹H-NMR spectrum of the soluble materials extracted from the polymer sample TUN50–DVB35–(NFO10–BFE5). The peaks at 4.0–4.2 ppm appear to correspond to the protons in the —CH_2— proton of the etherate initiator, and those at 4.3–4.6 ppm represent the triglyceride of the tung oil used in this study. Not many vinylic

hydrogens are detected at 5.3–5.5 ppm, which indicates that the soluble materials have considerably fewer carbon–carbon double bonds than do the oils employed in the polymerization. The DVB comonomer apparently polymerizes completely, since no aromatic protons are evident in the spectrum of the soluble substances shown in Figure 6. These results suggest that the structure of the bulk polymer is that of a crosslinked polymer network plasticized by a certain amount of unreacted free oil and initiator residue.

The structures of the resulting polymers are found to be closely related to their original compositions. Figure 7 shows the effect of the initiator concentration on the weight percent of the starting materials of the tung oil and the DVB comonomer converted to crosslinked polymers. The polymer conversions here are equivalent to the weight percent of the insoluble substances remaining after extraction of the bulk polymers by methylene chloride. The results show that no polymer is obtained in the absence of the initiator. However, 0.5 wt % of the initiator results in almost 100% of the starting materials being converted to the crosslinked polymer. As the initiator concentration increases, the polymer conversion, however, gradually decreases. A plateau appears at an initiator concentration above 3 wt %. Theoretically, the addition of an initiator is favorable for polymer conversion. But, as a result, the initiator residue in the bulk polymer also increases with increasing initiator concentration in the original
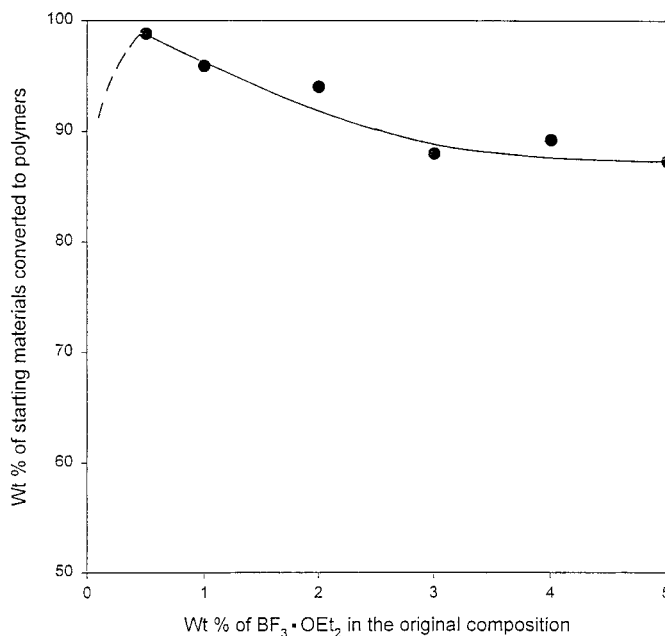
Figure 7 Weight percent of starting materials converted to crosslinked polymers versus BF$_3$·OEt$_2$ concentration in the original composition of the tung oil/35 wt% DVB systems. The initiator was modified by 10 wt % fish oil.

composition, which has been qualitatively verified by the ^{1}H-NMR spectra of the soluble substances extracted from the bulk polymers. Thus, the increased amounts of initiator residue apparently result in decreased polymer conversions as shown in Figure 7.
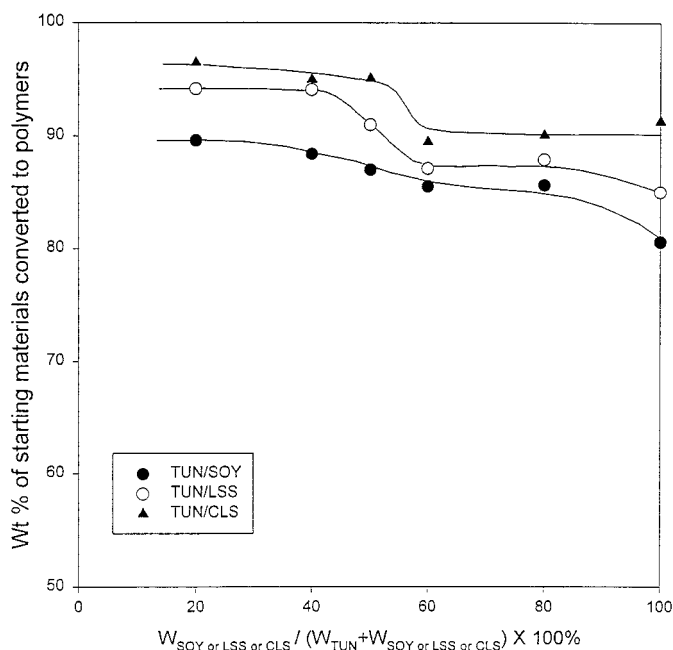

Figure 8 Effect of adding a second oil on the weight percent of starting materials converted to polymers using (NFO10−BFE5) and 35 wt % DVB in the original composition.
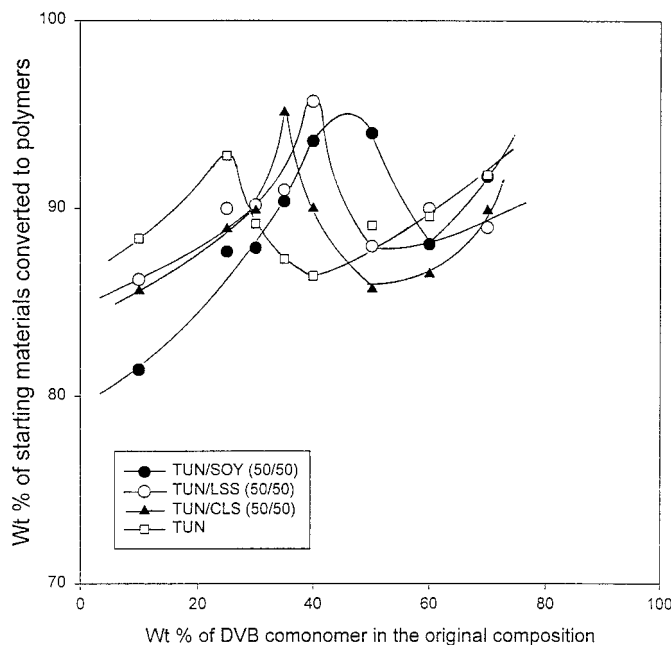
Figure 9 Effect of DVB comonomer concentration on the weight percent of starting materials converted to polymers initiated by (NFO10–BFE5) at 0°C.

Figure 8 shows the effect on the resulting polymer structures of adding a second natural oil to the tung oil systems. The results show that, for the same composition, the weight percent of the starting materials converted to the polymer is related to the type of oil employed or, more specifically, the reactivity of the second oil used in the reaction. Conjugated LoSatSoy oil exhibits higher reactivity than that of regular soybean oil or LoSatSoy oil, and the resulting tung oil/conjugated LoSatSoy oil polymers therefore exhibit higher polymer conversion over the whole composition range studied. However, no matter what the second natural oil is, the results of polymer conversion versus composition show a similar trend, typically a "Z" shape. The polymer conversion remains almost unchanged when only small amounts of the second natural oil are added to the tung oil. As the amount of the second natural oil increases to 40–60 wt % of $W_{\text{SOY or LSS or CLS}}/(W_{\text{TUN}} + W_{\text{SOY or LSS or CLS}})$, there appears an abrupt drop in polymer conversion and then the polymer conversion levels off. From soybean oil to LoSatSoy oil to the conjugated LoSatSoy oil, the position for the appearance of the abrupt drop in polymer conversion shifts to higher amounts of the second oil, and the drop becomes narrow and abrupt. The percent polymer conversion in Figure 8 is thus clearly related to the nature and concentration of the second oil in the original composition.

Figure 9 gives the dependence of the polymer conversion on the DVB comonomer concentration in various tung oil systems. Generally, the polymer conversion first increases with increasing comonomer concentration in the original composition. This peaks at 20–40 wt %, followed by a decrease in the polymer conversion. When the DVB comonomer concentration further increases, the polymer conversion gradually increases once again. For pure tung oil, this peak appears at a relatively low concentration of the comonomer. If conjugated LoSatSoy oil is added to the tung oil, the peak shifts to a higher comonomer concentration. If less reactive LoSatSoy oil or soybean oil is used instead of conjugated LoSatSoy oil, the corresponding peaks shift to still higher DVB concentrations. The reactant compositions corresponding to the polymer conversion peaks in Figure 9 correlate well with the compositions corresponding to the gel time peaks in Figures 2 and 5. This unusual correlation between polymer conversion and DVB comonomer concentration suggests that more than one mechanism for polymerization may be involved here. At present, the nature of those mechanisms is not clear. From the results in Figure 9, it is obvious that increasing DVB concentration in the original composition
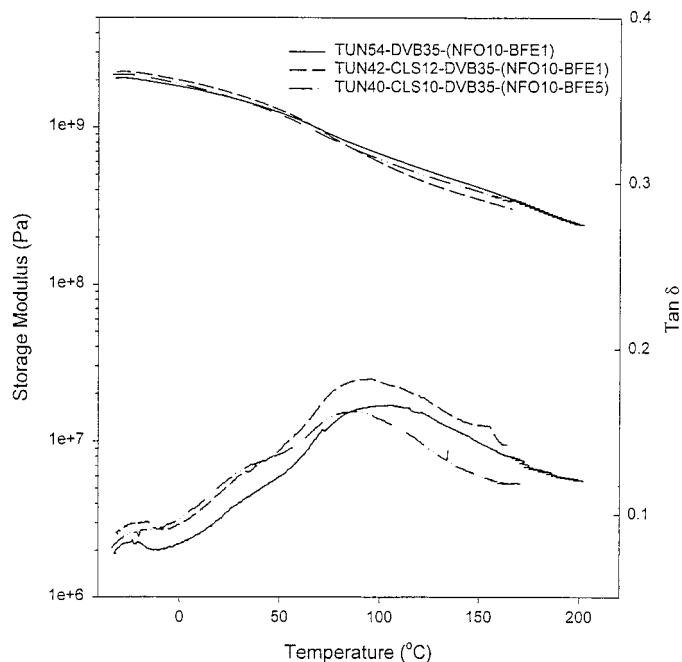
Figure 10 Temperature dependence of the storage modulus E' and the loss factor tan δ for the tung oil samples TUN54–DVB35–(NFO10–BFE1), TUN42–CLS12–DVB35–(NFO10–BFE1), and TUN40–CLS10–DVB35–(NFO10–BFE5).
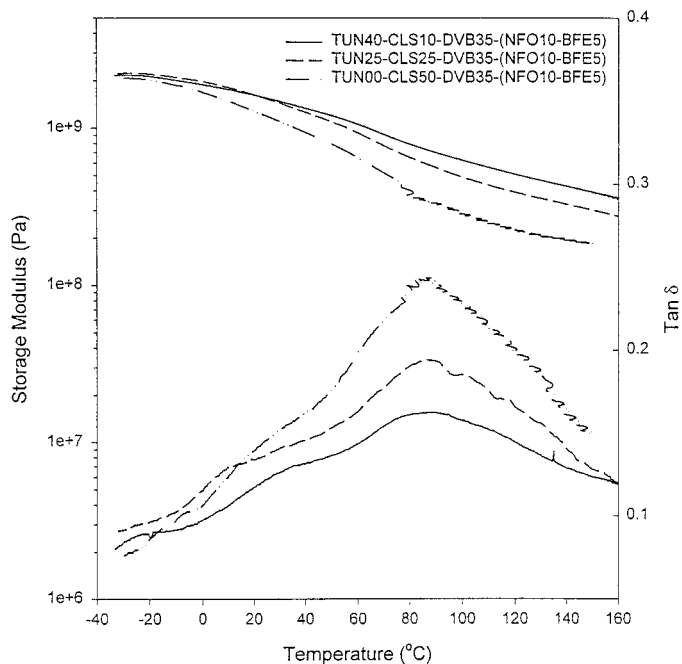

Figure 11 Temperature dependence of the storage modulus E' and the loss factor tan δ for the tung oil samples TUN40–CLS10–DVB35–(NFO10–BFE5), TUN25–CLS25–DVB35–(NFO10–BFE5),and TUN00–CLS50–DVB35–(NFO10–BFE5).
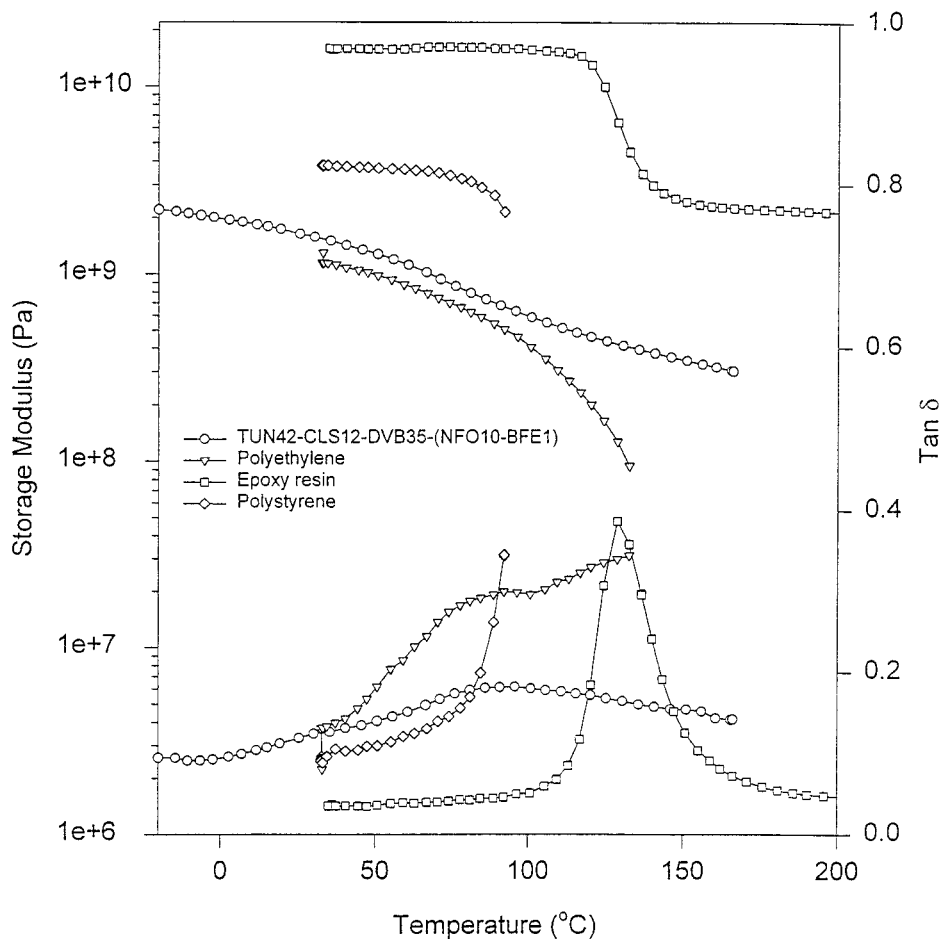
Figure 12 Temperature dependence of the storage modulus E' and the loss factor tan δ for the tung oil polymer sample TUN42–CLS12–DVB35–(NFO10–BFE1) and some commercial polymers.

does not necessarily favor polymer conversion. For some compositions, more reactive starting materials result in lower conversions than do less reactive starting materials. The above results are very important for structure and material design.

Dynamic Mechanical Behavior

Figure 10 shows the temperature dependence of the storage modulus E' and the loss factor tan δ for the tung oil polymer samples TUN54–DVB35–(NFO10–BFE1), TUN42–CLS12–DVB35–(NFO10–BFE1) and TUN40–CLS10–DVB35–(NFO10–BFE5). In general, the DMA curves for the different tung oil polymers are similar to each other. The storage moduli of the polymers are very similar over the whole temperature region studied. The figure shows that the storage moduli of the tung oil polymers at room temperature are approximately 2.0

$\times$ 10^9 Pa. As expected, the modulus gradually decreases with increasing temperature until the elastic plateaus appear at temperatures above 150°C. The elastic plateau in the DMA curves indicates the existence of a crosslinked network structure in the bulk polymers. Generally, a broad glass transition is observed from the loss factor behavior. The glass transition temperatures, the temperatures corresponding to the maximum tan δ, of the tung oil polymers are approximately 90–110°C. It is evident from the figure that the addition of some amount of the second oil (CLS) does not influence the storage modulus, but slightly decreases the glass transition temperature from 110 to 90°C [compare samples TUN54–DVB35–(NFO10–BFE1) and TUN42–CLS12–DVB35–(NFO10–BFE1)] as a result of decreased polymer conversion in the TUN/CLS system. Likewise, an increase in the initiator concentration slightly decreases the glass transition
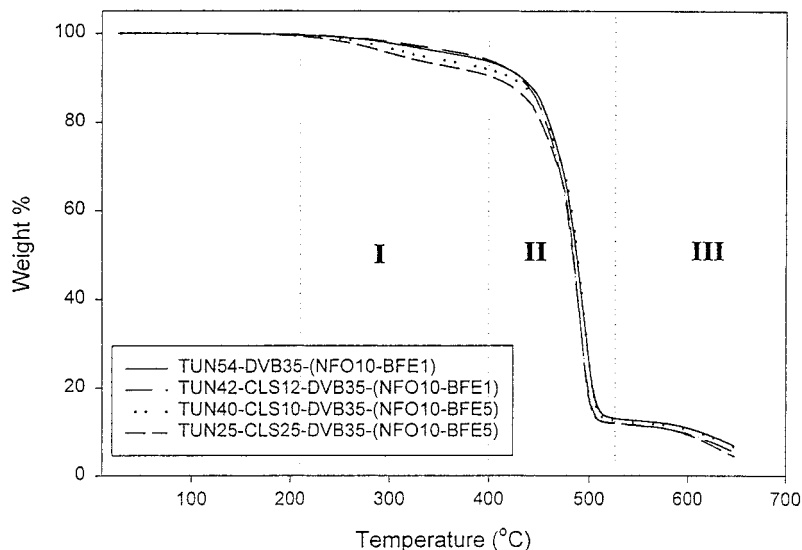
Figure 13 TGA curves of various tung oil polymers in air.

temperature of the resulting polymer [compare samples TUN42–CLS12–DVB35–(NFO10–BFE1) and TUN40–CLS10–DVB35–(NFO10–BFE5)]. This is probably due to an increasing amount of initiator residue in the bulk polymers, which is consistent with the results in Figure 7.

Figure 11 shows the effect of the concentration of the second oil (CLS) on the DMA behavior of the resulting tung oil polymers. An increase in the amount of CLS in the original composition evidently decreases the storage modulus of the resulting tung oil polymers, especially at higher temperatures [compare samples TUN40–CLS10–DVB35–(NFO10–BFE5) and TUN25–CLS25–DVB35–(NFO10–BFE5)], but the glass transition temperatures are not severely affected. The fact that the relative intensity of the loss factor and the area under the loss factor curves increase as a result of increasing the amount of CLS is a direct result of the decrease in the crosslinking density.[12] If tung oil is completely replaced by CLS in the original composition, the modulus of the resulting polymer further decreases, but the glass transition temperature remains unchanged, except for an increase in the relative intensity [TUN00–CLS50–DVB35–(NFO10–BFE5)].

Figure 12 provides a comparison between the tung oil polymer sample TUN42–CLS12–DVB35–(NFO10–BFE1) and some commercial polymers. The glass transition temperature of this tung oil polymer is approximately 100°C, which is similar to that of polystyrene, but lower than that of the epoxy resin used in this study. The storage modulus of this tung oil polymer at room temperature is 2.0×10^9 Pa, which is higher than that of commercial polyethylene. Due to the thermosetting nature of the tung oil polymer, it has a significantly higher storage modulus at higher temperatures (>150°C) than those of the thermoplastic polymers tested.

Thermogravimetric Analysis (TGA)

TGA was used to investigate the thermal decomposition behavior of the tung oil polymers in an air atmosphere. Figure 13 shows the TGA curves for various tung oil polymers. Like the other natural oil polymers that we have studied, three different decomposition stages are observed at 200–400, 400–560, and 560–800°C in the process.[10,13,14] The first temperature region appears to be primarily due to the evaporation of unreacted free oil in the bulk; the second region appears to be primarily due to conversion of the crosslinked polymer structure to carbon; and the third region is apparently due to oxidation of the carbon. These results suggest that stage-I, which relates to the unreacted free oil in the bulk polymer, plays a key role in determining the thermal stability of these materials. The temperatures at 10% weight loss, T_{10}, are used to evaluate the thermal stability of the tung oil polymers, and the results are listed in Table II. The temperature at 10% weight loss of the tung oil–DVB polymer sample is approximately 435°C. The data show

Table II   TGA Results for the Tung Oil Polymers in Air

Sample	Structure (wt %)		TGA (°C)	
	Insoluble	Soluble	T_{10}	T_{50}
TUN54–DVB35–(NFO10–BFE1)	96	4	435	487
TUN42–CLS12–DVB35–(NFO10–BFE1)	95	5	430	483
TUN40–CLS10–DVB35–(NFO10–BFE5)	96	4	422	488
TUN25–CLS25–DVB35–(NFO10–BFE5)	95	5	405	484

that adding conjugated LoSatSoy oil or increasing the initiator concentration in the original composition is not favorable for the thermal stability of the resulting tung oil polymers. However, due to the small difference in the amount of the unreacted free oils present in the bulk polymers, the thermal stabilities of these tung oil polymers is very good and very similar to one another.

Stage-II in the TGA curves appears to involve conversion of the crosslinked polymer network to carbon. The temperatures at 50% weight loss, T_{50}, are related to the crosslinked structures of the bulk polymers. From the T_{50} results in Table II, the values for all of the polymer samples are very similar, which means that the crosslinked structures in the above bulk polymers are similar to each other. The differences in the physical properties and thermal properties of the polymer samples are, therefore, primarily due to variations in the amount of low molecular weight oily substances present in the bulk polymers.

CONCLUSIONS

Tung oil is very reactive in cationic polymerization using the initiator $BF_3 \cdot OEt_2$. Its copolymerization with DVB results in hard plastics when employing appropriate compositions and reaction conditions. The gel time for such copolymerization ranges from a few seconds to 1 min. The addition of less reactive oils, such as soybean oil, LoSatSoy oil, and conjugated LoSatSoy oil, increases the gel time to minutes or hours. The conversions of the starting materials to crosslinked polymers, which vary from 80 to 96%, are closely dependent on the original composition of the mixtures. These tung oil polymers have proven to be typical thermosetting materials. Their storage modulus at room temperature is approximately 2.0×10^9 Pa. The glass transition

temperature is around 100°C with a rather broad transition range as a result of crosslinking. The tung oil polymers obtained have very good dynamic mechanical properties and thermal stabilities and may find application in replacing petroleum-based polymeric materials.

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