

Novel Thermosets Obtained by the Ring-Opening Metathesis Polymerization of a Functionalized Vegetable Oil and Dicyclopentadiene

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ABSTRACT: New polymeric thermosetting resins prepared by the ring-opening metathesis polymerization (ROMP) of a commercially available vegetable oil derivative, Dilulin, and dicyclopentadiene (DCPD) have been prepared and characterized. A thorough characterization of the modified oil itself has been carried out to elucidate its structure. Grubbs' second-generation catalyst has been used to effect the ROMP of the strained unsaturated norbornene-like rings in the commercial oil. Dynamic mechanical analysis of the resulting thermosetting resins has revealed that glass-transition temperatures ranging from 36 to -29°C can be obtained when the proper ratio of oil

to DCPD is employed. Thermogravimetric analysis has revealed that these resins have very similar temperatures of maximum degradation. Extraction analysis has indicated that all the samples had at least a 20% soluble fraction and that the soluble fraction was composed of oligomers, unreacted triglyceride oil, or both. The effect of the soluble fraction as a plasticizer has also been explored. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1788–1797, 2009

Key words: renewable resources; ROMP; thermogravimetric analysis (TGA); thermosets

INTRODUCTION

The recent increased interest in the production of plastics and rubbers from renewable and sustainable feedstocks has been driven by high and unstable petroleum prices and uncertainties about how long our petroleum supply can last. Although a great deal of attention has been focused on the production of ethanol from cellulose¹ and biodiesel from vegetable oil,² increasing research has been directed toward biobased materials and plastics from these and other renewable resources.³

Vegetable oils are a very promising renewable feedstock for polymer synthesis as either the triglyceride oil itself or derivatives thereof.⁴ Previous work has focused on the use of either condensation⁵ or free-radical polymerization⁶ to produce thermosetting resins. Our group has investigated cationic polymerization,⁷ free-radical polymerization,⁸ thermal polymerization,⁹ and, more recently, ring-opening metathesis polymerization (ROMP)¹⁰ of vegetable

oils or derivatives thereof to produce a variety of thermosetting resins.

ROMP constructs polymers by cleavage of the olefinic portions of strained ring systems that are then reconnected with olefinic portions of another ring system. Figure 1 shows a generalized ROMP mechanism. First, the phosphine ligand dissociates from the precatalyst (step 1). The resulting 14-electron transition-metal complex undergoes a [2 + 2] cycloaddition with the cyclic monomer to give a metallacyclobutane intermediate (step 2), which then undergoes [2 + 2] cycloreversion to give the ring-opened product (step 3). This process continues until the ruthenium carbene is quenched with ethyl vinyl ether, which terminates the polymerization (step 4).¹¹ Although much has been reported on the ROMP of various cyclic systems,¹² to our knowledge, our work on the ROMP of a functionalized castor oil containing a bicyclic moiety [bicyclic castor oil (BCO)] and cyclooctene is the first report of the ROMP of a triglyceride oil derivative.¹⁰ One disadvantage of the castor oil system is that castor oil is not all that readily available. In addition to that, BCO needs to be synthesized. Dilulin is a commercially available vegetable oil derivative prepared by the simple heating of dicyclopentadiene (DCPD) and linseed oil, which contains an unsaturated norbornene-like bicyclic moiety.¹³ We now report the synthesis and characterization of unique rubbery materials by the ROMP of Dilulin and DCPD.

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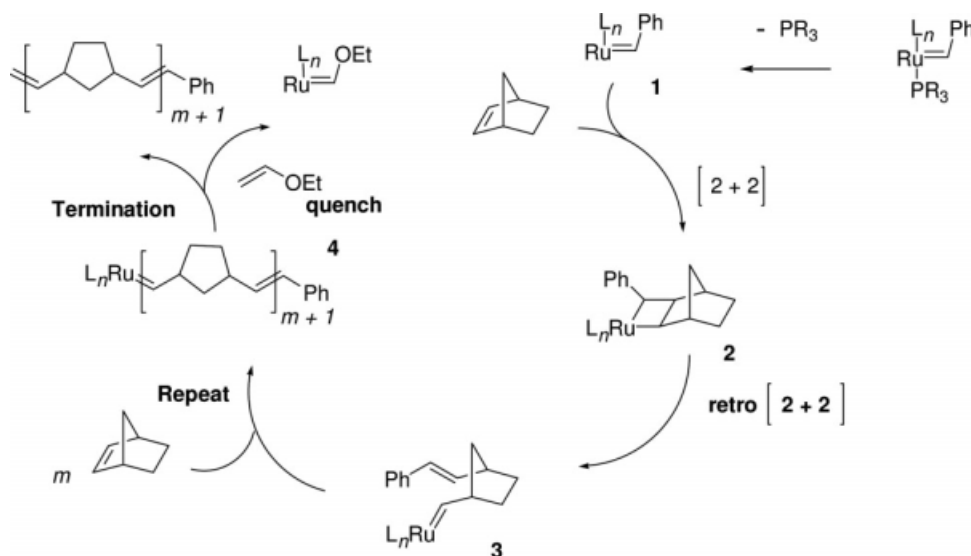


Figure 1 General mechanism of ROMP.

EXPERIMENTAL

Materials

Dilulin was obtained from Cargill (Minneapolis, MN). DCPD (>95%) was purchased from Alfa Aesar (Ward Hill, MA). Methylene chloride stabilized with amylene was supplied by Fisher (Fair Lawn, NJ). Grubbs' second-generation catalyst and potassium bromide [Fourier transform infrared (FTIR) grade $\geq 99\%$] were obtained from Sigma-Aldrich (Milwaukee, WI). Unless otherwise stated, all reagents were used as received.

Recrystallization of Grubbs' second-generation catalyst

To improve the solubility of the olefin metathesis catalyst with Dilulin and DCPD, Grubbs' second-generation catalyst was subjected to a freeze-drying process similar to that found in the literature.¹⁴ We used a modified procedure in which 0.5 g of the catalyst in a small beaker was dissolved in 10 mL of benzene and placed in liquid nitrogen for 5 min. The beaker was then removed from the liquid nitrogen, and a Kim-Wipe was placed around the top of the beaker, which was then placed in a vacuum oven overnight. This process produced a quantitative yield of crystals that were much larger than the original material and possessed a higher surface area.

Polymerization

A typical 5-g polymerization was carried out as follows: to a 20-mL vial was added 12.5 mg (0.25 wt %) of recrystallized Grubbs' second-generation catalyst. To this was added the appropriate amount (wt %) of Dilulin, which was stirred into the catalyst. Then, the appropriate amount (wt %) of DCPD was

added. Samples ranging from 50 to 100 wt % oil were prepared. Bulk polymerization was affected by a few minutes of stirring at room temperature and then by the pouring of the reaction mixture into a 55-mm-diameter Petri dish. The samples were cured in an oven for 1 h at 65°C and postcured for 3 h at 150°C. All of the samples gelled, and this resulted in transparent, amber rubbers with a slightly cured oil odor. For larger scale polymerizations (25 g), the resin was poured into a mold made of two 6-in. \times 8-in. glass plates separated by a 1/8-in. rubber gasket and clamped with paper binder clamps. The nomenclature adopted for these thermosets is as follows: a sample with 50 wt % Dilulin and 50 wt % DCPD is identified as Di150DCPD50.

Soxhlet extraction

All materials were characterized by Soxhlet extraction as follows. A 2–3-g sample was cut into a rectangular shape. The sample was placed into a cellulose thimble (Whatman, England), which was subsequently placed in a Soxhlet extractor equipped with a 250-mL, round-bottom flask containing 100 mL of methylene chloride and a stirring bar. A condenser was placed on top of the extractor, and the sample was refluxed ($\sim 60^\circ\text{C}$) for 24 h. Evaporation of the solvent yielded an oily residue (extract), which was dried for 24 h at an elevated temperature in a vacuum oven alongside the insoluble cross-linked portion. Both the extract and the insoluble portion were then weighed and analyzed further.

Purification of Dilulin

A 55-mm-diameter Buchner funnel with Whatman number 1 filter paper was fitted atop a 250-mL filter

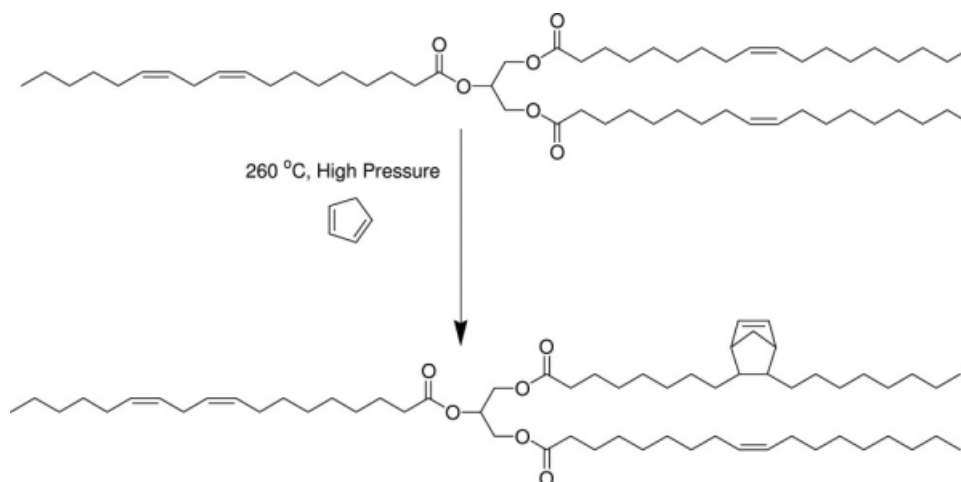


Figure 2 Diels–Alder reaction between linseed oil and cyclopentadiene.

flask connected to a water aspirator vacuum. Twenty-five milliliters of hexanes was passed through the funnel to wet the filter paper. Then, silica gel was poured onto the wet filter paper to a height of approximately 1.5 in. and then leveled. Another piece of filter paper was placed on top of the silica gel. Fifty milliliters of hexanes was poured through the flash column, and this was followed by 1 g of Dilulin dissolved in 10 mL of hexanes. An additional 150 mL of hexanes was poured through to elute the DCPD or oligomers. The vacuum was removed, and the filter flask was quickly emptied. Then, another 100 mL of hexanes was passed through while a vacuum was pulled. Thin-layer chromatography (TLC) showed no spot indicating DCPD or oligomers after the addition of 100 mL of hexanes. The oil was eluted by the placement of another 250-mL flask onto the flash column and the pulling of a vacuum. Approximately 200 mL of ethyl acetate was passed through the flash column. TLC showed no spot indicating oil after the addition of 200 mL of ethyl acetate. Each solvent fraction was put into a preweighed round-bottom flask and placed onto a rotary evaporator. After all of the solvent was removed, the flasks were placed in a vacuum oven for a few hours at 60°C. After each fraction was weighed, it was found that Dilulin contains the desired oil (ca. 95%) and unreacted DCPD or oligomers thereof (ca. 5%). The ratio of each of these, however, may vary from one batch of Dilulin to another.

Polymer characterization

$^1\text{H-NMR}$ spectroscopic analysis of the extract (soluble portion) was performed in CDCl_3 with a Varian (Palo Alto, CA) spectrometer at 400 MHz. FTIR analysis of the oils and insoluble portions were carried out on a Mattson (Madison, WI) Galaxy Series FTIR

3000 instrument. For the oils, a salt plate was the dispersing medium. For the insoluble portions, the samples were ground into a powder, mixed with KBr, and pressed into a pellet. The insoluble portions were also analyzed with cross-polarization/magic angle spinning $^{13}\text{C-NMR}$ on a Bruker AV600 spectrometer (Bruker America, Billerica, MA). The samples were examined at a spinning frequency of 12 kHz. Dynamic mechanical analysis (DMA) was recorded on a TA Instruments (New Castle, DE) Q800 dynamic mechanical analyzer with a film/fiber tension mode and a single cantilever mode. For the film/fiber mode, the specimens were cut into rectangular shapes approximately 24 mm long, 10 mm wide, and 1.5–2 mm thick. DMA multifrequency strain analysis was employed with an oscillation amplitude of 20 μm , a static force of 0.01 N, and a force track of 300%. Samples were cooled and held isothermally for 3 min at -60°C before the temperature was increased at $3^\circ\text{C}/\text{min}$ to 100°C . The single cantilever mode samples were about 30 mm long, 15 mm wide, and 3 mm thick. DMA multifrequency strain analysis with an oscillation amplitude of 15 μm was employed. Thermogravimetric analysis (TGA) of the specimens was carried out on a TA Instruments Q50 thermogravimetric analyzer. Samples were scanned from 50 to 650°C in air with a flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Characterization of Dilulin

Dilulin is synthesized by the presumed Diels–Alder reaction between the double bonds of linseed oil and cyclopentadiene formed by the cracking of DCPD at high temperatures and pressures¹³ (Fig. 2). TLC of Dilulin with 20 : 1 hexane/ethyl acetate reveals that the oil is a mixture of two components,

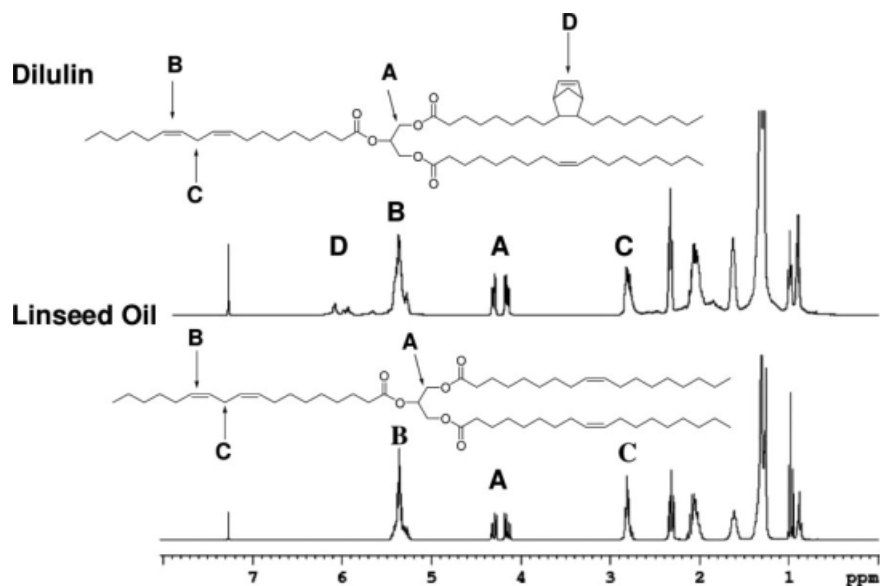


Figure 3 $^1\text{H-NMR}$ spectra of pure Dilulin and pure linseed oil.

one with a low retention factor (R_f) value (0.16) and the other with a high R_f value (0.74). The more polar, low- R_f material is the Dilulin itself. The less polar, high- R_f material consists of residual DCPD or copolymers thereof. The separation of Dilulin into the oil and residual DCPD was carried out on a flash silica gel column. It was found that the low- R_f fraction is approximately 95% of the Dilulin and that the high- R_f portion makes up about 5% of the Dilulin. FTIR and $^1\text{H-NMR}$ spectroscopy of the "purified Dilulin" provided results essentially identical to those of the nonpurified Dilulin (mentioned next); therefore, only characterization of the nonpurified Dilulin is discussed.

A representative structure of the main component of Dilulin was determined with $^1\text{H-NMR}$ spectroscopy. Figure 3 shows both the structures and $^1\text{H-NMR}$ spectra for Dilulin and regular linseed oil. Regular linseed oil was chosen as the oil for structural comparison because Dilulin is synthesized from linseed oil. Figure 3 shows peaks at 4.1 and 4.3 ppm, which correspond to the methylene protons of the glycerol moiety, for both oils. At 5.35 ppm, there are peaks for both oils that correspond to both the vinylic protons in the fatty ester chains and the methine proton in the glycerol moiety. The peaks at 6.1 and 6.2 ppm for Dilulin are due to a norbornene-like moiety. The integration of these peaks reveals an average of one norbornene-like unit per triglyceride. In actuality, the norbornene number for any particular triglyceride may vary from one to six, as found in previous work with norbornenylized oils.¹⁵ However, molecules ranging from three to six norbornene-like moieties are quite low in number. The small peak at 5.65 ppm is that of either the cyclopentene portion of the residual DCPD (proven from TLC) or that of an ene-type reaction (discussed

later). Figure 4 shows the $^{13}\text{C-NMR}$ spectra of Dilulin and regular linseed oil. Peaks that are characteristic of the norbornene-like moiety appear in the Dilulin spectrum at 136 ppm [Fig. 4(A)] for the vinylic carbons and at 48 ppm [Fig. 4(B)] for the methylene carbons of the ring. In addition to these peaks, a peak corresponding to the bridgehead carbon appears around 42 ppm (C).

Figure 5 shows the FTIR spectra of both regular linseed oil and Dilulin. Evidence for the incorporation of the norbornene-like unit is seen by the presence of a small peak at 1570 cm^{-1} . The purified Dilulin also shows this peak; this indicates that it is not due to residual DCPD. Most vegetable oils have naturally occurring cis double bonds. Regular linseed oil and Dilulin are no exception to this, with a peak at 725 cm^{-1} . However, the FTIR spectrum of

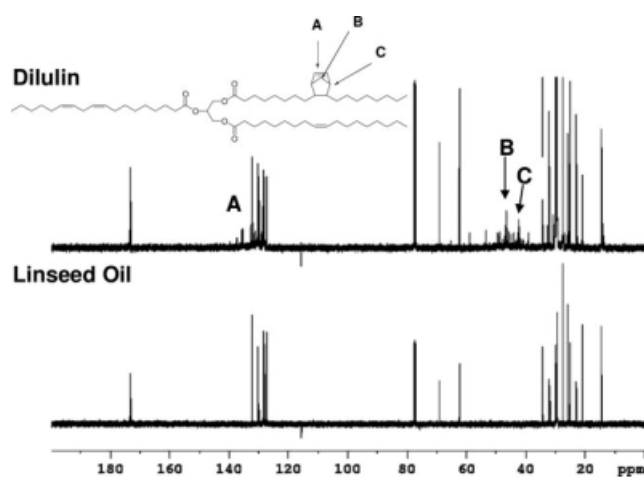


Figure 4 $^{13}\text{C-NMR}$ spectra of pure Dilulin and pure linseed oil.

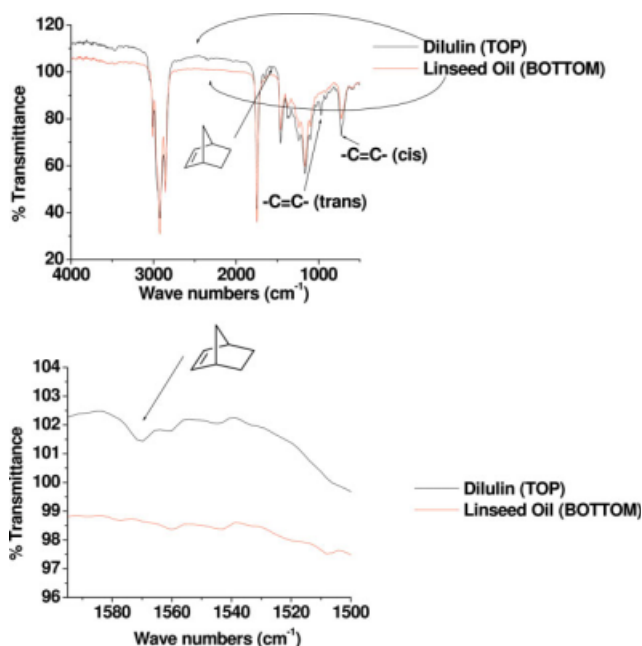


Figure 5 FTIR spectra of pure Dilulin and pure linseed oil (top) and an enlargement of the norbornene region (bottom). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Dilulin also indicates the presence of a trans double bond detected at approximately 970 cm^{-1} . We believe that this is due to two possible isomerization routes. One route involves isomerization of the double bond by an ene-type reaction between the bisallylic hydrogens in the oil and cyclopentadiene (Fig. 6) during the synthesis, which would allow for the formation of a trans double bond and a cyclopentene moiety. This is further evidenced in the $^1\text{H-NMR}$ spectrum by a peak at 5.65 ppm (Fig. 3) corresponding to a cyclopentene moiety. A similar reaction with maleic anhydride involving the bisallylic protons in a vegetable oil has been reported previously.¹⁶ The second route may be a thermally related isomerization of the double bonds at the high temperature used to synthesize Dilulin. Both of these could be responsible for the trans double bond.

From these characterization techniques, we have determined that (1) Dilulin is a mixture of the desired oil containing the unsaturated norbornene-like moiety and DCPD or copolymers thereof; (2) there is an average of approximately one bicyclic moiety per triglyceride; and (3) during the synthesis of Dilulin, two possible isomerization routes may occur: an ene-type reaction of the oil with cyclopentadiene introducing a cyclopentene group into the oil causing isomerization of the double bonds and/or a thermal isomerization of the double bonds in the triglyceride oil.

To verify that Dilulin does have an unsaturated bicyclic moiety that can undergo ROMP, regular lin-

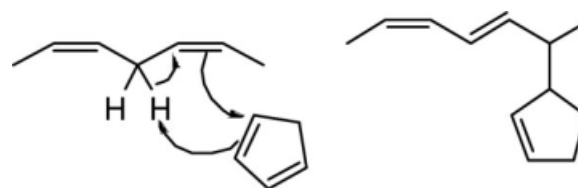


Figure 6 Ene reaction between cyclopentadiene and the bisallylic hydrogens in the triglyceride.

seed oil and, in a separate experiment, a 50 : 50 (wt %) mixture of regular linseed oil and DCPD were polymerized in the presence of Grubbs' second-generation catalyst (0.125 wt %). Neither of these resulted in any desirable crosslinked thermoset. Rather, the pure linseed oil gave an oily substance, and the 50 : 50 mixture also yielded an oily substance with a weak film on top. All of the Dilulin thermosets presented in this study, including the one composed of pure Dilulin, resulted in desirable crosslinked thermosets, and this suggests that Dilulin does indeed possess an unsaturated bicyclic moiety capable of undergoing ROMP.

Optimization of the catalyst concentration

The first step in this study was to determine the optimum concentration of the catalyst. In our previous work using BCO and cyclooctene, we found the best concentration of Grubbs' second-generation catalyst for all of the explored thermosets to be 0.5 wt %.¹⁰ This, however, is a high catalyst concentration and a hindrance for scale-up. In this study, the concentration of the catalyst was reduced to as little as 0.03 wt % and studied up to 0.25 wt % while the Dil50DCPD50 composition was used. All of the concentrations employed produced crosslinked materials. However, the sample that used a 0.03 wt % concentration of the catalyst was still quite oily after the curing sequence. Soxhlet extraction analysis of the thermosets prepared with various concentrations of the catalyst was employed to determine how effective each catalyst concentration was at producing a crosslinked thermoset. Table I shows the soluble portions obtained for each of the catalyst concentrations employed. For 45% soluble materials, the 0.03 wt % sample had the greatest soluble

TABLE I
Effect of the Catalyst Concentration on the Soluble Fraction

Catalyst concentration	Soluble (%)	Insoluble (%)
0.03 wt %	45	55
0.06 wt %	22	78
0.125 wt %	21	79
0.25 wt %	19	81

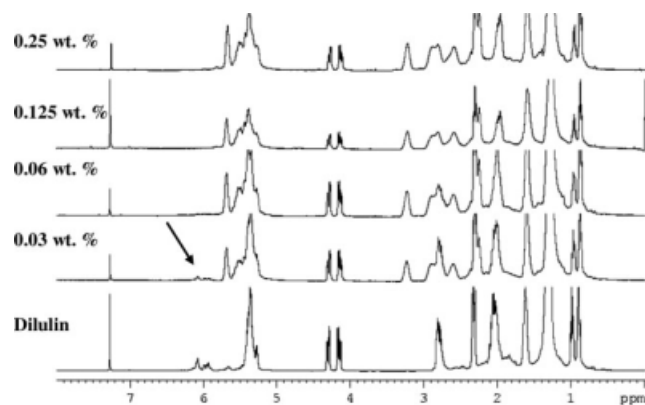


Figure 7 $^1\text{H-NMR}$ spectra of the extracts obtained with different catalyst concentrations.

fraction, yet this value was actually lower than what it should have been because the sample was quite oily and some of the residual surface oil was lost when the sample was weighed. Table I reveals that as the catalyst concentration was increased from 0.06 to 0.125 to 0.25 wt %, the soluble fraction was 22, 21, and 19%, respectively. A more detailed analysis of the compositions of these soluble fractions is discussed later. Figure 7 shows the $^1\text{H-NMR}$ spectra of the soluble fractions with different catalyst concentrations. The sample prepared with a 0.03 wt % catalyst concentration still possessed protons corresponding to the unsaturated bicyclic moiety, and this indicated that this concentration of the catalyst was too low to allow for efficient incorporation of Dilulin into the thermoset. All of the other samples with different catalyst concentrations underwent ring opening and the incorporation of the unsaturated bicyclic moiety of the oil into the thermoset. With these data in hand, the chosen optimum catalyst concentration was 0.125 wt %. Even though the 0.06 wt % sample had roughly the same soluble portion as the 0.125 and 0.25 wt % samples, this amount of the catalyst failed to produce desirable thermosets when more than 50 wt % oil was used. Because the goal of this study was to examine the range of oil incorporation into the thermosets, the 0.125 wt % catalyst concentration was chosen as the optimum concentration.

Extraction analysis

Table II shows the extraction analysis carried out on these Dilulin–DCPD thermosets. As the amount of oil increased, the soluble fraction or unreacted component also increased, from 21 wt % for the Dil50DCPD50 specimen to 28 wt % for the Dil100 specimen. Surprisingly, this is a rather small difference (ca. 7 wt %). Nonetheless, Dilulin's reactivity is lower than DCPD's reactivity. This is attributed to the fatty ester chains, which may hinder coordination between the catalyst and the norbornene-like moiety of the Dilulin. Figure 8 shows the $^1\text{H-NMR}$ spectra of extracts from the thermosets along with the spectrum of pure Dilulin. The extracts appeared to be either oligomers of a Dilulin–DCPD copolymer, unreacted triglyceride oil, or both. These oligomers may actually be cyclic in nature, as this is a common occurrence in ROMP polymerizations.¹⁷

As the amount of DCPD in the feed ratio of the thermoset increased, the intensity of the peaks at 2.6, 2.8, 3.15, 5.45, and 5.65 ppm, which corresponded to oligomers containing DCPD, increased. Proof that the peaks corresponded to oligomers or low-molecular-weight polymer was provided by the broadening of the peaks at 2.6, 2.8, and 3.15 ppm, which usually indicates oligomer or polymer formation. The peak at 5.45 ppm corresponded to the metathesized carbon–carbon double bonds of the polymeric backbone. The peak at 5.65 ppm corresponded to the cyclopentene-like vinylic hydrogens of the DCPD. This peak was fairly intense when DCPD was employed in the feed ratio. When no DCPD was used, as in the Dil100 sample, the extract appeared to be mainly unreacted triglyceride oil. This was evidenced by the absence of a peak at 5.45 ppm, which indicated no oligomerization, along with the absence of norbornenyl peaks at 6.1 and 6.2 ppm. The small peak at 5.65 ppm can be attributed to the ene-type product mentioned earlier.

It is interesting that when CDCl_3 was added to the Dil50DCPD50, Dil70DCPD30, and Dil90DCPD10 soluble fractions, small needlelike materials appeared. These materials are insoluble in common solvents at room temperature and are thought to be lightly crosslinked oligomeric species. $^{13}\text{C-NMR}$

TABLE II
DMA, TGA, and Extraction Data

Sample	T_g (°C) ^a	Tan δ	Storage modulus at 25°C (MPa)	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)	Soluble (%)	Insoluble (%)
Dil50DCPD50	36 (64)	0.64	228	427 (426)	461 (461)	462 (461)	21	79
Dil70DCPD30	−9 (27)	0.67	6.35	414 (385)	453 (451)	462 (457)	26	74
Dil90DCPD10	−30 (−14)	0.75	1.88	362 (348)	440 (441)	459 (457)	28	72
Dil100	−29 (−4)	0.71	—	376 (344)	438 (437)	459 (457)	28	72

^a T_g corresponds to the larger peak if there is phase separation.

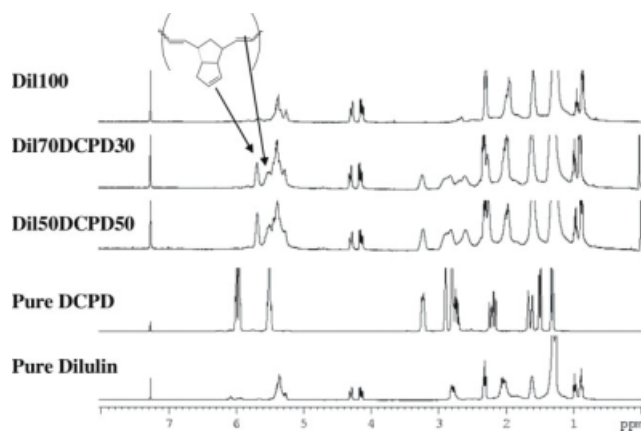


Figure 8 $^1\text{H-NMR}$ spectra of the Dilulin-DCPD extracts.

analysis (not shown) revealed the structure of these materials to be similar to that of the insoluble cross-linked thermoset, which is discussed later.

Generally, these thermosets have a high amount of a soluble material (nothing less than 20% soluble). One possible reason for this is that the catalyst, which is highly active, may initially favor the formation of cyclic oligomers. Once significant polymer formation and crosslinking occur, many of these oligomers may still exist, resulting in a high soluble fraction. Indeed, it is known that in the ROMP of cycloalkenes, the product consists of a high-molecular-weight portion and a low-molecular-weight portion that is composed of cyclic oligomers.¹⁷ Also, it has been shown that in the ROMP of *endo*-DCPD with certain reactive catalysts, the formation of cyclic oligomers occurs within minutes and decreases with time, whereas a high-molecular-weight polymer is formed only slowly.¹⁸ These previous findings are applicable to these Dilulin-DCPD thermosets and may help to explain the high soluble fraction. Another reason for the high soluble fractions present in these materials may be cross metathesis between the double bonds in the fatty acid chains and the growing polymeric network. It has been shown that Grubbs' second-generation catalyst is quite effective at the cross metathesis of internal olefins.¹⁹ This could effectively reduce crosslinking and thus reduce the incorporation of the Dilulin and DCPD into the thermoset.

FTIR was carried out on the insoluble crosslinked portions that remained behind after the extraction process. The FTIR spectra of the insoluble portions of the Dil50DCPD50 and Dil100 samples are shown in Figure 9. The peak corresponding to the norbornene-like moiety at 1570 cm^{-1} in both insoluble portions was gone, and this suggested a ring-opened product in the crosslinked thermoset. Also, both *cis* and *trans* double bonds could be seen around 725 and 970 cm^{-1} , respectively. However, we cannot say

with certainty whether the *cis* and *trans* peaks were due to the metathesized carbon-carbon double bonds or to the carbon-carbon double bonds in the fatty ester side chains.

Thus, extraction analysis showed that the resulting thermosets were composed of (1) a soluble fraction that was mainly composed of oligomers of Dilulin and DCPD, triglyceride oil, or both and (2) a cross-linked polymeric network containing both monomers of Dilulin and DCPD (if it was used). The *cis/trans* configuration of the crosslinked network could not be elucidated, and it was assumed that it was fairly random. The impact of Dilulin incorporation and the soluble fraction percentage are examined in the next section in the discussion of DMA.

DMA

DMA was carried out on the polymeric samples with single cantilever and film/fiber tension modes. The two methods gave similar glass-transition temperature (T_g) values. Thus, for simplicity, we report only the single cantilever results. The T_g values are based on the maximum peak height of the $\tan \delta$ curves. As shown in Table II, T_g decreased from 36 to -29°C as the concentration of the oil in the sample increased. This is most easily explained by the increasing amount of unreacted oil (soluble fraction) that could plasticize or soften the thermoset,

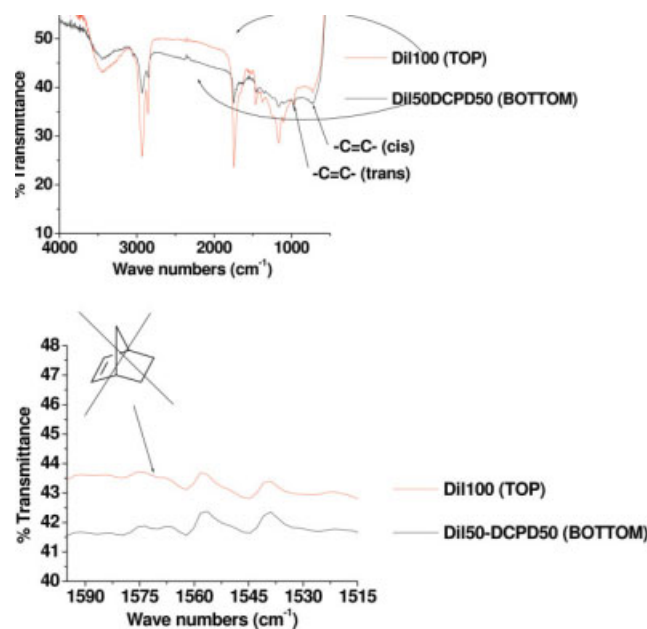


Figure 9 FTIR spectra of the insoluble portions of Dil50DCPD50 and Dil100 (top) and an enlargement of the norbornene-like region indicating an absence of norbornene-like moieties (bottom). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

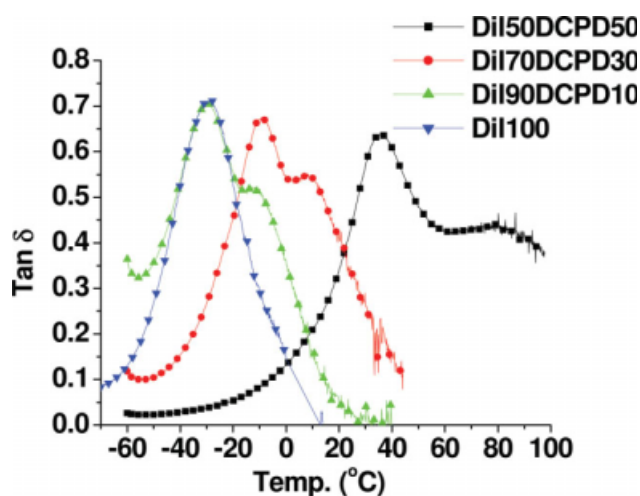


Figure 10 Tan δ curves for the non-solvent-extracted samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

resulting in a lower T_g value. In addition, with larger concentrations of oil incorporated into the final thermoset, a decrease in T_g could also occur because of the increased number of fatty ester chains in the oil that could internally plasticize the thermoset.²⁰

Figure 10 shows the DMA curves for the analyzed specimens. The DiI100 curve has a relatively narrow single peak. The DiI50DCPD50, DiI70DCPD30, and DiI90DCPD10 curves are broad with two peaks, which indicate phase separation. In these curves, the lower T_g peak corresponds to a more oil-rich phase, and the higher T_g peak corresponds to a more DCPD-rich phase. In addition, the tan δ values for the lower T_g peaks are greater than those for the higher T_g peaks, pointing to less stiffness and cross-linking in these oil-rich regions. As for the DiI100 sample, no phase separation was seen with the homopolymer of the thermoset. The phase separation was likely due to the differences in the reactivity of the DiIulins and DCPD. The tan δ values for all of these samples ranged from 0.65 to 0.72. The DiI50DCPD50, DiI70DCPD30, and DiI90DCPD10 materials could be attractive in damping applications because their tan δ values were all above 0.3 and covered a temperature range of at least 60°C.²¹

Also in Table II are the storage modulus values at room temperature. The storage modulus of the DiI50DCPD50 sample was much higher than those of the other samples. This could be attributed to the fact that at room temperature the DiI50DCPD50 sample was below its T_g and not in the rubbery plateau like the other samples; this gave rise to the high storage modulus (Fig. 11). The DiI50DCPD50 sample had not yet reached its rubbery plateau at 100°C, whereas the DiI70DCPD30 and DiI90DCPD10 samples had reached their rubbery plateaus around

10°C and then broke around 40°C; this indicated the weakness of these samples. The DiI100 sample, which broke before 20°C, had the consistency of gelatin and was quite weak.

We have also explored the effect of the soluble fraction as a plasticizer. In general, a plasticizer is usually a high-boiling, oily organic liquid that is mixed with a polymer to impart softness or flexibility, which in turn lowers the T_g .²⁰ To measure the plasticizing effect of the oil in our system, samples were extracted in a Soxhlet extractor for 24 h and then dried in a vacuum oven at 70°C overnight. The solvent-extracted samples, which possessed cracks and small voids after the extraction process, were less flexible than their non-solvent-extracted counterparts. The T_g values of these samples are shown in parentheses in Table II. As one can see, the plasticized samples had lower T_g values than those with no plasticizer (solvent-extracted), and this followed the expected trend. The DiI90DCPD10 and DiI100 samples still possessed relatively low T_g 's. This was due to both the higher content of the flexible triglyceride oil in the crosslinked polymer backbone, which contained fatty ester chains that plasticized (internally) the thermoset, and the lower content of the rigid crosslinker DCPD.

In Figure 12, the tan δ curves for the solvent-extracted samples seem to possess some of the phase separation seen in the non-solvent-extracted samples. However, the differences in the peak heights of the oil-rich and DCPD-rich portions in the tan δ curves of these two materials are quite different. This indicates removal of the soluble fraction and suggests that the unreacted triglyceride oil or oligomers thereof became more entangled with the fatty ester side chains in the oil-rich regions of the

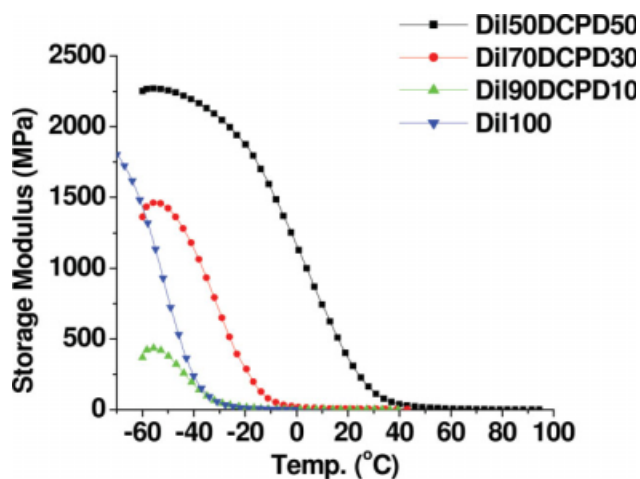


Figure 11 Storage modulus curves for the non-solvent-extracted samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

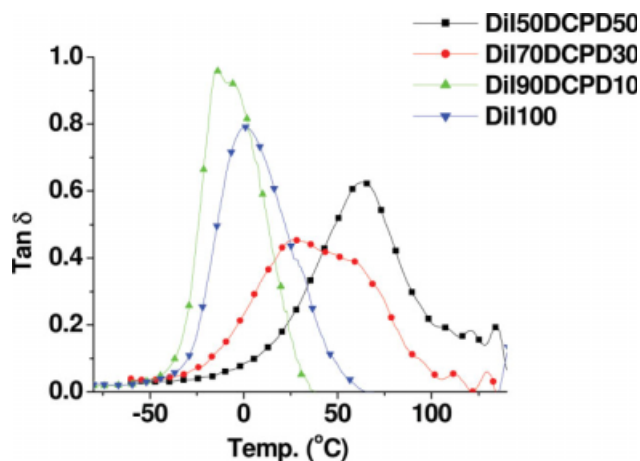


Figure 12 Tan δ curves for the solvent-extracted samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thermoset. In effect, this enhanced the tan δ values of the oil-rich regions in the non-solvent-extracted samples, creating a larger difference in tan δ between the oil-rich and DCPD-rich regions.

TGA

TGA was carried out on these thermosets. Figure 13 shows the degradation curves of the thermosets in air. A three-stage degradation curve can be seen for the thermosets. The first stage, from 200 to 400°C, is degradation of the triglyceride oil or free fatty ester components that remain in the crosslinked thermoset. The second stage (400–500°C) is the stage of maximum degradation and represents degradation of the crosslinked thermoset. The third stage (500–650°C) consists of a short-lived plateau whose height in terms of the weight percentage is greater when greater amounts of DCPD are present in the thermoset. The third stage is degradation of the char, which remains behind.

The temperatures of 10 and 50% weight loss (T_{10} and T_{50} , respectively) were determined to evaluate the thermal stability of the bulk polymer and the consistency of crosslinking in the bulk polymer, respectively.²² Table II reveals that, with the exception of the DiI100 sample at T_{10} , all of the samples had decreasing T_{10} and T_{50} values with increasing amounts of oil and decreasing amounts of the DCPD crosslinker. This trend was more pronounced in the T_{10} values for the DiI90DCPD10 and DiI100 samples, which had T_{10} values below 400°C, probably because the bulk polymer for these samples contained more oil. The oil portions of the backbone were not as thermally stable as those containing DCPD, thereby giving a lower T_{10} value. The maximum degradation temperature (T_{max}) values are shown in Table II as well. All of these samples had roughly the same

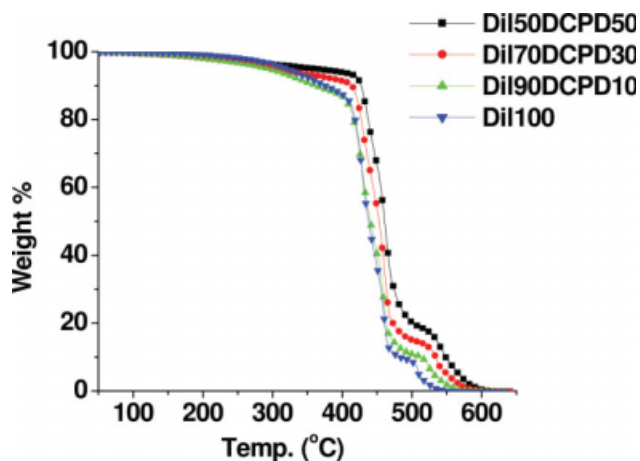


Figure 13 TGA of the non-solvent-extracted samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

T_{max} values around 460°C. Without any valid method to test for this, we are assuming at this time that this is related to thermal crosslinking of the double bonds in the unreacted fatty ester chains or the metathesized carbon–carbon double bonds, yielding roughly equal thermal stability among the samples in this region.

TGA was also performed on the solvent-extracted thermosets. Figure 14 shows the same three-stage degradation curves found for the non-solvent-extracted samples. The solvent-extracted samples followed a trend similar to the non-solvent-extracted samples in terms of the T_{max} values, in that all of the samples, regardless of the oil concentration, had similar values. Again, we attribute this to thermal crosslinking occurring during the temperature ramp of TGA. The T_{50} values (shown in parentheses) decreased with decreasing DCPD crosslinker

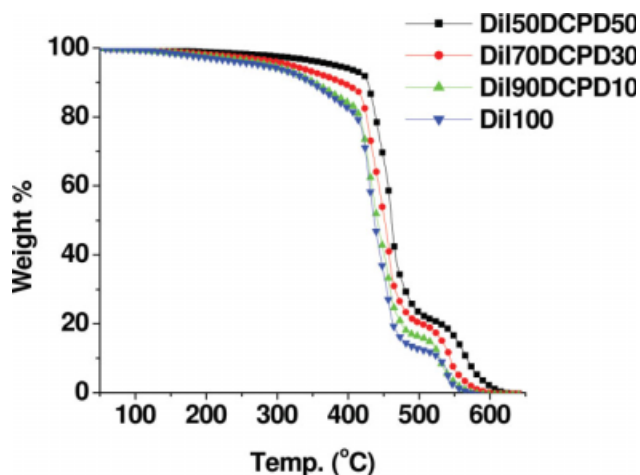


Figure 14 TGA of the solvent-extracted samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

content, and this suggested less crosslinking in the bulk polymers that contained increased amounts of oil. The T_{\max} and T_{50} values for the solvent-extracted and non-solvent-extracted samples were the same. However, a major difference between the solvent-extracted and non-solvent-extracted samples can be seen in the T_{10} values. The solvent-extracted T_{10} values were lower than those of the non-solvent-extracted samples. A plausible reason for this is a synergism between the soluble fraction and the bulk polymer, which enhanced the thermal stability of the non-solvent-extracted thermosets in this temperature region. It has been stated that the stability of a polymeric matrix is related not only to the characteristics of the polymer but also to the various interactions between the macromolecules and molecules²³ (i.e., the polymer and the plasticizer). Thus, a positive synergistic effect between the soluble fraction and the bulk polymer may exist in this temperature region, which delays the degradation of the bulk polymer, yielding a higher T_{10} value with a non-solvent-extracted sample.

CONCLUSIONS

Dilulin, a commercially available modified linseed oil, was characterized and found to have an average of approximately one norbornene-like unit per triglyceride and to be an approximately 95 : 5 mixture of the desired oil and unreacted DCPD and/or oligomers of DCPD. Materials possessing anywhere from 50 to 100 wt % oil were synthesized by the copolymerization of Dilulin and DCPD and characterized. Increasing the oil content and decreasing the DCPD content resulted in samples with lower T_g 's. Solvent-extraction analysis revealed that the soluble fraction acted as a plasticizer, as did the fatty ester side chains incorporated into the thermoset, which internally plasticized these materials. The samples had T_{\max} values that were all relatively similar, and this may have been due to the added stability imparted by the double bonds remaining in the thermoset. We are presently looking to improve the oxidative stability of these materials by attempting to enhance their mechanical properties with different reinforcing fibers and fillers.

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