Corn Oil-Based Composites Reinforced with Continuous Glass Fibers: Fabrication and Properties

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ABSTRACT: Novel thermosetting composites have been successfully developed using glass fibers to reinforce regular corn oil (COR) and conjugated corn oil (CCOR) resins prepared by cationic copolymerization with styrene (ST) and divinylbenzene (DVB). The dependence of morphology and physical properties of the composites on the contents of glass fibers and DVB was determined by scanning electron microscopy, dynamic mechanical analysis, thermogravimetric analysis and tensile testing. The glass fiber loading and polymer matrix composition play an important role in improving the mechanical properties and thermal stability of the resulting composites. As the glass fiber content increases from 0 to 45 wt %, the COR-based composites show an increase in Young's modulus from 4.1 to 874 MPa and tensile strength from 1.7 to 8.4 MPa. Furthermore, the composites exhibit good damping properties and are suitable for applications where reduction of both unwanted noise and vibration is important. Compared with the composites from COR, the CCOR-based composites exhibit slightly higher thermal stabilities and mechanical properties, due to higher reactivity of CCOR with comonomers. Increasing the DVB content improves the crosslink density of the polymer matrix, leading to a significant improvement in the thermal stabilities and mechanical properties of the resulting composites. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3345–3353, 2006

Key words: composite; corn oil; cationic polymerization; glass fibers; renewable resources

INTRODUCTION

Advances in petrochemical-based polymers have brought many benefits to mankind. However, it is becoming increasingly evident that the ecosystem is being badly damaged as a result of these nondegradable plastic materials. Thus, the use of renewable resources as starting materials for the synthesis of new polymers has become the focus of considerable recent scientific research.[1] Natural oils, possessing a triglyceride structure with highly unsaturated fatty acid side chains, are considered to be one of the most important classes of renewable sources for the production of biodegradable polymers.[2] Natural oils are now used in everything from margarine to meals for livestock to refined biodiesel fuels, as well as environmentally friendly lubricants and coatings.[3–6] Recently, considerable research has been concentrated on the development of bio-based polymers using natural oils or their derivatives as the main comonomer.[7–17] Wool and colleagues[7–9] and Aranguren and colleagues[10,11] have, respectively, developed a series of polymer resins using multifunctional soybean and linseed oil derivatives as a main compo-

nent and styrene (ST) as a comonomer. Bio-based epoxy resins,[12] polyurethane thermosets,[13,14] and aqueous dispersions[15,16] have also been developed from derivatives of linseed, soybean, castor, and rapeseed oils. In our previous work, we have taken advantage of the carbon–carbon double bonds in soybean,[17–20] linseed,[21] tung,[22,23] corn,[24] and fish oils[25,26] to develop a wide variety of new polymeric materials by cationic or thermal copolymerization of these natural oils with ST and divinylbenzene (DVB) (Fig. 1). The resulting thermosetting polymers can be varied from elastomers to tough and rigid plastics by simply changing the stoichiometry, the type of oil, and the alkene comonomers. These new polymers exhibit thermophysical and mechanical properties that are comparable to those of commercially available elastomers and conventional plastics and may serve as replacements for petroleum-based polymers in many applications.

The major problems with polymers in engineering application are their low stiffness and strength when compared with metals. To offset these deficiencies, the fibers and particles are always used to reinforce the polymers for preparation of composites.[27] A fiber-reinforced polymer (FRP) composite typically consists of a mass of reinforcing fibers combined with a polymer resin matrix, which is used to combine with and bond to the reinforcing fibers, so that applied loads are supported by the latter and transmitted through the material from fiber to fiber.[28] The main advantages
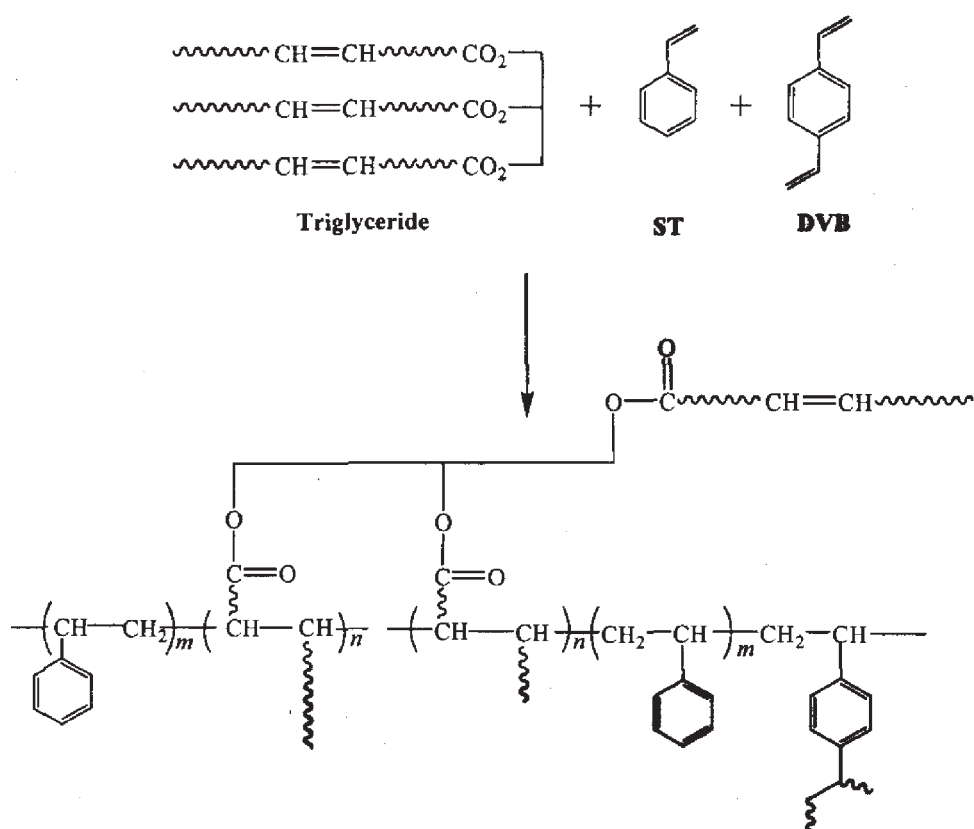
Figure 1 Cationic or thermal copolymerization of triglyceride oils with styrene (ST) and divinylbenzene (DVB).

of FPR materials are their low weight, high specific strength and stiffness, environmental resistance and long life, which has resulted in their wide use in the aerospace, automotive, marine, infrastructure, military, sports, and industrial fields.[29] Among the existing polymer matrix composites, glass fiber-reinforced polymer composites are widely used, because of their cost effectiveness, and their mechanical, electrical, and thermal properties.[30] Recently, thermosetting resins for polymer composite matrices have been developed from renewable resources, such as soybean and linseed oils.[11,31,32] Corn oil consists of triglyceride molecules with, on average, ∼ 4.1 C=C double bonds per molecule present in the fatty acid side chains. This makes it possible to copolymerize corn oil directly with other comonomers, such as ST and DVB, by cationic polymerization,[24] and thus prepare new FRP materials. The objective of this work was to show the feasibility of utilizing corn oil-based resins to prepare glass fiber-reinforced composites. Novel composites from cationically polymerized corn oil-based thermosetting resins and glass fibers have been prepared using compression molding. The morphology, structure, thermophysical, and mechanical properties of the resulting composites have been investigated by scanning electronic microscopy (SEM), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and tensile testing.

EXPERIMENTAL

Materials

The 100% pure Mazola corn oil used in this work was purchased at the local supermarket. The conjugated corn oil (CCOR) was synthesized by rhodium-catalyzed isomerization of regular corn oil using a method developed previously by us.[33] The degree of conjugation was calculated to be about 100% based on ^{1}H-NMR spectral analysis performed on a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 300 MHz. ST, DVB (80 mol % DVB and 20 mol % ethylvinylbenzene), and distilled-grade boron trifluoride diethyl etherate (BFE) were purchased from Aldrich Chemical and used directly as received. Norway Pronova fish oil ethyl ester EPAX 5500 EE (NFO) was used to modify the cationic initiator. The random continuous glass fiber mat was provided by Creative Composites of Brooklyn, Iowa. The polytetrafluoroethylene (PTFE) release agent MS-122DF was purchased from Miller-Stephenson Chemical (Morton Grove, IL).

Fabrication of corn oil-based resins and composites

The corn oil-based resins were prepared by the cationic copolymerization of COR or CCOR with ST and DVB

initiated by modified BFE initiators using our previously procedure.[24] The following procedure is representative. Briefly, 25 g of ST and 10 g of DVB were added to 50 g of the oil, and the mixture was then vigorously stirred while adding 15 g of the modified BFE initiator, which was prepared by mixing the NFO with BFE in a 2 : 1 weight ratio. The NFO is added for production of more homogeneous reactions and polymers. The resulting reactants were then injected into a glass mold, which was subsequently sealed by a silicon adhesive, and cured at 60°C for 10 min, 80°C for 20 min, and then 110°C for 24 h.

The composite materials were prepared by compression molding. The glass fiber mat was first cut into about 15 cm × 15 cm squares, dried, weighed, and then placed into the cavity of the stainless steel mold coated with the PTFE release agent (MS-122DF). The mixture of oil, ST, DVB, and modified initiator with the same composition as the final CORP and CCORP resins were poured into the mold to totally wet the fiber mat. Then, the mold was closed and the resulting materials were cured at 60°C for 10 min, 80°C for 20 min, and 110°C for 2 h under 1500 psi, followed by 110°C for 22 h in an oven. By changing the layers of the glass fiber mat, a series of composites with different glass fiber loadings have been obtained. The nomenclature adopted in this work for the composite samples is as follows: CORP and CCORP represent the polymer matrix from regular corn oil and conjugated corn oil, respectively. The following number indicates the loading of the glass fibers in the composite. For example, CORP-45 corresponds to a composite sample prepared from CORP resin with 45 wt % glass fibers.

To study the effect of composition of polymer matrix on the properties of the resulting composites, a series of composites has been prepared in which the glass fiber content was held constant at about 20 wt %, while changing the DVB concentration. The total content of the comonomers ST and DVB was kept at 35 wt % in the polymer matrix, while using the same amount of oil and initiator, as well as the cure sequence outlined earlier. Similar to the nomenclature mentioned above, CORP(DVB15)-20 corresponds to a composite sample reinforced with 20 wt % glass fibers prepared from a COR based-resin where the amount of DVB concentration is 15 wt %. Thus, the amount of ST is 20 wt %.

Characterization

Soxhlet extraction was used to characterize the structures of the pure polymer resin and the resulting composites. A 2.0 g sample was extracted for 24 h with 100 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the insoluble material was totally dried in vacuo for several hours before it was weighed.

The densities of the composites were determined by picnometry (a buoyancy method using distilled degassed water as the displacement medium), using at least three specimens of each sample. The theoretical densities of the composites were calculated from the rule of mixtures as follows:

$$\frac{1}{\rho_c} = \frac{w_m}{\rho_m} + \frac{w_f}{\rho_f} \tag{1}$$

where ρ is the density and w is the weight fraction, and the subscripts c, m, and f correspond to the composite, the matrix, and the fiber, respectively. The values of ρ_m (1.02 g cm^{-3} for the COR-based resin and 1.04 g cm^{-3} for the CCOR-based resin) were determined experimentally, and ρ_f was taken as 2.64 g cm^{-3} for the glass fiber.[30]

The morphology of the fracture surfaces of the samples after the tensile strength test was carefully observed using scanning electron microscopy (Hitachi 2460N, Japan) at 20 kV.

The dynamic mechanical properties of the bulk polymers and the composites were obtained using a PerkinElmer dynamic mechanical analyzer (Pyris-7e) (PerkinElmer, Norwalk, CT) in a three-point bending mode. A rectangular specimen of about 2 mm in thickness and 5 mm in depth was cut from the samples. Each specimen was first cooled to about −60°C, and was then heated at 5°C/min at a frequency of 1 Hz under helium.

A PerkinElmer Pyris-7 thermogravimeter was used to measure the weight loss of the samples under an air atmosphere. The samples were heated from 50 to 650°C at a heating rate of 20°C/min. Generally, 8–12 mg samples were used for the thermogravimetric analyses.

The tensile tests were conducted at 25°C according to ASTM D638 using an Instron universal testing machine (model 4502) at a crosshead speed of 5 mm/min. The dogbone-shaped test specimen (type - V specimen in ASTM D638M) had a gauge section with a length of 63.5 mm, a width of 3.18 mm, and a thickness of about 3 mm.

RESULTS AND DISCUSSION

Structure and morphology

Void content is a major concern in manufacturing composite materials, since it influences the quality and strength of the resulting composites.[32] A void-trapped composite usually exhibits a lower density than a compact composite. Figure 2 shows the theoretical and experimental densities of the corn oil-based composites prepared by compression molding. As expected, the CCOR resin exhibits a slightly higher crosslink density than the COR resin, since
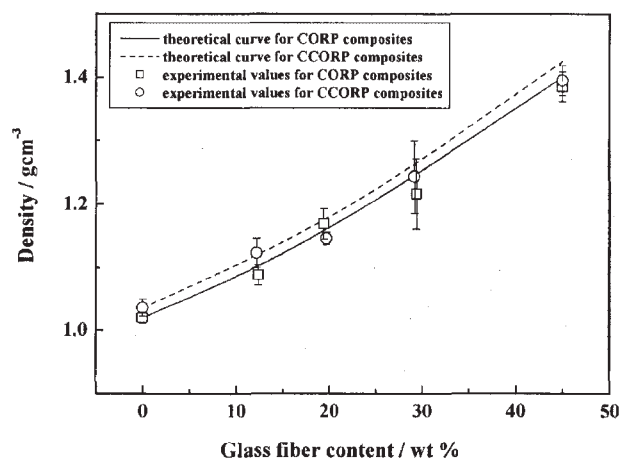
Figure 2 The density of the composites as a function of glass fiber content.

the higher reactivity of the CCOR with ST and DVB reduces the free volume of the resulting polymer and, hence, leads to higher density. The experimental density of the composites increases with increasing glass fiber content for both the CCORP and CORP composites and fits well with the theoretical values calculated by using the mixing rule. This indicates that all of the fibers were totally wet and a compact structure was formed for the composites during the cure under pressure.

Figure 3 shows the dependence of the soluble materials from the polymer matrix (not the total composite) on the glass fiber and DVB content. The CCORP resin consists of 20 wt % of soluble substances and 80 wt % of crosslinked polymer. A relatively high percentage of soluble substances is observed for the CORP resin because of the lower reactivity compared with CCOR. It has been found by ^{1}H-NMR spectral analysis that the soluble substances are composed primarily of initiator fragments, triglyceride molecules, and polymers containing polystyrene segments with aromatic protons.[18,24] As the glass fiber content increases in the polymer matrix, an increase in soluble materials from 31.4 to 41.3 wt % is observed in the CORP composite. Before experiment, the glass fiber mat used as the reinforcement was dried for 2 h at 100°C, so the increase in soluble materials is due to the glass fiber itself rather than hydrolysis of the oil due to the introduction of water by the glass fibers. Incorporating glass fiber into the reactant affects diffusion of the initiator or chain propagation during polymerization, resulting in the decreased crosslink density and the loose network structure of the composite matrix. Similar results have also been observed in other systems.[34–36] However, only a slight increase in soluble materials from 19.7 to 22.1 wt % is found in the matrix of CCORP composite when the glass fiber content is increased

from 0 to 45 wt %, indicating that the glass fibers have less of an effect on the copolymerization between CCOR and the comonomers because of their higher reactivity. DVB has proven to be an effective crosslinking agent for the natural oil/styrene system,[18,21,22] so the percentage of soluble materials is dramatically decreased as the DVB content is increased in the composite for both CORP and CCORP. This plays an important role on the structure and properties of the resulting composites, as discussed later.

Many of the properties of the composite materials have a very close relationship to their morphology. Figure 4 shows SEM micrographs of the CCORP composites after tensile fracture with 12, 29, and 45 wt % glass fibers. Two phases can be clearly seen for the composites. The fractured surfaces show that the fibers protrude out of the polymer matrix, where the ductile fracture is observed. Some glass fibers show adhesion of the resin onto the surface (images b, d, and f). However, the gaps between the fibers and the matrix and the holes due to the fiber pulling out are obvious on the fracture surfaces of the composites. These findings suggest that a weak interaction occurs between the matrix and the glass fibers, resulting in less interfacial adhesion and, therefore, an incompatible polymer composite. The poor interfacial adhesion between the fiber and the matrix indicates that fiber surface treatment and interfacial-coupling agents are needed for this system.
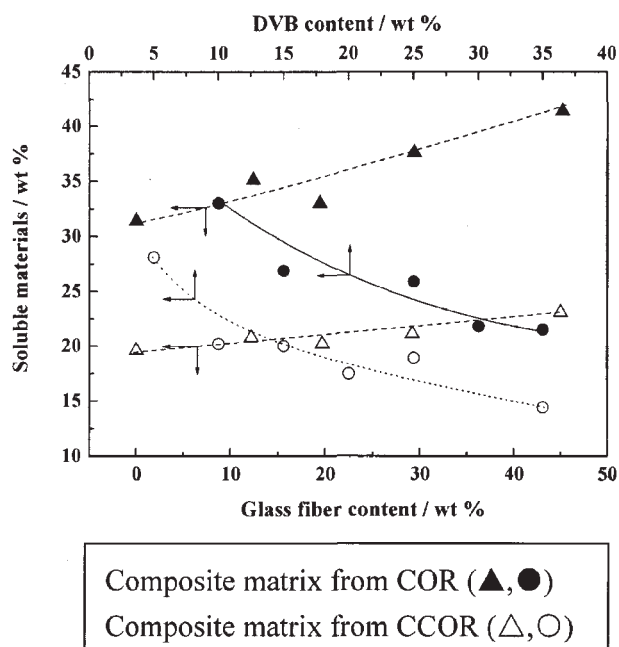

Figure 3 The dependence of the soluble substances of the polymer matrix for composites on the glass fiber and DVB content.
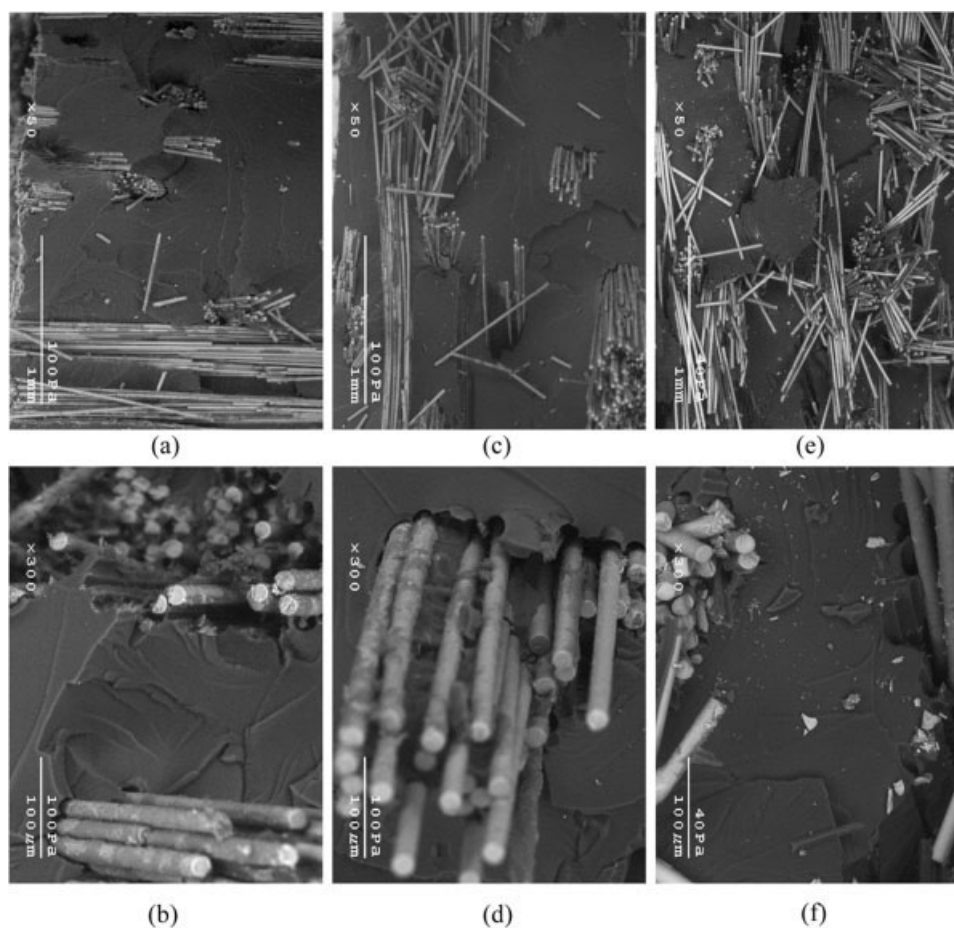
Figure 4 SEM images of the composite CCORP-12 (a,b), CCORP-29 (c,d), and CCORP-45 (e,f).

Thermophysical properties

The dynamic mechanical behavior of both the storage modulus and the loss factor (tan δ) for the CORP composites is shown in Figure 5. The storage modulus of the CORP composites greatly increases with increasing glass fiber content over the whole range of testing temperature, especially for temperatures where the rubbery plateau modulus occurs. The plateau modulus of the composite CORP-45 at 100°C is 10 times higher than that of the CORP resin, indicating the reinforced rigidity and increased thermal stability of the resulting composites. This improvement in stiffness can be attributed to the fact that the glass fiber embedded in the polymer matrix reduces the mobility and deformability of the polymer matrix.[11] The tan δ–T curves of the composites show a single relaxation peak in the temperature range from −25 to 75°C. The tan δ peak corresponds primary relaxation process of the polymer matrix and shifts from 24 to 19°C with an increase in the glass fiber content from 0 to 45 wt %, as a result of the loose network structure of the matrix due to addition of the fibers as indicated in Figure 2.[34–36] As expected, the height of the tan δ peak decreases as the glass fiber content

increases, since the polymer matrix fraction is reduced correspondingly and the introduction of glass fiber restricts in the mobilities of the polymer chain segments.[11] However, these CORP composites still exhibit a tan δ peak height higher than 0.3 over a 53–70°C temperature range, indicating that these CORP composites have very good structure damping properties and potential applications where reduction of both unwanted noise and resonance vibrations is important.[37]

The DMA behavior of the CCORP composites is shown in Figure 6. Similar to the CORP composites, the CCORP composites also show an increased storage modulus with increasing glass fiber content. An increase in storage modulus of 21.7 and 15.6 times at 50 and 100°C, respectively, is observed for the composite CCORP-45 when compared with the CCORP resin. However, no shift in tan δ peak position is observed in the tan δ–T curves. This can be explained by the fact that copolymerization of CCOR of relatively high reactivity with the comonomers is less affected by incorporating glass fibers, which leads to approximately the same crosslink density of the matrix and thus a similar relaxation temperature, which is consistent with the results from extraction.
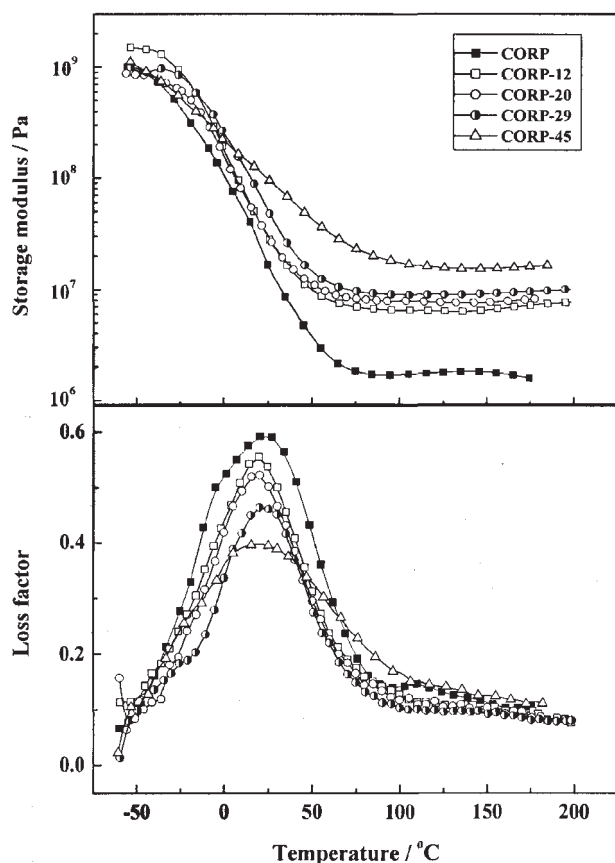
Figure 5 DMA behavior of the CORP composites with variation in the glass fiber content.

Figure 7 shows the DMA behavior of the approximately 20 wt % glass fiber reinforced composites from CCOR crosslinked with different DVB content. As expected, the storage modulus of the resulting composites increases dramatically with an increase in the DVB content in the matrix, due to the high crosslinking. Compared with CCORP-20, the significant improvements of 1755% and 1926% in the moduli at 50 and 100°C respectively, are achieved for the composite CCORP(DVB35)-21. The tan δ peak of the composite flattens, broadens and shifts from 11.7°C to 33.5°C as increasing the DVB content from 10 to 20 wt % in the polymer matrix. It is known that the ester groups in the polymer backbone in the matrix greatly contribute to the damping intensities of the materials.[38] Crosslinking increases the segmental heterogeneities of the polymer backbone and, thus, effectively broadens the glass-transition (damping) regions of the composite matrix. At the same time, however, crosslinking restricts the segmental motion and, thus, reduces the polymer's ability to dissipate mechanical energy. Thus, the damping intensity is reduced to some extent. Further increasing the DVB content from 25 to 35 wt %, however, results in two broad relaxation processes in the temperature range from −50 to 50°C and 50–175°C, respectively. The reactants used in this work

have a relatively large difference in their reactivity. At the very beginning of the reaction, the high concentration of the more reactive DVB (25–35 wt %) results in homopolymerization or copolymerization with ST to form a segment with a "DVB-rich phase" (hard domain), which is evidenced by the white flakes forming at the beginning of the experiment. As the DVB concentration decreases, a certain amount of the oil is incorporated by copolymerization with DVB or ST to form an "oil-rich phase" (soft segment). Therefore, the matrix with a high DVB loading appears as a complex heterogeneous structure composed of a "DVB-rich" phase and an "oil-rich" phase with their own individual relaxation transitions: the high temperature relaxation transition (from 50 to 175°C) intrinsic to a "DVB-rich" phase and the low temperature relaxation transition (from −50 to 50°C) intrinsic to an "oil-rich" phase. Similar results have been observed in plastics prepared previously by the cationic polymerization of other vegetable oils with ST and DVB.[20]

Figure 8 shows the TGA curves for the CORP resin and the resulting composites with different glass fiber content. The CORP resin shows a three-stage weight loss: the initial loss, beginning at around 200°C, attributed to evaporation and decomposition of unreacted oil and other soluble components in the bulk materi-
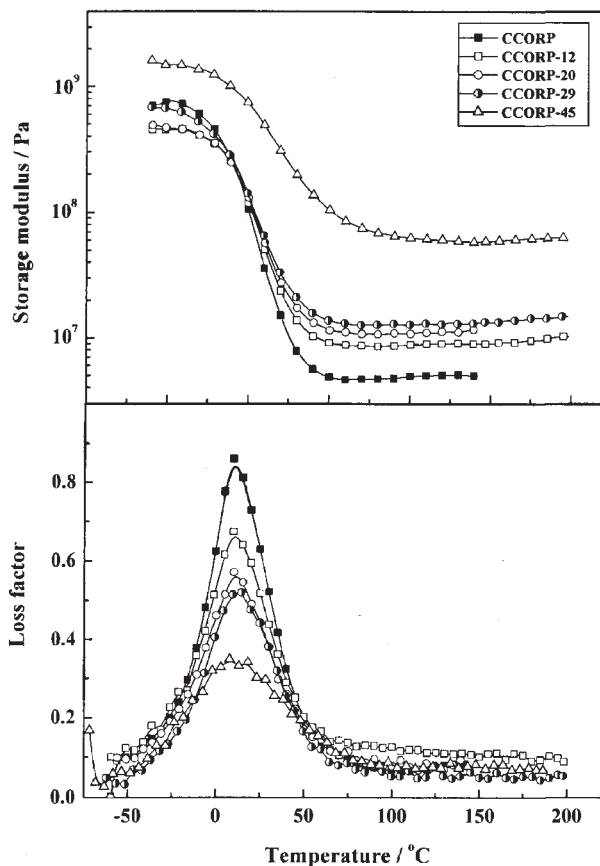

Figure 6 DMA behavior of the CCORP composites with variation in the glass fiber content.
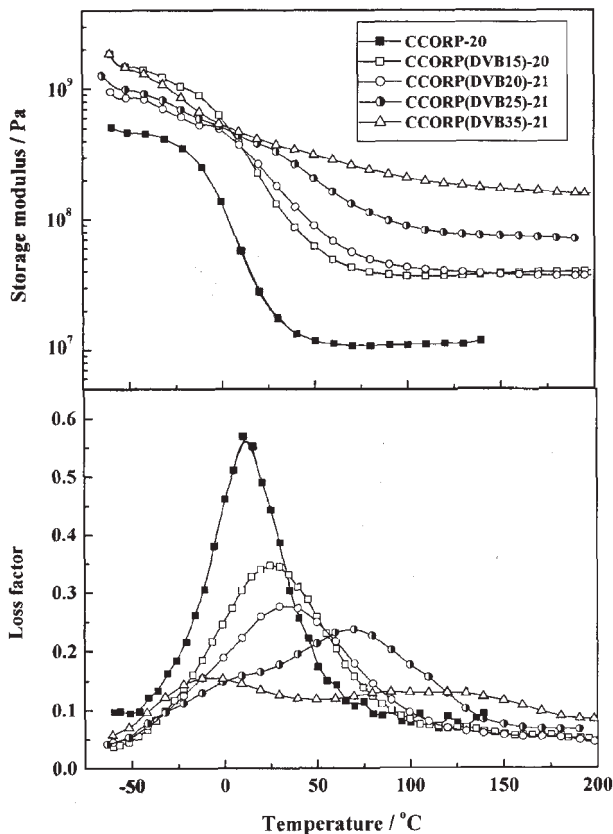
Figure 7 DMA behavior of 20 wt % glass fiber reinforced composites from CCOR with differing DVB content.

als.[18] A second loss at around 400–500°C is believed to be caused by thermal degradation of the crosslinked polymers.[39] The final loss at around 600°C is indicative of complete decomposition of the smaller fragments and oxidation of the carbon residue.[27] The thermal decomposition behavior of the composites is largely influenced by the glass fiber loading. For example, the temperatures for 20 wt % (T_{20}) and 40 wt % (T_{40}) loss shift from 357 to 421°C and from 448 to 475°C as the glass fiber content increases from 0 to 45 wt %. A similar increase is also found in the CCORP composites (entries 10–14 in Table I). Compared with the CORP resin and composites, the CCORP resin and composites exhibit a slightly higher value for T_{20}, T_{40}, and T_{max}, because of their dense structures. The incorporation of more glass fibers increases the composite residual weight. Not much difference in the temperature of maximum degradation (T_{max}), located at around 478°C, is observed for the composites with different glass fiber loadings. This phenomenon may be attributed to the weak interfacial interaction between the glass fiber and the polymer matrix as seen in the SEM images.

The TGA curves for the composites from CCOR with different DVB content are shown in Figure 9 and the TGA data for the composites from COR (entries 3 and 6–9) and CCOR (entries 11 and 15–18) are sum-

marized in Table I. Increases in the T_{20} values from 424 to 446°C and T_{40} values from 463 to 481°C are observed for the composites from CCOR with an increase in DVB content from 10 to 35 wt %. At the same time, the T_{max} increases from 476 to 490°C. A similar phenomenon is also observed in the composites from COR. Thus, increasing the DVB content can effectively increase the thermal stability of the resulting composites, due to the high crosslinking, which is in good agreement with the results from the extraction experiments.

Mechanical properties

The mechanical properties of the composites are summarized in Table I. The CORP (entry 1) and CCORP (entry 10) resins exhibit typical elastomer behavior. The ultimate tensile strength (σ_{max}) and Young's modulus (E) of the CORP composites (entries 2–5) increase with increasing glass fiber content. The E and σ_{max} of the CORP-45 composite increase by 213 and five times compared with the CORP resin. For the CCORP composites (entries 11–14), similar increases in the mechanical properties are also observed. The E and σ_{max} values for CCORP-45.0 are 227 and six times higher than those of the CCORP resin. The elongation at break (ε_b) of both the CORP and CCORP composites decreases with increasing glass fiber content. The CCORP composites exhibit higher E and σ_{max} values than the corresponding CORP composites.

Entries 3 and 6–9, and entries 12 and 15–18 in Table I show that the mechanical properties of the composites from COR and CCOR are greatly affected by the DVB concentration. When increasing the DVB content from 10 to 35 wt %, the σ_{max} of the resulting composites first increases and reaches its maximum at about 25–30 wt % DVB. Further increasing the DVB content results in a decreased σ_{max}
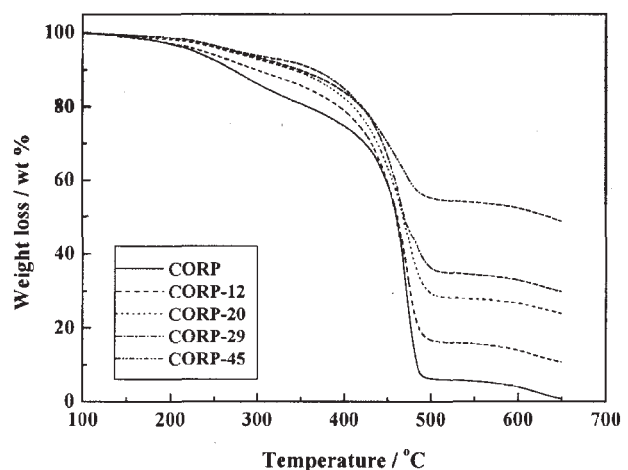

Figure 8 TGA curves for the CORP composites with variation in the glass fiber content.

TABLE I
Thermal and Mechanical Properties of the Thermosets and Their Resulting Composites

Entry	Composites	TGA			Mechanical properties		
		T_{20} (°C)	T_{40} (°C)	T_{max} (°C)	E (MPa)	σ_{max} (MPa)	ε_b (%)
1	CORP	357	448	472	4.1 ± 0.6	1.7 ± 0.2	76.2 ± 3.6
2	CORP-12	394	449	473	78.9 ± 27.8	2.1 ± 0.2	23.9 ± 4.8
3	CORP-20	411	455	471	188.1 ± 32.0	2.3 ± 0.5	16.2 ± 5.2
4	CORP-29	419	459	473	386.2 ± 75.8	3.2 ± 0.4	12.6 ± 1.1
5	CORP-45	421	475	472	873.6 ± 188.5	8.4 ± 0.7	8.4 ± 0.8
6	CORP(DVB15)-21	412	459	474	349.9 ± 36.0	4.1 ± 1.3	6.1 ± 1.6
7	CORP(DVB25)-20	415	464	481	703.2 ± 45.1	8.2 ± 1.6	4.2 ± 1.3
8	CORP(DVB30)-20	421	465	480	886.2 ± 60.5	11.4 ± 3.8	5.6 ± 3.7
9	CORP(DVB35)-21	426	468	479	911.9 ± 166.1	5.9 ± 1.0	3.4 ± 0.4
10	CCORP	386	454	478	4.7 ± 1.3	2.0 ± 0.1	64.3 ± 3.3
11	CCORP-12	422	462	480	139.3 ± 43.2	2.1 ± 0.4	13.9 ± 6.2
12	CCORP-20	424	463	476	205.9 ± 42.6	2.5 ± 0.5	12.8 ± 1.6
13	CCORP-29	427	469	477	413.2 ± 93.8	3.8 ± 0.3	9.1 ± 1.2
14	CCORP-45	430	481	476	933.2 ± 197.1	11.9 ± 1.6	6.6 ± 1.4
15	CCORP(DVB15)-20	433	471	483	491.9 ± 42.6	5.6 ± 1.4	6.3 ± 1.6
16	CCORP(DVB20)-21	438	473	487	740.9 ± 75.4	5.7 ± 0.9	6.6 ± 1.7
17	CCORP(DVB25)-21	442	478	490	1000.6 ± 52.3	8.3 ± 1.0	3.4 ± 0.3
18	CCORP(DVB35)-21	446	481	490	1254 ± 188.5	5.6 ± 0.8	2.2 ± 0.5

value for the composites from both COR and CCOR. This suggests that high crosslinking reduces the number of conformations that the polymer can adopt while being loaded. As a crack becomes a failure due to the force applied, the matrix can dissipate only a small amount of energy, leading to a low ultimate tensile strength. A similar phenomenon has been observed in the resins prepared by the cationic polymerization of fish oil, ST, and DVB.[26] When increasing the DVB content from 10 to 35 wt %, the Young's modulus increases from 188.1 to 911.9 MPa and from 205.9 to 1254.2 MPa for the composites from COR and CCOR, respectively, indicating the stiffness improvement of the composites due to higher crosslinking of the polymer matrix.

To assess the effectiveness of the fibers at contributing to the composite moduli, some models to predict the behavior of the elastic modulus of a fiber reinforced material have been examined, including parallel [upper bound, eq. (2)],[32,40] and series [lower bound, eq. (3)][40] as well as Cox-krenchel [eq. (4)] models:[41,42]

$$E_c = \phi_f E_f + (1 - \phi_f) E_m \qquad (2)$$

$$E_c = \frac{E_f E_m}{\phi_f E_m + (1 - \phi_f) E_f} \qquad (3)$$

$$E_c = (1 - \phi_f) E_m + \xi \phi_f E_f \qquad (4)$$

where E represents the elastic modulus, ϕ the volume fraction, and ξ the fiber efficiency factor for the composite modulus considering the effects of fiber length and orientation. The subscripts c, f, and m indicate composite, fiber, and matrix, respectively.

An E_f value of 73 GPa was taken for the glass fiber.[30] Uniform strain and uniform stress are assumed for the parallel and series models, respectively.

Figure 10 shows the experimental Young's moduli and those predicted by the three models mentioned earlier. The experimental data lay between the predictive values from the parallel and series models. This is expected, because the assumptions of either uniform stress or uniform strain used in the composites are clearly an oversimplification.[40] However, it is found that eq. (4) fits well with the experiment values. From the curve fitting shown in Figure 10, the fiber efficiency factors, ξ, have been calculated to be approximately 0.038 and 0.042 for the CORP and CCORP composites, respectively. The ξ values in this system are relatively low compared with other natural fiber rein-
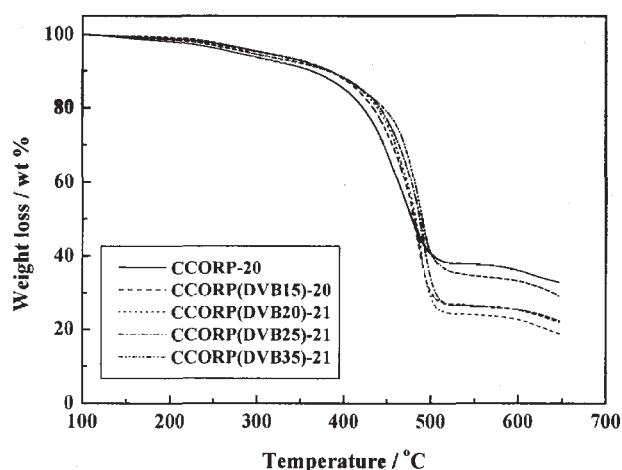
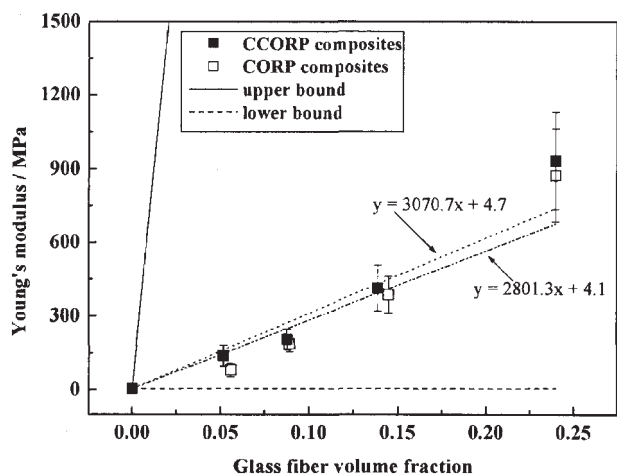**Figure 9** TGA curves for the composites from CCOR with variation in the DVB content.

Figure 10 Modeling the Young's moduli of the composites as a function of glass fiber volume fraction.

forced plant oil-based resins.[32] This can be explained by the extreme disparity in stiffness between the matrix and the glass fibers, and by the imperfect interfacial adhesion between the fiber surface and the matrix, which results in ineffective load transfer from the matrix to the fibers, leading to a reduction in the reinforcement efficiency of the glass fibers.

CONCLUSIONS

Novel composite materials have been prepared from corn oil-based polymer resins initiated by BFE using glass fibers for reinforcement. The resulting composites exhibit a significant increase in thermal stability and mechanical properties when compared with the pure polymers. With increasing the glass fiber loading from 0 to 45 wt %, the modulus and tensile strength of the CCOR-based composites increase from 4.7 to 933 MPa and from 2.0 to 12 MPa, respectively. The Young's moduli of the composites based on COR and CCOR are consistent with the theoretical values. Increasing the DVB content results in the increased crosslink density of the polymer matrix, leading to dramatic improvement in thermal stability and mechanical properties of the resulting composites. It is worth noting that these composites show good damping properties and potential applications where both reduction of unwanted noise and the prevention of fatigue failure are important.

Work is currently underway on improving the interfacial adhesion between the fibers and the matrix by treating the fiber surface and/or incorporating a coupling agent.

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