Fabrication and Mechanical Characterization of Glass Fiber Reinforced UV-Cured Composites from Epoxidized Vegetable Oils

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ABSTRACT: Novel fiberglass-reinforced composites were fabricated by the ultraviolet and visible (solar) irradiation of epoxidized vegetable oils in the presence of onium salt cationic photoinitiators. A variety of layup techniques and experimental conditions were explored to optimize composite fabrication. It was demonstrated that composites prepared by wet layup techniques containing up to five plies of glass cloth could be cured by a direct, 25-min exposure to solar irradiation. A series of composite samples were prepared using mixtures of epoxidized vegetable oils and synthetic epoxy resins, and their mechanical properties were evaluated. Based on these measurements, it may be concluded that photochemical routes to the fabrication of composites derived from epoxidized vegetable oils provide a simple, direct, and inexpensive route to the fabrication of composites with many potential low-performance applications. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2073–2087, 1997

Key words: composites; photocuring; epoxidized vegetable oils; solar curing

INTRODUCTION

The high strength- and stiffness-to-weight ratios of organic matrix composite materials are the chief advantages of these materials over metals in structural applications. These types of composites and methods for their fabrication have been the subject of considerable materials research within the past three decades. However, the majority of this research has been directed toward the fabrication of high-performance composites with exceptional mechanical properties and thermal resistance for the aerospace and sporting goods industries. By contrast, there has been little emphasis on the development of organic matrix composite materials for applications in the consumer sector or simple applications such as housing, boats, water storage and distribution systems, and sewage systems. Further, most composite fabrication techniques involve complex layup procedures, long processing times at high temperatures, and complex curing equipment. There is a general need for novel fabrication technology which would permit the construction of serviceable composites for low-performance applications from inexpensive starting materials by relatively unskilled workers.

An effort has been underway in our laboratories to identify and use materials derived from renewable resources to synthesize polymers using
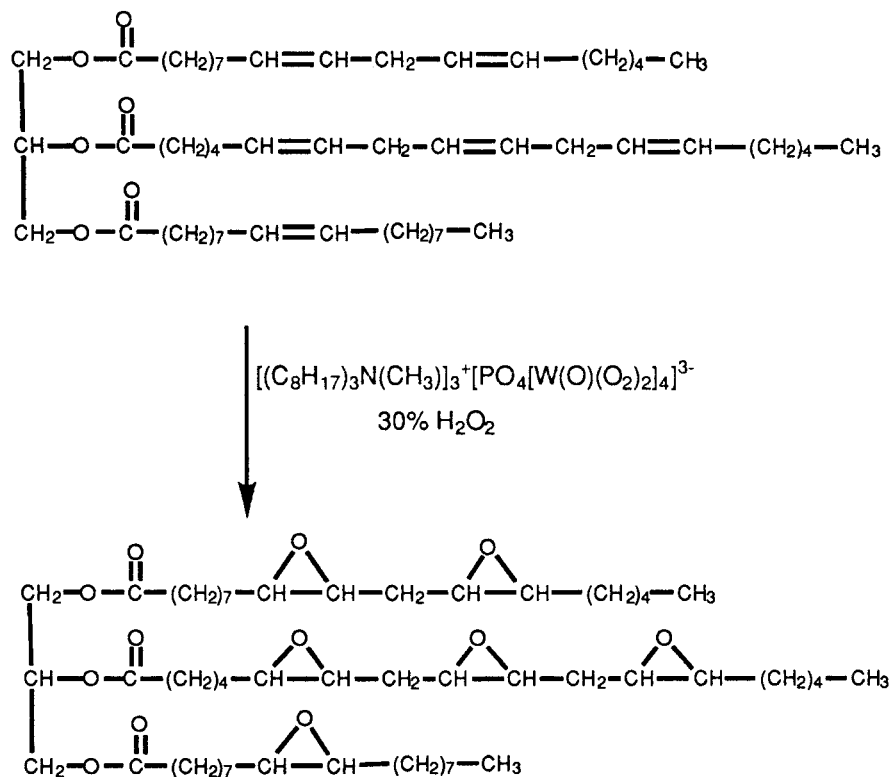
Epoxidized Soybean Oil

Scheme 1

energy-efficient and pollution-free methods.[1-3] Previously, we have reported that it is possible to prepare photopolymerizable epoxide monomers from naturally available unsaturated triglycerides such as soybean and linseed oils, through efficient, solvent-free routes.[1] Scheme 1 shows a typical example of the epoxidation of soybean oil using 30% hydrogen peroxide and a tungsten-containing phase transfer catalyst. These epoxides were polymerized as depicted in Scheme 2 using onium salt cationic photoinitiators developed in this laboratory[4] to give crosslinked thin film coatings and films using ultraviolet (UV) or visible light. The resulting polymers have numerous potential applications in areas such as coatings, adhesives, and printing inks.

High-energy radiation in the form of electron-beam irradiation has been used to fabricate carbon fiber−epoxy laminates,[5] and wood composites have been made by crosslinking of vinyl mono-

mers using high-energy γ radiation from a ^{60}Co source.[6,7] UV light-induced free radical crosslinking polymerization has also been used in the preparation of fiberglass-reinforced unsaturated polyester composites,[8] and the same chemistry has been applied in the fabrication of glass ionomer-reinforced dental composites using multifunctional methacrylate monomers.[9] Although epoxides have found wide use as matrices in composites made by conventional thermal curing, the use of cationic UV curing in the fabrication of fiberglass−epoxy composites has not been extensively studied. A recent patent revealed the use of a free radical−cationic dual-cure two-stage process to make fiberglass composite preforms.[10] In two recent publications, Udagawa and coworkers[11,12] have reported the preparation of composites by the photopolymerization of traditional biscycloaliphatic epoxide resins. This article reports the results of studies involving the use of photopolymerizable epoxidized

Epoxidized Linseed Oil

$h\nu$

$Ar_3S^+ SbF_6^-$
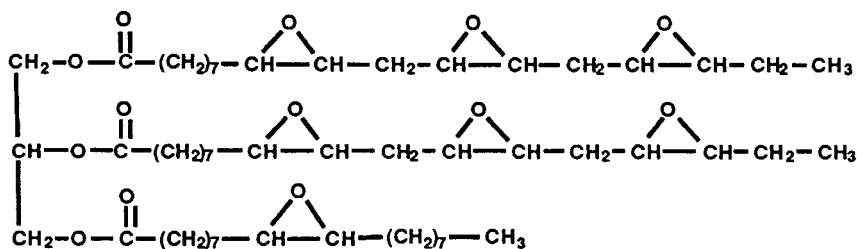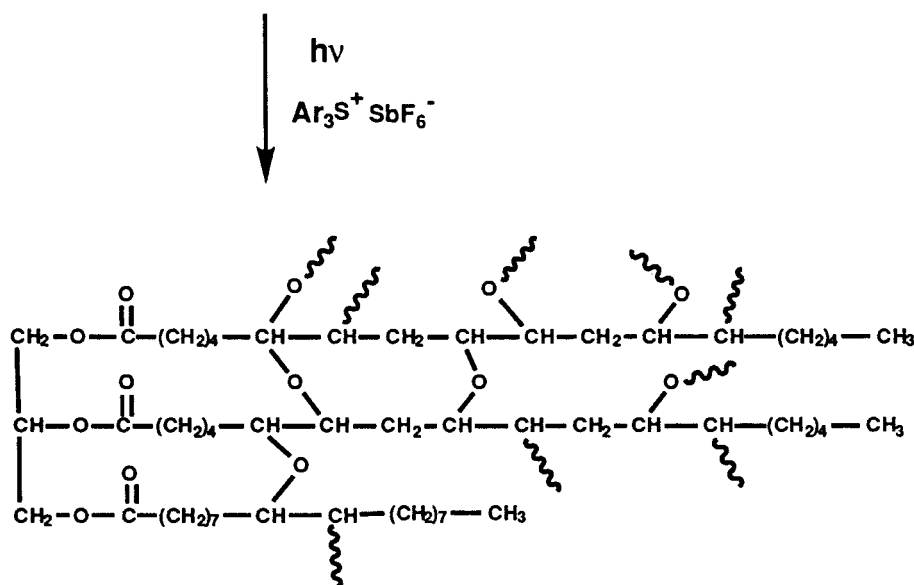
Crosslinked Network Polymer

Scheme 2

triglyceride oil monomers for the fabrication of glass fiber-reinforced composites and the characterization of their mechanical properties.

EXPERIMENTAL

Materials and Equipment

Woven fiberglass cloth (E-glass, 6 and 10 oz/sq. yard, style 120, even-weave, 550 finish) was obtained from Northern Fiberglass Sales Inc., Hampton, NH. Teflon-coated fiberglass used as the base release layer for the cured composite was obtained from the same source. Epoxidized linseed oil (ELO, 9.4% oxirane oxygen) and epoxidized soybean oil (ESO, 6.8% oxirane oxygen)

were purchased from Elf-Atochem (Bloomington, MN). 3,4-Epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate, ERL-4221 (ERL), was obtained from Union Carbide Co. (Danbury, CT) Photoinitiator GE1014 (General Electric Co., Waterford, NY) used in this work was a mixture of triarylsulfonium hexafluoroantimonate salts supplied as a 50% solution in propylene carbonate. (4-Thiophenoxyphenyl)diphenylsulfonium hexafluoroantimonate (SSb) was prepared according to a literature procedure.[4] Cyclohexanone, γ-butyrolactone, propylene carbonate, and acetone were purchased from the Aldrich Chemical Co. (Milwaukee, WI) Gel time measurements were performed on a Gel Pointe-2 instrument[13] (Gel Pointe Scientific Instruments Co., Bellbrook, OH) fitted with a temperature-programmable heater.

The radiation intensity received by the composite was measured using a Control Cure radiometer (UV Process Supply Co., Northbrook, IL) which was calibrated at a wavelength of 365 nm. Glass transition temperatures (T_gs) were determined using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a cooling accessory. The differential scanning calorimetry runs were performed under a nitrogen flow rate of 40 mL/min and at a heating rate of 10°C/min.

Removal of the Sizing Agent on Glass Fibers and Measurement of Gel Times of Photocured Monomers Used in Composite Fabrication

A 10-g sample of 6-oz-weight glass cloth was placed in a Soxhlet extractor and the sizing was extracted with 150 mL acetone for 24 h. The extract was concentrated to 2 mL using a rotary evaporator. This process was also repeated for 10-oz-weight fiberglass cloth. A solution containing 2 g of ELO, 0.06 g of SSb photoinitiator, and 0.0006 g of the extract was prepared. This solution was drawn into a 0.5-mm borosilicate capillary tube which was then sealed at one end and placed in the Gel-Pointe instrument. All gel time studies were performed at a constant temperature of 40°C. The capillary was exposed to a 100 W UV light using a fiberoptic cable. The intensity of the UV light received by the sample was 18 mW/cm². The time required for gelation was recorded using a chart recorder. This process was repeated with cyclohexanone, γ-butyrolactone, propylene carbonate, and acetone as the carriers for the photoinitiator.

Preparation of Matrix Resins

A typical preparation is given as follows. To a 1-L three-neck flask fitted with a mechanical stirrer was added 500 g of ELO (9.4% oxirane oxygen) and 30 g of GE1014 photoinitiator. This corresponded to a 3 wt % solution of the photoinitiator. The solution was vigorously stirred using a mechanical stirrer for 10 min and heated and maintained at 45°C using an oil bath until a clear solution was obtained. The mixture was degassed prior to composite layup by applying a mild vacuum. This process was repeated for blends of ELO and ERL and for blends of ESO and ERL.

Evaluation of the Depth of Cure

In preliminary experiments, 1.5 in. × 1.5 in. patches of 6-oz-weight fiberglass were cut and a five-layer laminate was laid up in a 0,90 fiber orientation using a 0.5-mil polyethylene film as the base release layer, in a manner described in the next section. The matrix resin consisted of a mixture of 60 (ELO) : 40 (ERL) wt/wt containing 3 wt % of GE-1014 photoinitiator. In order to measure the light intensity at the bottom of the composite, a radiometer was placed at a distance of 30 cm from an air-cooled GE H3T-7 200 W medium pressure Hg arc UV lamp. First, a patch of the above polyethylene film was placed over the sensor of the radiometer and the magnitude of radiation received was recorded over a 60-s period. Next, the polyethylene film was replaced with the film bearing the uncured composite. The composite was exposed to UV light and similar measurements of radiation intensity were performed over 1-min intervals for a total exposure time of 25 min. After that time, the composite was inspected to detect any uncured polymer in the bottom layer and then removed from the base polyethylene film. This process was repeated for 3-, 7-, and 9-layer laminates.

Fabrication of Photocured Composites

On a 3 ft × 1.5 ft steel or tempered glass plate was placed a Teflon-coated fiberglass cloth of dimensions 24 in. × 12 in. × 0.004 in. The cloth was taped to the base in such a way as to exclude most of the air trapped between the two surfaces, and then thoroughly washed with acetone to remove impurities. Next, a layer of the matrix resin was brushed onto the cloth and the first 10 in. × 10 in. layer of 6-oz-weight fiberglass cloth (±45 fiber orientation) was placed on the resin and allowed to wet out. More matrix resin was applied as required with a nylon brush to ensure complete wetting of the fibers. Excess resin and air bubbles were removed using a rubber squeegee. After allowing the sample to wet out completely (10 min), the entire process was repeated for the next layer. In the case of vacuum-bagged samples, the resin-impregnated layers of glass were covered with a polyethylene film, the film was taped down, and vacuum was applied for 1.5 h to remove air bubbles trapped within the wet composite layers.

The uncured mats were cured by exposure to sunlight between noon and 3:00 p.m. on clear, dry days in Troy, New York (located at 42° 40′ north latitude and 73° 31′ west longitude), between the months of June and August. Photocured composites were also fabricated by exposing the uncured

samples to UV light using a 200 W medium pressure Hg arc lamp placed at a distance of 30 cm from the samples. The radiation received was recorded using the radiometer described above. Depending on the light intensity, the exposure time was varied in such a way that the total incident radiation received was held constant at 12 J/cm^2 for all the samples, whether cured by UV light or solar irradiation. Exposure of the 5-layer composites on the top surface was sufficient to induce photopolymerization throughout the thickness of the composite. For 10-layer composites, the photocuring was carried out in two steps. First, the top layers were irradiated for a period corresponding to a total dose of 6 J/cm^2. Next, the partially cured samples were removed from the base and then the reverse side was irradiated again for a total dose of 6 J/cm^2. The cured composite was removed from the base release layer, and samples 6 in. $\times$ 0.5 in. $\times$ 0.042 in. were cut and their mechanical properties evaluated using the tests described in subsequent sections.

A separate experiment was designed to study the effect on the mechanical properties of UV-cured composites after removing the sizing on the glass fibers. The glass cloth was immersed in either 450 mL of acetone or concentrated sulfuric acid solution for 24 h. The acetone from the immersed fibers was decanted and the cloth rewashed with fresh acetone to remove any sizing extracts on the surface of the fibers. After drying in air at room temperature, the fiberglass cloth was placed in a vacuum oven at a pressure of 0.1 mmHg at 45°C for 18 h. The acid-treated glass cloth was washed with copious amounts of deionized water until the pH of the wash water was neutral. These latter fiberglass samples were dried in the same way as the acetone-treated samples. Ten-layer composites using 60 : 40 wt/wt ERL : ELO were fabricated using UV irradiation as described above. The composites were then subjected to mechanical testing as described below.

Mechanical Tests on Photocured Composites

Measurement of Tensile Properties

Tensile tests on photocured composites were performed on an Instron-4204 tensile testing machine, according to the guidelines set forth in ASTM test D3039-76. The Instron instrument was interfaced with a data acquisition card and a computer and the data obtained were plotted as stress−strain curves. Elastic moduli data were collected at room temperature (20°C) and at low stress values of 1200 to 2400 psi (8.2−15.5 MPa). An extensometer with a gauge length of 0.5 in. (0.0127 m) was used to measure the true strain. The crosshead speed in all experiments was 0.2 in./min.

Measurement of Viscoelastic Properties

Viscoelastic data of the photocured composites were obtained using a Dynastat Mechanical Spectrometer.[14] The composite samples (2.25 in. $\times$ 0.500 in. $\times$ 0.082 in.) were tested in a three-point bending mode with free sample ends. The samples were prestressed to 10 MPa (1,450 psi) and the thermomechanical data obtained in a frequency range of 1−25 Hz and at temperatures of 30−150°C. At each temperature, the sample was equilibrated for 5 min to ensure that the moduli data collected at that temperature were under isothermal conditions. The composite samples for these tests consisted of 10-layer laminates using 6-oz-weight woven glass fibers in a 0,90 fiber orientation. Various blends of ELO and ERL were used as the matrix resin and the composites were photocured as described above using a UV lamp.

Measurement of Fiber and Resin Weight and Volume Fractions in the Photocured Composites

The fiber-to-resin ratio for the composites was determined by placing a preweighed sample of the composite in an open crucible and heating it on a Meeker burner until all the organic combustible matter had burned off and only the carbon-free glass fibers remained. Typically, this process took about 1 h. To ensure that complete removal of the organic material had occurred, one of the samples which had been heated for 1 h was reheated for an additional hour. No further weight loss was observed. Hence, all other samples were heated for only 1 h. The weight fractions were calculated from this resin-burnoff test. The volume fractions were determined according to the formula $V_f = [1 + W_r r_f / W_f r_r]^{-1}$, where V, W, and r are the volume fraction, weight fraction, and density of the resin (subscript r) and fiber (subscript f), respectively. The resin densities were obtained by first photocuring neat samples of appropriate monomers and then measuring their densities according to the guidelines of ASTM test method D792-91. In

the evaluation of the volume fractions, the density of E-glass was taken to be 2.56 g/cm^3.[15]

RESULTS AND DISCUSSION

In our previous study of the cationic photopolymerization of epoxidized vegetable oils we observed that the rate of polymerization and cross-link density were dependent on the number of epoxy groups present in the monomer. Those oils with low epoxy contents give low T_g and flexible films and castings, whereas correspondingly high epoxy content oils give higher T_g, rigid polymers. Fully epoxidized linseed oil (Scheme 2) possesses the greatest number of epoxy groups per molecule of any of the common epoxidized vegetable oils. Hence, this oil would appear to be the most suitable for use as a composite matrix intended for structural applications. At the same time, epoxidized soybean oil (Scheme 1) has on average 6 epoxy groups per molecule and would be expected to give more flexible, damage-tolerant composites. Both ESOs and ELOs are commercially available in large quantities and are relatively inexpensive. Accordingly, these two materials were selected as the main monomers for use in this study.

To assess the viability of the fabrication and cure of composites from epoxidized vegetable oils by photochemical techniques, it was necessary first to seek answers to several fundamental questions. We wished to know the effect of the glass type, weight, and sizing on the photopolymerization reaction; the irradiation conditions necessary to conduct the photopolymerization; the thickness of the composite which could be attained; and the best method of fabrication. Hence, the following studies were undertaken preparatory to the layup of composites for the detailed measurements of their mechanical properties.

Effect of the Sizing Agent on the Fiberglass on Photopolymerization Reaction

For photopolymerization to proceed throughout the depth of the sample, the reinforcement material must be reasonably transparent to the radiation incident upon it. This was found to be the case with the fiberglass cloth used in this work. In fact, it was observed that glass fiber-reinforced composites could be cured to greater thicknesses more rapidly than the pure resin. This effect may result from a greater penetration of light in the

Table I Effect of Solvents and Fiber Sizing Agent on the Gel Time of ELO

Sample Type[a]	Gel Time (s)
Control	7
3 wt % acetone	10
3 wt % cyclohexanone	10
3 wt % propylene carbonate	15
3 wt % γ-butyrolactone	25
0.3 wt % sizing extract (6 oz cloth)[b]	20
0.3 wt % sizing extract (10 oz cloth)[b]	32

[a] Each sample was composed of ELO with 3 wt % (SSb) as the photoinitiator.
[b] Refers to the type of glass cloth from which the sizing was extracted.

composite due to both light-scattering and wave-guiding effects from the glass fibers.

During the manufacture of fiberglass articles, the fibers spun from the melt are coated with sizing agents in order to improve ease of handling, to bind fibers together during twisting and weaving operations, and to minimize reduction in strength of the fibers due to abrasion.[15] The sizing materials may include, among others, materials such as starch, oils, gelatin, and fatty amines, as well as various combinations of the above. Since cationic photopolymerizations (Scheme 2) are inhibited by the presence of amines and other basic materials, it was necessary to determine the effect of sizing agents on the photopolymerization reaction. In addition, some solvents used as carriers for the photoinitiator can also retard the photopolymerization. The possible retardation effects of these agents were investigated using a Gel-Pointe instrument.[13] This technique consists of filling a capillary tube with a photopolymerizable liquid sample and then oscillating the meniscus of the liquid across an infrared photocell detector using a pump. Initially, since the photocurable sample is uncured, a large oscillation corresponding to the motion of the relatively fluid sample is recorded. As the sample polymerizes upon UV irradiation, its viscosity increases and hence the amplitude of oscillation decreases. At the gelation point, the motion ceases altogether; this time is recorded as the gel time. Measurements of the gel time are reproducible to within ±5% and can be employed to monitor the effects of polymerization accelerators or retarders in a given system. The gel times for the photopolymerization of ELO in the presence of extracts containing the fiberglass

sizing agent and various solvents were measured and compared to a control sample which consisted only of ELO; times are given in Table I. At least five individual gel-point measurements were made for each set of data reported. The data in Table I shows that there is a retarding effect on the gel time due both to the sizing agent and to the four added solvents; however, the retardation is not strong enough to completely inhibit the photopolymerization. It should be noted that since the sizing agent is located only on the surface of the glass fibers, retardation effects should mainly be located there and the overall effect on the polymerization of the resin should be considerably less than observed in the gel-time measurements. On the basis of these observations, it was decided not to attempt to remove the sizing agent from the fiberglass cloth prior to its use in the fabrication of the composites.

Depth of Cure in Photocured Composites

Since composites gain their mechanical properties from multiple layers of resin and reinforcing agents, it is important to determine the maximum thickness of a composite that can be cured under a specific set of irradiation conditions. The depth of cure in any photocurable system is dependent on a complex set of variables, including the light intensity, its wavelength, and the length of irradiation duration. In addition, the response of a given system is also dependent on the photosensitivity of the photoinitiator, the UV absorption characteristics and reactivity of the monomer or monomers, and lastly, the configuration of the sample.

In preliminary experiments, it was discovered that a 25-min exposure to direct radiation from ambient sunlight in the summer months was sufficient to cure through 5 plys of fiberglass−epoxy composites with a total thickness of approximately 0.8 mm. This corresponds to a total dose of 7.5 J/cm^2 and this dose was taken as an arbitrary practical standard irradiation time and light intensity (flux) with which to assess the limitations of thickness for photocurable composites in this investigation.

Accordingly, a set of four composite samples of varying thicknesses were made and the UV radiation received at the bottom ply was measured. Figure 1 shows that the radiation received by the bottom layer decreases exponentially with the thickness of the sample. After a total radiation
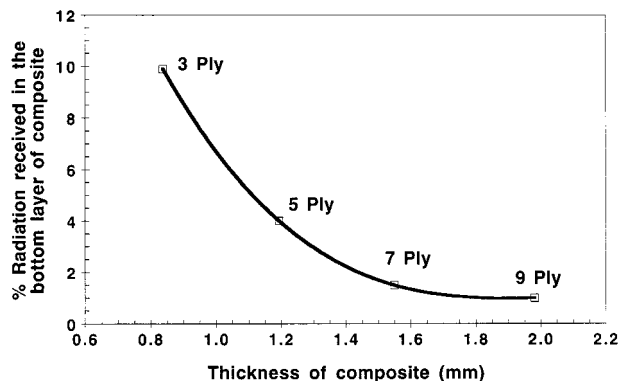

Figure 1 Depth of cure versus incident radiation intensity in a UV-cured fiberglass/ELO composite.

time of 25 min, for a total radiation dose of 7.5 J/cm^2, samples of thickness up to 1−1.6 mm (5−7 layers) could be cured. Under the same conditions, however, the bottom layer of a 9-ply laminate (2 mm thick) was not cured. Thus, for samples with thickness greater than 1.6 mm, it is necessary to irradiate the reverse side of the composite for an additional 20 min in order to ensure cure within the entire sample. In this way, composites up to 2−2.5 mm thick were fabricated using a single 200 W medium pressure Hg arc lamp. Alternatively, it was observed that exposure to solar irradiation at the same intensity gave similar results.

Survey of Composite Fabrication Techniques and Evaluation of Tensile Properties of Photocured Composites

Composites can be fabricated by a wide variety of techniques, including hand layup, spray layup, vacuum bagging, pultrusion, and resin transfer molding.[16] The simplest fabrication technique, the hand layup method, was chosen for our initial experiments. Five-layer composites were laminated in a ±45 fiber orientation using 6 oz woven fiberglass cloth with ELO as the matrix resin. The composites were then exposed for 25 min to direct solar irradiation. It should be noted that when solar irradiation is employed for curing composites, some inherent variability is to be expected. The irradiations were carried out under conditions described in detail in the Experimental section. Table II depicts the tensile test data for 6 sets of these composites made at different times on the same day. With the exception of set 5, the tensile moduli and tensile strength are in the

Table II   Comparison of the Tensile Data for Various Sets of Solar Cured Composites

Set No.	Number of Samples per Set	Tensile Modulus (ksi)[b]	Standard Deviation of Modulus (ksi)	Peak Stress (ksi)	Peak Strain (%)	Resin (wt %)
1	5	352	49.0	5.40	6.91	39
2	5	483	56.0	6.90	6.05	38
3	4	433	56.0	6.30	6.84	36
4	4	685	64.0	11.1	7.12	38
5	4	470	32.0	7.60	7.70	38
6	3	473	20.0	6.90	6.41	37
7[a]	4	411	32.0	3.45	2.55	25
8[a]	4	465	35.5	4.03	2.03	24
9[a]	4	449	19.4	4.08	2.82	25

Five-layer ELO composites fabricated in the ±45 fiber orientation using 6-oz-weight woven cloth.
[a] 10-oz cloth.

range 350–483 ksi (2.4–3.3 GPa) and 5.5–7.2 ksi (38–52 MPa), respectively. The reason for the high values of strength and modulus for set 5 is not known. The values given in Table II are comparatively lower than those obtained for bisphenol-A diglycidyl ether (DGEBA) fiberglass–epoxy composites (e.g., tensile strength 25 ksi, 172 MPa, fiber orientation not specified) prepared by conventional thermal curing methods.[17] DGEBA-based monomers are not ideally suited for use in UV curing of composites because the cationic photopolymerization of these monomers is slow due to the competitive absorption of available UV light by the aromatic groups present in the resin and due to the sluggishness with which glycidyl ethers undergo cationic polymerization. On the other

hand, the modest values of tensile modulus for ELO-based photocured composites is due to the inherent structure of these polymers. The segments between crosslinks in the polyether network which is obtained after photopolymerization are long and very flexible, resulting in a comparatively low crosslink density polymer network.

Figure 2 gives typical stress–strain curves for the above ELO-based composites. The curves show that the matrix undergoes considerable extension after reaching the point of maximum stress. While this is indicative of a rather ductile matrix, this ductility is at the cost of reduced tensile strength and modulus. Table II and Figure 3 also show that there is a standard deviation of about 10–15% in the values of tensile modulus in a given set of data. This can be attributed to the
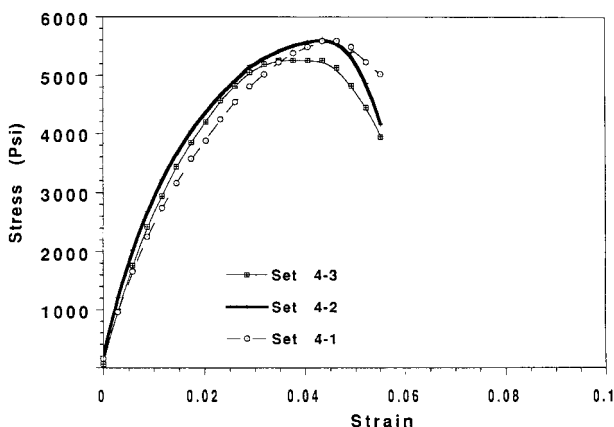

Figure 2   Variation in the modulus and strength for three samples from the same UV-cured fiberglass/ELO composite.
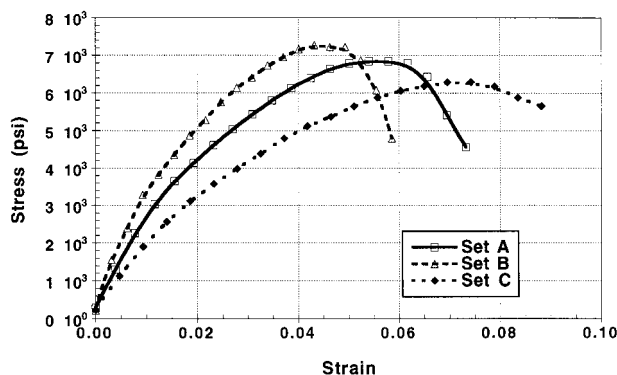

Figure 3   Variation in the modulus and strength for three samples from the different UV-cured fiberglass/ELO composites.

Table III   Tensile Data for 10-oz, Five-Layer Vacuum Bagged ELO Photocured Composites in (±45) Fiber Orientation

Set No.	Sample No.	Cross-Head Speed (in./min)	Modulus (psi)	Peak Stress (psi)	Peak Strain	Resin (wt %)
10-12	1	0.2	451000	3600	0.0257	25
10-12	2	0.2	421000	3500	0.0268	—
10-12	3	0.2	388000	3300	0.0251	24
10-12	4	0.2	382000	3400	0.0247	—
10-13	1	0.2	489000	4000	0.0194	24
10-13	2	0.2	464000	4100	0.0197	—
10-13	3	0.2	492000	4000	0.0201	23
10-13	4	0.2	416000	4000	0.0221	—
10-14	1	0.2	440000	4200	0.0263	25
10-14	2	0.2	431000	3900	0.0271	—
10-14	3	0.2	449000	4000	0.0291	24
10-14	4	0.2	476000	4200	0.0306	—

variations in resin and fiber weight ratios, inhomogeneities in the distribution of resin within the composite, slight differences in the extent of curing of the monomers in the different sets of composites, and experimental error in the conduct of the tensile tests. In addition, the photocuring was conducted outdoors and, although the relative humidities were low on all days that curing was conducted, the values of relative humidities were not identical. All these factors may contribute to the observed scatter in the tensile properties of the solar-cured composites.

The technique of vacuum-bagging generally results in improvements in the mechanical properties of composites due to the reduction of voids and better consolidation and uniformity in the prepegs.[18] In order to determine if there was a beneficial effect in this additional step, three sets of five-layer composites were prepared and photocured by solar irradiation after vacuum-bagging

the wet composite. It was observed that when the vacuum-bagging technique was applied, the cured laminates were clearly inhomogeneous, having considerable resin loss in the bottom portions of the composites. This is due to the low viscosity (6.6 s) of the ELO monomer. The depletion of the monomer in these samples is further evidenced by the lower resin weight ratio of 25% for the vacuum-bagged laminates as against 37% for the five layer composite samples prepared without vacuum-bagging. Table III shows the mechanical properties for vacuum-bagged composite specimens. While the tensile moduli of the vacuum-bagged composites compare well with the hand-laid-up samples, their tensile strengths are typically lower. Since the function of the matrix is to act as a load transfer medium, the nonuniform distribution of the resin may be the reason for lower values of strength in these composites. Comparable values for the tensile moduli in the

Table IV   Comparison of the Tensile Properties of Sunlight-Cured Composites Fabricated Using Blended Epoxide Matrices

Weight Ratios of Blended Epoxide Monomers	Number of Samples per Set	Modulus (ksi)	Peak Stress (ksi)	Peak Strain (%)	Resin (wt %)	Epoxy (average equivalent weight)
ELO (100) : ERL (0)	4	471	7.63	7.70	38	154
ELO (60) : ERL (40)	4	824	10.0	7.13	42	143
ELO (0): ERL (100)	4	1,784	21.5	5.83	43	126
ESO (60): ERL (40)	4	604	8.85	6.65	39	190
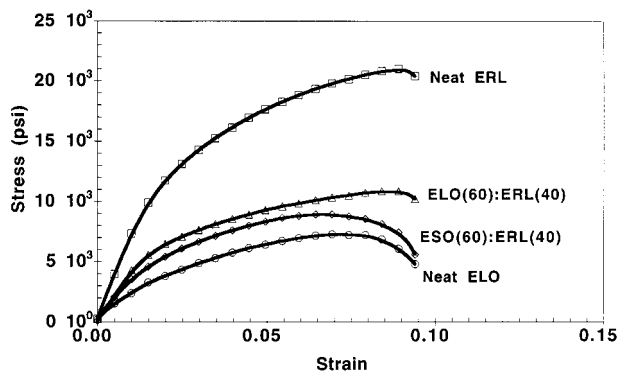
Figure 4 Effect of epoxy resin composition on the mechanical properties of photocured fiberglass composites.

Figure 5 Influence of the length of the room temperature postcure on the mechanical properties of photocured fiberglass/ELO composites.

two types of composites may also be due to the low values of stress at which the moduli were measured. Since no substantial advantage was realized by vacuum-bagging, all the subsequent composites were fabricated by the hand-layup technique.

With the aim of improving upon the modest values for the tensile modulus and strength of photocured composites obtained from neat ELO monomers, a series of five-layer solar-cured composites were made using blends of ELO and ESO with the commercially available biscycloaliphatic epoxide ERL, and their tensile properties were evaluated. The results of the tensile properties measurements are displayed in Table IV and Figure 4. On photocuring, the ERL composite has the highest stiffness with a modulus of 1.8 million psi (12.3 GPa) while the ELO composite has the lowest modulus (0.47 million psi, 3.2 GPa). The modulus and the strength of the composites increase as the weight fraction of ERL increases in blends with both ELO and ESO. This may be attributed to the expected greater stiffness of the matrix obtained from the relatively rigid ERL resin as compared with the comparatively low modulus expected for the matrix from the highly flexible, aliphatic ELO and ESO monomers. Measurement of the resin content of the above composites gave values of from 39 to 42% resin.

Postcure and Moisture Effects in Photocured Composites

Cationic photopolymerizations are known to proceed even after the light source has been removed. This is manifested in these systems as a postcure effect.[19] To determine the effect of the postcure
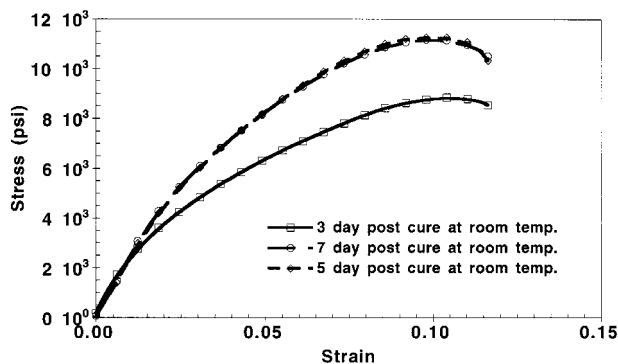
reaction on the tensile properties of sunlight-cured composites, a 10-layer laminate using only ELO and a 5-layer laminate using a 60 : 40 w/w blend of ELO and ERL were laid up in the ±45 fiber orientation. The tensile moduli of these composites were tested after various periods of postcure at room temperature. Figure 5 shows the results of these tests. The modulus of the 10-ply ELO sample increased from 408 ksi (2.8 GPa) to 535 ksi (3.7 GPa) from 3 to 5 days of postcure, and then remained constant thereafter. However, as shown in Figure 6, for a five-ply composite made from blended epoxies, the room-temperature postcure is essentially complete within 1 day. The average tensile modulus in this case was 820 ksi (5.7 GPa). It is clear from these experiments that the duration of the postcure depends on the thickness and the composition of the resin in the composite.

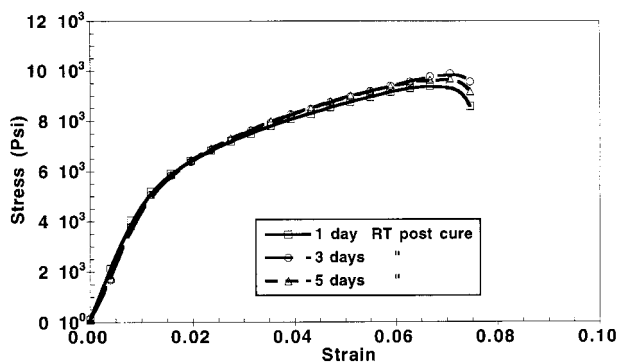The long postcure time at room temperature

Figure 6 Effect of the length of the room temperature postcure on the mechanical properties of photocured fiberglass/60% ELO/40% ERL composites.
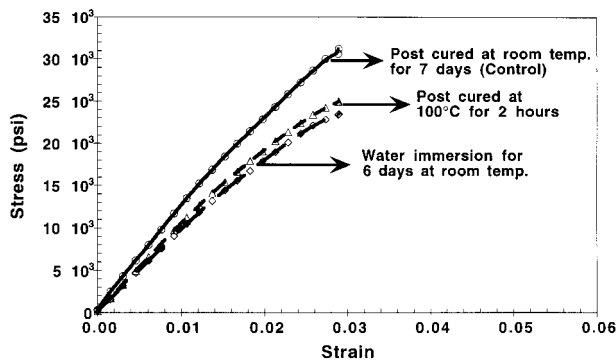
Figure 7 Influence of a thermal postcure on the tensile properties of a photocured fiberglass/ELO composite.

indicates the presence of unreacted epoxide groups in the initially obtained photocured composite. This is undesirable because the mechanical and thermal properties of the composite will continue to change over time as the cure continues. This problem can be overcome by accelerating the postcure by incorporating a thermal bake after the radiation curing step. To determine the effects of a thermal postcure on the tensile properties of the solar-cured composites, a 10-ply composite was made in the 0,90 fiber orientation using neat ELO monomer. Tensile specimens were prepared and divided into two sets: one set was postcured in an oven in air at 100°C for 2 h and the other set was allowed to postcure at room temperature for 7 days. The results of the tensile tests conducted on these samples are presented in Figure 7. When the laminates are subjected to a thermal bake, there is only a slight (10%) decrease in the modulus but a much greater decrease (33%) in the tensile strength of the composite. The decrease in the peak stress in this sample was 33%. It was also noted that the surface of the initially light-yellow composites became considerably darker after the thermal postcure. This indicates that an oxidative degradation of the matrix may have occurred as the temperature increased beyond the T_g (66°C) of the polymer. At 100°C, the polymer is in the rubbery region with increased diffusion of oxygen due to the higher segmental motion of the polymer chains. The oxidative degradation of the matrix causes an effective reduction in the crosslink density of the polymer and probably also reduces the extent of fiber–matrix adhesion; hence the tensile strength of these composites is reduced.

This decrease in strength of fiberglass–epoxy

and other composites exposed to heat and moisture has been well documented in the literature.[20] To study the effect of moisture on photocured composites prepared in this investigation, a 10-ply composite was laid up in the 0,90 fiber orientation using neat ELO and subjected to solar irradiation as described above. Tensile specimens were cut and first postcured at room temperature for 6 days and then immersed in water for an additional 6 days. Measurements showed that the tensile modulus and the strength decreased by 20 and 21%, respectively. Much greater reductions in tensile properties (>60%) have been reported in the literature for composites cured by conventional methods and then subjected to similar environmental effects.[21,22] For the samples that were immersed in water, the weight gain of the composites was monitored over a period of 144 h and the results plotted as Figure 8. Initially, the water uptake was quite rapid with the weight gain reaching a value of 0.3% after a 25-h immersion period. The moisture content reached an equilibrium value of 0.6%. This value is lower than that obtained for composites made from commercially available DGEBA epoxies which have equilibrium moisture contents of 0.8–1.0% at 25°C and is the result of the inherent hydrophobic nature of the epoxidized vegetable oils.

Fiber Orientation and Sizing Effects on the Mechanical Properties

As shown in Figure 9 there is a large difference in tensile modulus and strength of composites, depending on whether the fibers are placed in a
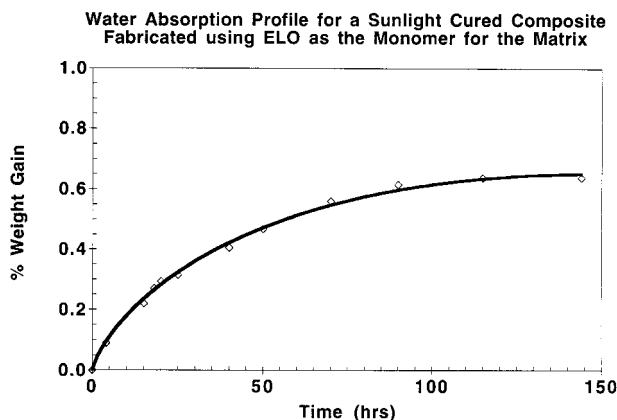

Figure 8 Profile of the water absorption with time of a photocured fiberglass/ELO composite.
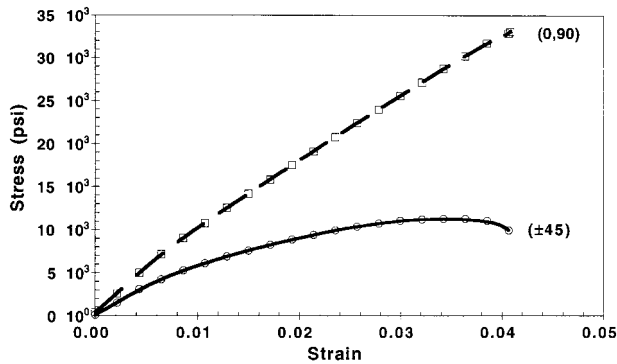
Figure 9   Effect of the fiber orientation on the tensile strength of a photocured fiberglass/ELO composite.

±45 or in a 0,90 orientation to the direction of applied stress. For example, 10-ply laminates laid up in the ±45 and 0,90 orientations were made using 6-oz.-weight cloth and postcured at room temperature for 7 days. These composites had an average modulus of 2,160 ksi (14.9 GPa) and strength of 32.9 ksi (227 MPa) for the 0,90 fiber orientation and a modulus of 543 ksi (3.70 GPa) and strength of 11 ksi (76.0 MPa) for the ±45 fiber orientation, respectively. The higher modulus obtained in the 0,90 fiber orientation was expected since in this orientation, the fibers are the major load-bearing components, whereas in the ±45 fiber orientation the tensile properties are more reflective of the shear behavior of the matrix.

The effect of removal of the fiber sizing on the modulus of UV-cured composites was investigated using dynamic mechanical analysis on 3-point bend specimens, and the results are shown in Figure 10(a,b) as the magnitude of dynamic modulus and loss factor (both at 1 Hz), respectively. In these composites a 60 : 40 w/w blend of ERL : ELO was used as the matrix. The initial moduli (at 30°C, which is below the matrix T_g) of the acetone, acid-treated, and untreated (control) composites were 11.7, 13.8, and 15.8 GPa, respectively. The lower initial moduli of the acetone and acid pretreatment composites suggest significantly lower fiber–matrix adhesion in the pretreated samples than in the untreated sample. The T_gs of all samples are virtually identical (118°C), which implies that the pretreatments had little or no effect on the curing process.

It should be noted that laminate type composites (i.e., with reinforcement in two directions only, as is the present case), when tested in 3-point bending, will exhibit pronounced dependence of bending stiffness on the effective in-plane shear modulus of the composite. Thus, even when a 0,90 glass reinforcement layup is used, the bending stiffness is very sensitive to matrix stiffness and fiber–matrix adhesion. The same sensitivity can be seen in graphite/epoxy laminates when tested through the T_g of the matrix.[23]

Evaluation of Viscoelastic Properties of Photocured Composites

The dynamic mechanical analysis (DMA) curves obtained for a 10-layer composite fabricated with neat ELO as the matrix are shown in Figure 11(a) magnitude of the dynamic modulus) and in Figure 11(b) (loss factor), both for three frequencies, namely 1, 10, and 25 Hz. The initial modulus for this composite is 12–13 GPa at room temperature and falls off quite rapidly as the polymer passes through the T_g at 68°C. The behavior of this
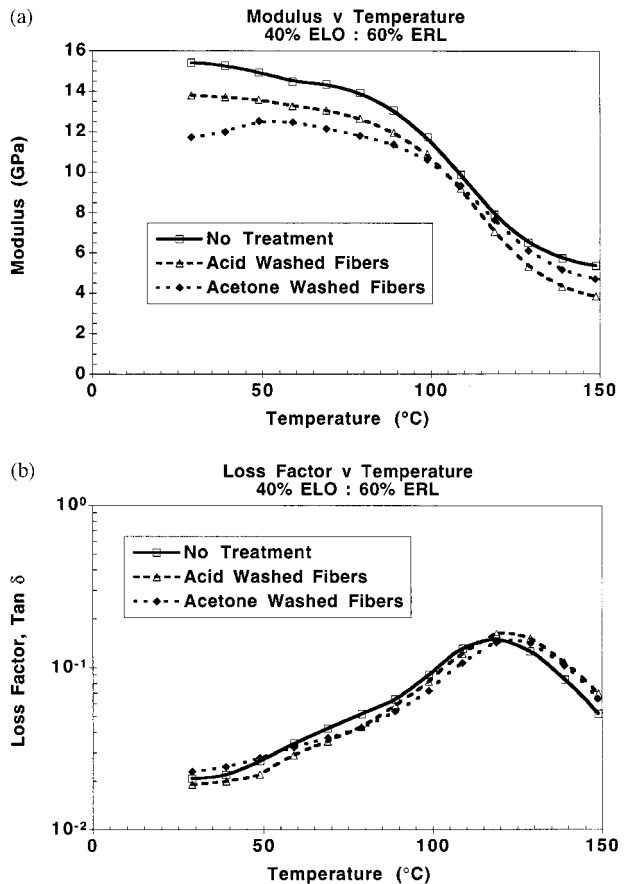

Figure 10   Study of the influence of fiber treatment on the dynamic mechanical properties of photocured fiberglass 60/40 ELO/ERL composites.
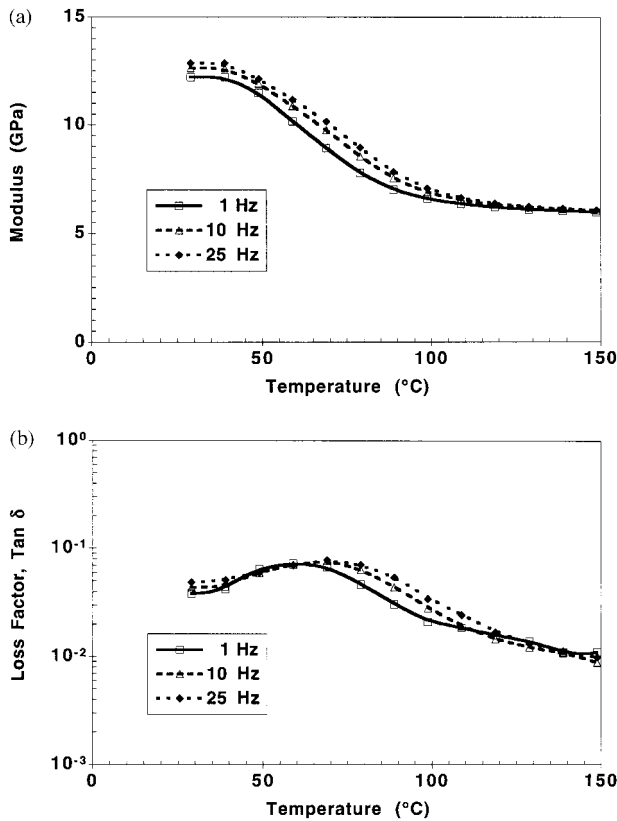
Figure 11 Study of the influence of frequency on the dynamic mechanical properties of photocured fiber-glass/ELO composites.

Figure 12 Dynamic mechanical analysis curves for photocured composites based on various ERL/ELO blends.

composite is typical of laminates tested in bending, as discussed above and elsewhere.[23] The dynamic modulus for the ELO composite remains fairly constant at 6 GPa, even at 40–50°C beyond the T_g. Above the T_g of the matrix, the bending modulus is representative of the glass fiber–soft matrix composite, which will always be higher than the shear modulus of the neat matrix. Thus, the softening of the matrix is responsible for the dramatic decrease of the bending modulus as the glass transition of the matrix is approached and exceeded [from 30 to 100°C in Fig. 11(a)], while the fiber reinforcement serves to limit the above-glass-transition bending modulus to a nearly constant value. Of course, the crosslinked character of the matrix also tends to limit the high temperature modulus falloff as well, but it is primarily the high volume fraction of fibers that tends to determine the high temperature behavior.

The DMA curves at 10 Hz for a series of composites fabricated using various blends of ERL and ELO as the matrices are depicted in Figures
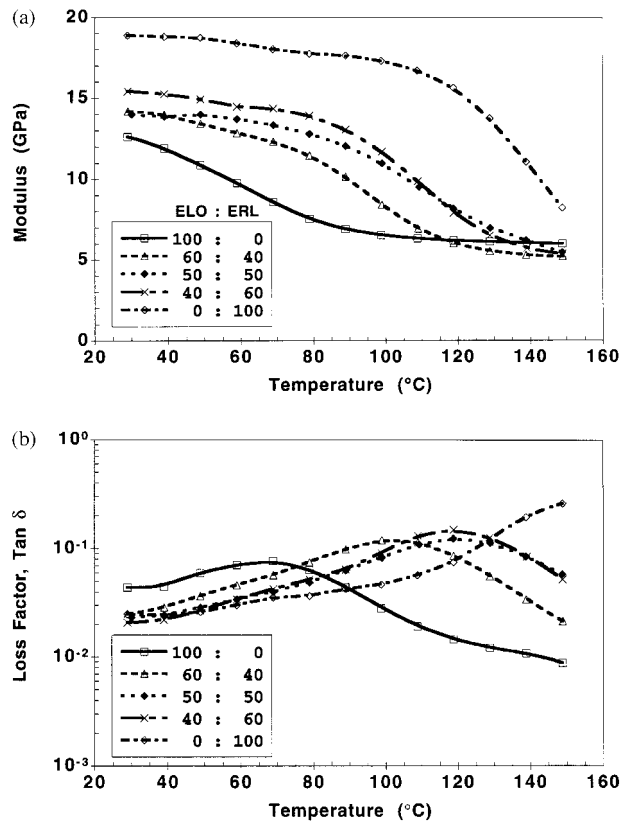
12(a) (magnitude of dynamic modulus) and Figure 12(b) (loss factor). These curves exhibit some striking features. All the polymer matrices show a single broad glass transition, suggesting that

Table V Variation in Complex Modulus and T_g as a Function of Monomer Weight Fractions in UV Cured Fiberglass–Epoxy Composites

ELO (Weight Fraction)	T_g (Calcd)[a] (°C)	T_g (Found)[b] (°C)	Modulus (GPa)[c]
1.0	68	68	12.8
0.6	96	100	13.8
0.5	104	115	14.1
0.4	114	118	15.5
0.0[d]	165	165	18.8

Ten-layer laminates made in (0.90) fiber orientation.
[a] Calculated using the Pochan equation.
[b] Obtained as the peak value of tan δ in the DMA curves.
[c] Initial magnitude of complex modulus (E^*) at 30°C.
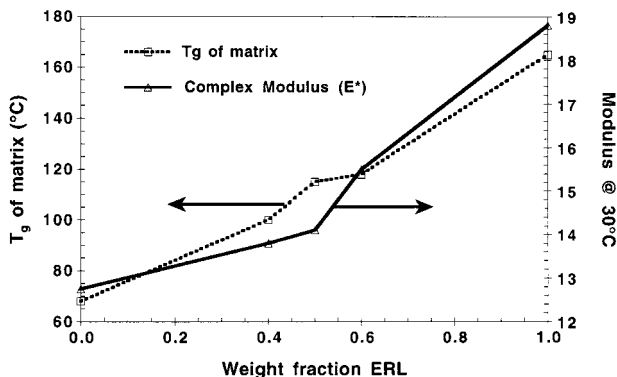[d] Weight fraction ERL = 1.0.

Figure 13 Variation in the initial modulus and T_g as a function of the composition of the matrix resin for UV-cured composites.

the ERL and ELO are molecularly mixed and that they form copolymers. Both the initial modulus (at 30°C) and the T_g increase as a function of the weight fraction of ERL and ELO, as shown in Table V and plotted as Figure 13. Bearing in mind that all samples have about the same volume fraction, layup, and type of reinforcement, the effect of matrix stiffness on the effective bending stiffness of a laminate is particularly well illustrated by Figure 12(a).

$$\ln T_g = M_1 \ln T_{g1} + M_2 \ln T_{g2}. \qquad (1)$$

The T_g value correlates well with the Pochan equation [eq. (1)], which describes the changes in T_g for thermodynamically miscible blends as a function of the weight fraction of the blend components.[24] In this equation T_g, T_{g1}, and M_i are the glass transition temperatures of the blend, the pure components, and the weight fractions of the components, respectively. The initial moduli values measured at 30°C vary from 12.5 GPa to 19 GPa for pure ELO and ERL, with intermediate values for the blends. This trend parallels the tensile modulus data presented in the previous section for ELO, ERL, and their blends. The increase in the modulus is indicative of the higher crosslink density of the ERL matrix and consequently its superior stiffness. Conversely, the flexible ELO polymer chains act as a plasticizer or a softening agent when it is copolymerized with ERL. Since the DMA experiments were conducted only up to 150°C, literature T_g values were used for cationic UV-cured polymers of pure ERL monomer in the calculation involving eq. 3.[12] One reason for the broad loss factor curves for all these polymers may

be the presence of a wide distribution of molecular weight segments between crosslinks. This could be the result of the difference in the reactivity of the two monomers ERL and ELO, which leads to each monomer undergoing a different extent of photoinduced copolymerization.[24] In addition, since all the T_g values are well above the temperatures at which the photopolymerization was conducted (22°C), it is likely that those composite samples which were postcured at room temperature possessed unreacted epoxide groups which underwent further polymerization as the temperature was increased during the DMA measurements.

CONCLUSIONS

Composite matrix resins can be produced from naturally derived epoxidized vegetable oils such as ESO or ELO crosslinked with either visible or UV light and offer an inexpensive, rapid, and low-energy means to fabricate custom shape composites on-site and without complex processing machinery. The composites have sufficient mechanical properties to be used in a wide variety of low-performance applications, such as low pressure piping, roofing, culverts, boats, and casts for medical use, to name a few. In addition, the resins are nontoxic, have near infinite shelf life when kept in the dark, and do not need refrigeration.

The novel chemistry used in the fabrication of these composites consists of irradiating mixtures of epoxidized vegetable oils and synthetic epoxy resins with UV or visible light in the presence of an onium salt photoinitiator. On irradiation, the photoinitiator decomposes releasing species which rapidly and efficiently catalyze the crosslinking polymerization of the resin mixture. Once initiated, a typical cationic addition polymerization takes place which proceeds to completion in the dark at room temperature.

Fabrication of cured composite components up to 2 mm in thickness consists of standard wet-layup techniques after which the laminates are exposed to UV light or sunlight. Tests to determine the performance of the glass fiber-reinforced composites showed that the cured composite matrices produced from ELO are quite tough but have a fairly low T_g. Accordingly, synthetic epoxy/epoxidized vegetable oil blends were prepared which give both higher glass transitions and stiffer matrices. The low water absorption charac-

teristics of these composites make them attractive candidates for use in electronic and other applications. Further, the prospect of using an economical system of composite fabrication for common objects employing sunlight and naturally derived matrix materials has many potential applications, especially in developing countries.

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