Thermal Degradation Analysis of Thermoset Resins

Amit Chatterjee

Center for Composite Materials, University of Delaware, Newark, Delaware 19716

ABSTRACT: Dynamic mechanical analysis, thermogravimetric analysis, and dielectric analysis (DEA) were conducted for three thermoset resin systems: bismaleimide, epoxy, and vinyl ester. The resin samples were subjected to various degrees of thermal exposure (400, 270, and 330°C for 5–150 min). Dielectric constants were measured along with the thermomechanical properties. The glass-transition temperature, modulus, and weight loss were important parameters for correlating the material property changes with the heat exposure. A linear relation was determined between the thermomechanical properties and the dielectric properties of the resins under the selected exposure conditions. Therefore, DEA can be introduced as a significant technique for evaluating thermally exposed polymer materials. Interestingly, it is a nondestructive evaluation process. In the future, it could be used for onsite health monitoring of thermally exposed polymer matrix composite structures. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1417–1425, 2009

Key words: degradation; dielectric properties; glass transition; modulus; thermosets

INTRODUCTION

Fiber-reinforced composites are playing important roles in the production of high-performance vehicles as well as critical aerospace structures and primary structures for commercial and military aircraft. Typically, structural composites for the marine and infrastructure industries are based on glass-reinforced polyester, vinyl ester (VE), or epoxy (EP) resins.[1–5] Moreover, these thermoset resins are widely used in defense and civilian applications.[6–8] Civilian and military aerospace applications generally use graphite or carbon reinforcement, with a variety of these resin systems depending on the application requirements. Therefore, the safety and reliability of these materials must be ensured. In high-temperature applications of the aerospace industry, composites exposed to elevated temperatures[1] become irreversibly damaged. Organic resins [e.g., EP, VE, bismaleimide (BMI), and polyester] used in the manufacture of polymer matrix composites (PMCs) with fibers (e.g., graphite, glass, Kevlar, and organic fibers) are significantly susceptible to irreversible thermal oxidative degradation.[6–8] Thermal degradation involves subjection to temperatures above or within a narrow window of the upper service temperatures. In fact, the exposed temperatures are sufficiently high to cause resin degradation. As a result, these materials experience a drop in the glass-transition temperature (T_g) that effectively lowers the upper service temperature and significantly reduces the room-temperature mechanical properties of these composites.[2,3] Below a certain exposure threshold, the composites can apparently appear visually and microscopically to be undamaged. However, in reality, they lose a significant percentage (<60%) of their strength.[4]

The extent of heat damage is typically evaluated by mechanical analysis. A mechanical test requires the collection of a sample plug from the structure. Mechanical testing may not be a viable option for a particular purpose because the mechanical testing of a heat-damaged composite component currently in service is impossible. Suitable nondestructive evaluation (NDE) techniques must be developed for heat-damage detection. The measurement of heat damage on PMCs by NDE is a real concern; the damage may result from a combination of thermal cycling of PMCs above the T_g of the polymer and oxidative degradation of the polymer or polymer–fiber interface.[1–3] At present, suitable NDE procedures are unavailable to assess the heat damage of advanced composite components.[8] The lack of NDE techniques for characterizing the damage of these materials causes a delay in certification and even disposal of the full aircraft for safety reasons. Therefore, the development of NDE for detecting the heat damage of PMC has become a unique challenge.

The NDE methods found in the literature for detecting the heat damage of PMCs are shearography, thermal imaging, backscattered X-rays, multi-sensor techniques, diffuse reflection infrared Fourier

Correspondence to: A. Chatterjee (chatterjeamit@yahoo. com).

transform, and laser-induced fluorescence.[5,6,8–11] Most traditional NDE techniques, such as ultrasonic measurements, radiography, and thermography, are capable of detecting physical anomalies such as cracks and delamination. To measure thermal degradation, NDE techniques must be capable of detecting initial heat damage, which occurs on a molecular scale.[9,12–17] These techniques essentially detect molecular changes in the polymer matrix subjected to thermal exposure. However, these NDE methods are based on chemical surface analysis, so they are still questionable for the prediction of bulk mechanical properties.

Dielectric property measurement is one of the best known methods for quantifying the cure kinetics of crosslinking polymers. It involves the measurement of the dielectric constant (E_r) and loss factor as a function of the curing time over a wide range of frequencies. The cure behavior of several thermoset polymers, such as EP–amine, VE, and polyester, has been studied with the dielectric technique. Traditionally, dielectric measurements have been laborious and time-consuming, using manual or semiautomated bridges.[5,18] The advent of frequency response and network analyzers has allowed the development of automated dielectric measurement systems over the frequency range of 10^{-5} to 10^9 Hz and high-precision time domain reflectometry measurements. High-frequency dielectric measurements have also been used for NDE of adhesive joints.[12–14] The influence of humidity on dielectric properties is well documented for thermoset resins and their composites.[19–23] E_r and the loss factor increase with humidity. Publications are also available for the evaluation of the dielectric properties as a function of the thermal history.[24,25] The effects of postmold curing and thermal aging on dielectric properties and physicochemical properties have been reported.[25] Many studies have been concerned with the effect of annealing on dielectric relaxation at T_g[26,27] and sub-T_g relaxations. In these studies, the temperature has always been limited to a few tens of degrees above T_g. In our previous publications, we also exposed a BMI resin for a long time (hours to days) below T_g of the resin. The mechanical and dielectric analysis (DEA) properties were measured and correlated with one another[6,8] for the long-term thermal aging of BMI resins. However, very few data were reported about the effects of high temperatures on the dielectric properties of thermoset resins.[27,28]

In this effort, thermoset resins (BMI, EP, and VE resins) were exposed to temperatures well above the glass transition for a short period of time. The changes in the dielectric properties of the resins were studied to evaluate their sensitivity to thermal exposure and to predict the mechanical performance of heat-exposed resins. Correlations between E_r and

T_g and the storage modulus (E') were developed. These correlations will help us to envisage the conditions of heat-exposed resins and composites.

EXPERIMENTAL

Thermal degradation analysis

Three different classes of thermoset resins—EP (Applied Poleramic, Inc., Benicia, CA), VE (VE411-350, Dow Chemicals, Midland, MI), and BMI (Cytec 5250-4, Cytec Engineering Materials, Anaheim, CA)—were used in this study and processed as recommended by the manufacturer. The BMI resin was heated in a mold at 93.3°C, and this was followed by degassing to remove trapped air and subsequent curing at 191°C for 6 h and at 227°C for 6 h. The samples were exposed to a 400°C isothermal condition in an air oven for a period of time (60 min). The samples were taken out from the oven after 5, 10, 15, 25, and 60 min. EP was cured at room temperature overnight and postcured at 121°C for 4 h. The samples were exposed at 270°C for 30, 60, 90, and 120 min. The VE resin was cured at room temperature and postcured at 120°C for 2 h. The resin was exposed to 330°C up to 150 min. The samples were taken out after a 30-min interval. The exposure temperatures of 400, 270, and 330°C were chosen for BMI, EP, and VE, respectively, to determine the heat-induced damage in these systems. Figures 1 and 2 show the measured weight-loss characteristics. At exposure to 400°C, significant weight loss was observed for BMI. At 270 and 330°C, significant weight loss was observed for EP and VE. Weight loss continued with the exposure time. The fully cured resin plaques were used for DEA, thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) measurements. A rectangular sample (13 mm × 3 mm × 60 mm) was used for DMA, and a circular sample (1.5 mm × 25 mm) was used
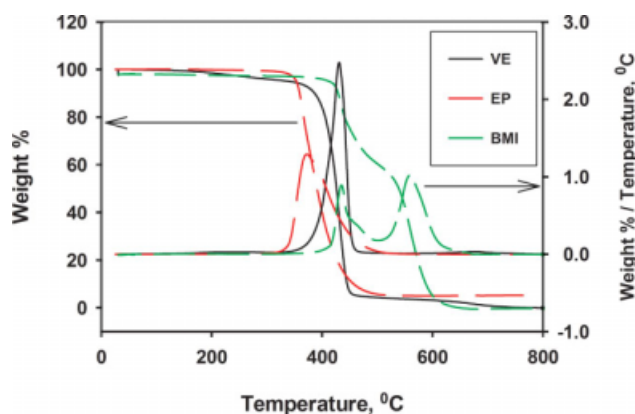
Figure 1 Degradation behaviors of the cured BMI, EP, and VE resins (TGA). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
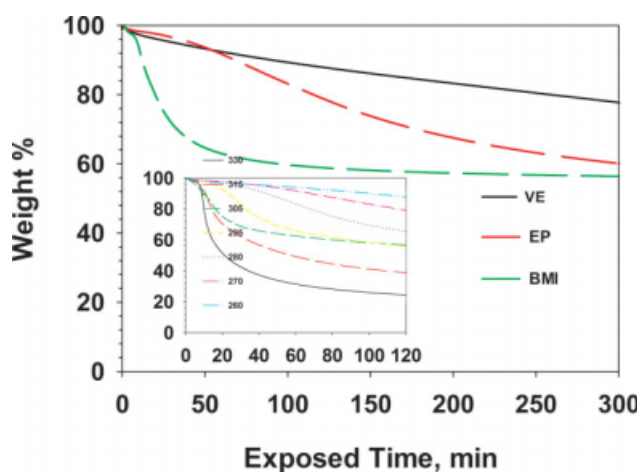
Figure 2 Isothermal degradation behavior of the cured BMI (400°C), EP (270°C), and VE (330°C) resins at different temperatures. The inset shows the isothermal degradation behavior of the cured EP at different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for dielectric measurements. A small sample (5–10 mg) from the resin plaque was cut and placed in a TGA pan for degradation analysis.

DMA

A DMA-2980 from TA Instruments (New Castle, DE) was used to thermally characterize the samples. The DMA instrument was operated in the double-cantilever mode at a frequency of 1 Hz to measure the temperature dependence of the viscoelastic modulus [E' and loss modulus (E'')] in the temperature range of 25–250°C. The samples were tested at an oscillatory displacement amplitude of 15 μm. A heating ramp of 1–5°C/min was used. E' and E'' were continuously recorded through the temperature ramp by the DMA machine. T_g of the polymer is reported to examine the E'' peak at the frequency of 1 Hz. Details about DMA were published previously.[6–8]

Dielectric measurements

A Hewlett–Packard 4294A precision impedance analyzer with a parallel-plate system (HP Test and Measurement, Englewood, CO) was used to evaluate the bulk dielectric properties. The samples were scanned in the frequency range of 1 kHz to 5 MHz. More details about the dielectric measurements were published previously.[6–8]

Thermogravimetric measurements

A Q-500 instrument from TA Instruments was used to identify the thermal degradation patterns of EP,

VE, and BMI resins under an air environment. The machine was operated from room temperature to 900°C with a heating ramp of 20°C/min. In addition, several isothermal experiments were also performed at 260–330, 330, and 400°C for EP, VE, and BMI resins to understand the weight-loss and degradation characteristics of the resins. Further details about the thermogravimetric measurements are presented in our previous publications.[6–8]

RESULTS AND DISCUSSION

Degradation analysis

TGA for the fully cured BMI, EP, and VE resin samples was conducted to identify the decomposition characteristics. Figure 1 shows the weight losses of the samples as a function of temperature. The BMI resin was stable up to 200°C with no measurable weight loss, and this correlates well with the published data from the manufacturer. The initial 1.0% weight loss was observed at 344°C, indicating the loss of moisture and volatiles. The next significant loss (5%) occurred at 425°C because of decomposition of the resin. The third weight loss (42%) occurred at 510°C, and this was followed by 99% weight loss at 670°C. The same experiment was conducted for the EP and VE resins (Fig. 1). The VE system was stable up to 180°C and started to decompose after 180°C with 1% weight loss. At 230°C, VE lost 2% of its weight, and at 338°C, 5% weight loss occurred. VE lost 95% of its weight at 456°C, and this was followed by 99% weight loss at 630°C. The EP system was stable up to 270°C after it lost 1% of its weight. At 353°C, 5% weight loss was observed, and at 523°C, 5% of the weight remained in the system.

The isothermal TGA experiments were performed to identify weight loss as a function of exposure time (Fig. 2). Isothermal exposures at different temperatures were performed for the EP system to determine the decomposition characteristics with time. At the selected exposure temperature, the degradation behavior of EP was measured. The inset of Figure 2 illustrates the results. This clearly indicates that the EP resin was very sensitive to the exposure time. Similar experiments were done for the BMI and VE systems to determine the decomposition temperature. The exposure temperatures of 400, 270, and 330°C were chosen for BMI, EP, and VE, respectively, to observe the heat-induced damage in these systems, as described previously in the Experimental section. Figure 2 shows the measured weight-loss characteristics. At exposure to 400°C, significant weight loss was observed for BMI. At 330°C, significant weight loss was observed for VE, and the weight loss continued with time. Although 1%
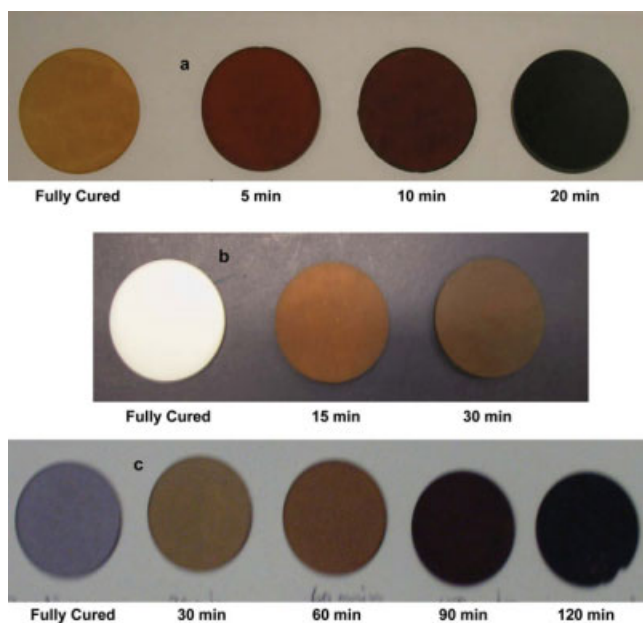
Figure 3 Effect of the thermal exposure on the color for the (a) BMI, (b) EP, and (c) VE resins. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

weight loss occurred for the VE system at 180°C, which may have been unreacted monomer, solvent, and moisture, the onset of decomposition was initiated at a higher temperature (325–330°C). This was due to the stability of the highly crosslinked VE–styrene system. The SC-15 resin system contained low-molecular-weight second-phase toughener particles.[29] These polymer particles were phase-separated during curing. Therefore, these molecules had less thermal stability and decomposed in advance (270°C) during heat exposure (Figs. 1 and 2). The low thermal stability of the amine–alcohol moiety of the EP system was another cause of the early decomposition of EP in comparison with the BMI and VE systems.[6–8,29] The VE polymer system had a higher decomposition temperature than EP. This was due to the high crosslink density and low free volume of the system.[30] Therefore, the exposure temperature of 330°C was used to obtain heat-induced changes. Initially, a very low weight loss was observed for each resin. However, the resin color changed [Fig. 3(a–c)]. A longer period of thermal exposure caused decomposition of the resins,[6–8] and weight loss occurred (Figs. 2 and 3); this was detected with the TGA system. The correlation of the weight loss with the exposure time for the three resin systems was determined. A linear correlation was found. The correlation coefficient (R^2) was 0.96–0.98 (shown later in Table II). The heat-exposed samples were examined and photographed to observe the color variation. Figure 3(a–c) indicates the color difference due to the isothermal tempera-

ture exposure with time (5–150 min). Raising the exposure temperature and/or time significantly changed the resin color. The color change was correlated with surface oxidation.[17] There was sufficient evidence that the exposure time caused resin decomposition,[1,6,7,17,22] which was visualized with the photographs. However, the magnitude of damage was immeasurable by visual inspection.[6,7] The color change was measured by the CIELAB technique with a Cary 5 ultraviolet–visible/near-infrared spectrophotometer (Varian Instruments, Walnut Creek, CA) in the reflection mode with a diffusion reflection accessory for Cary 4/5 equipment. The scan was done from 380 to 780 nm at a scan rate of 1 nm (full slit height and double beam mode). The weight-loss percentage and E_r with the color change (CIE A, CIE C, and CIE D65 for L^*, a^*, and b^*) were plotted for the EP, BMI, and VE systems. Results showed that the CIE A–L^* values decreased with the exposure time. Figure 4 represents the CIE A–L^* values with the weight-loss percentage for EP. No direct correlation was observed. However, this is a very preliminary investigation. Further investigation is needed in this direction. Thermal degradation changes the polymer chemical structure; this includes oxidation, chain scission, and crosslinking.[6,7,17] Depending on the exposure temperature and time, all three changes could occur simultaneously or individually. The chemical degradation of the polymer matrix was reviewed by Lee and Neville.[17] The presence of aromatic groups in a cured resin network tends to increase thermal stability. In nonaromatic resins, the linear chain is degraded initially. For amine- or amide-cured epoxies, the nitrogen linkages exhibit relatively poor thermal stability in comparison with ether or ester
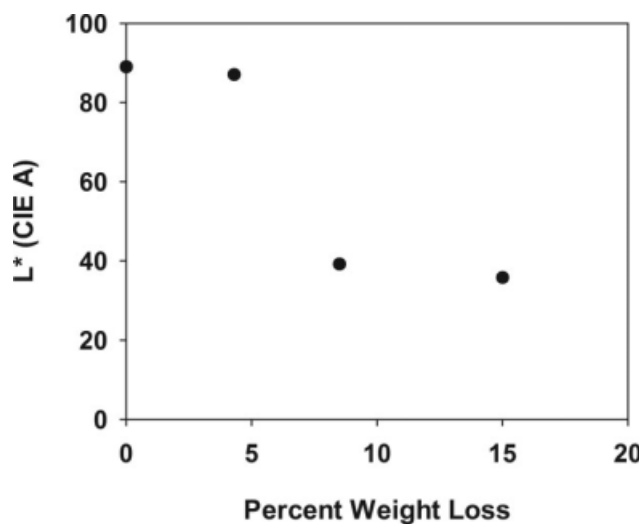
Figure 4 Correlation between the L^* (CIE A) and weight loss (%) for the EP system. The heat-exposure conditions are given in Table I.

Resins	Exposure time (min)	E' (MPa)	T_g (°C)	Error (%; $n = 3$)[a]	E_r	Error (%; $n = 3$)[a]	Reproducibility (%)[b]
BMI	0	3400	348	0.7	3.45	3.36	4.01
	5	2700	305	1.00	3.27	3.85	4.82
	15	1200	210	2.2	3.01	4.85	5.56
	20	700	180	3.49	2.79	6.52	7.93
EP	0	2410	101	2.9	3.82	0.24	1.01
	15	2250	91	3.37	3.67	0.58	2.67
	30	1709	78	3.85	3.55	1.07	3.43
	60	1605	67	4.74	3.41	1.81	4.56
VE	0	2540	127	1.91	3.35	0.81	1.29
	30	2442	126	2.10	3.28	1.20	2.86
	60	2350	123	3.25	3.24	1.56	3.35
	150	1977	117	4.27	3.10	2.01	4.97

[a] The error was determined from the RSD of E_r for three successive analyses.
[b] The RSD of E_r for three analyses was performed on three different days.

linkages.[6,7] The hydroxyl groups are particularly vulnerable to degradation, especially at higher temperatures. It has been reported that narrow-molecular-weight fractions of diglycidyl ether of bisphenol A degrade the weakest segment in the molecular chain.[17] That is the amine–alcohol moiety —N[CH$_2$CH(OH)CH$_2$O—]$_2$. A diglycidyl ether of bisphenol A backbone EP resin was used in this study and was cured with cyclohexane amine. The amine–alcohol moiety was the prime linkage and might degrade at a low temperature in comparison with BMI and VE systems. Hence, the EP system had low thermal stability (270°C in comparison with BMI and VE.[6–8,30]

Viscoelastic property measurements

It is well known that changes in T_g can be correlated well with the resin morphology and degradation mechanisms of chain scission. Therefore, DMA measurements were taken to assess T_g and modulus changes in the samples. The E'' peak temperature was used for T_g calculations. E' and T_g for various isothermally exposed BMI, EP, and VE resin samples are tabulated in Table I. Figure 5 shows typical graphs of E' and E'' for isothermal exposure at 400°C for the BMI resin. The modulus and T_g decreased with increasing exposure time. Similar types of graphs were obtained for the EP and VE systems. The measured T_g values showed a linear decrease with the thermal exposure time (see Table I for the three thermoset systems). The onset of chain scission (breakdown of the crosslinked network) is generally characterized by a subsequent decrease in T_g, as seen here. E' and T_g decreased linearly with increasing time (Table II). The higher temperature exposure samples showed a consistently high T_g

falloff in comparison with the lower exposure samples. The same trend was observed for the EP and VE systems exposed at 270 and 330°C for 5–150 min. These facts clearly indicate that each system decomposed with exposure. The viscoelastic properties were degraded. The rate of decomposition was highest for the BMI system followed by the EP and VE systems. In the case of thermooxidation, it is accepted that degradation is diffusion-limited.[22] Thermooxidation implies the transport of oxygen from the surface toward the bulk or the transport of mobile groups from the bulk toward the surface, where they react with oxygen.[11,19–22] As a result, below 250°C, the effects of thermooxidation are generally observed to be limited to a few tens of micrometers below the surface.[24] In the case of thermolysis, bond scission and chemical transformation occur because of the effect of elevated
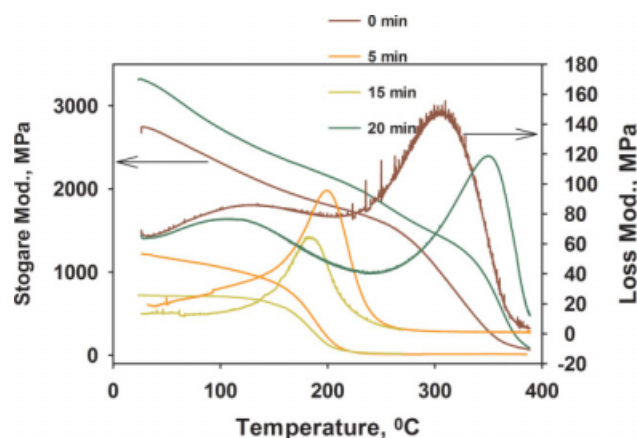
Figure 5 Variation of E', E'', and T_g with the exposure time for the heat-exposed (400°C) BMI resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Correlation Potential Between E_r and E', T_g, and Weight Loss of the Three
Different Resin Systems

Correlation parameter	Resin system	Equation	R^2
Exposure time (min) versus E_r	BMI	$Y = -0.0316X + 3.45$	0.991
	EP	$Y = -0.0067X + 3.79$	0.964
	VE	$Y = -0.0016X + 3.34$	0.993
T_g (°C) versus exposure time (min)	BMI	$Y = -8.62X + 347$	0.995
	EP	$Y = -0.569X + 99$	0.964
	VE	$Y = -0.069X + 127$	0.989
E' (MPa) versus exposure time (min)	BMI	$Y = -138X + 3380$	0.996
	EP	$Y = -14.22X + 2467$	0.845
	VE	$Y = -3.79X + 2555$	0.996
Weight loss (%) versus exposure time (min)	BMI	$Y = 1.045X - 1.24$	0.984
	EP	$Y = 0.249X + 0.086$	0.995
	VE	$Y = 0.088X + 1.33$	0.961
Weight loss (%) versus E_r	BMI	$Y = -32.65X + 111$	0.969
	EP	$Y = -36.91X + 140$	0.979
	VE	$Y = -53.66X + 181$	0.982
E' versus E_r	BMI	$Y = 4302X - 11464$	0.976
	EP	$Y = 2165X - 5828$	0.908
	VE	$Y = 2315X - 5179$	0.982
T_g (°C) versus E_r	BMI	$Y = 268.5X - 580$	0.973
	EP	$Y = 84.9X - 222$	0.992
	VE	$Y = 42X - 12.9$	0.966

temperatures.[19,24] However, in this study, both processes happened, depending on the exposure time.[6,7,19–20,31] An increase in the exposure time may facilitate transient oxygen diffusion into the resin system and/or facilitate the chemical decomposition of the three-dimensional network.[19–20,31] The decomposed network is loosely bound to the parent structure, and this may ultimately reduce the crosslink density of the polymers. Interchain bond breakage may occur, and that increases chain mobility through transient oxygen diffusion. During oxygen diffusion, the broken chains may further oxidize. As a result, the bindings of the main network system loosen further, and this may cause the network systems to be more floppy. Hence, the modulus and T_g decrease.[6,7,19–26,31]

Dielectric property measurements

The dielectric properties and log frequency of the cured EP resin exposed for different times showed a decreasing response. E_r decreased with increasing time of exposure and frequency. The capacitance factor (C_p) and E_r responses showed a frequency dependence.[19–26] The same trend was observed for the VE and BMI resin systems. There are three components of molecular polarization—electric polarization, atomic polarization, and dipole orientation polarization—and these influence E_r of polymers.[14–16] The three types of polarization can respond to an applied electric field at 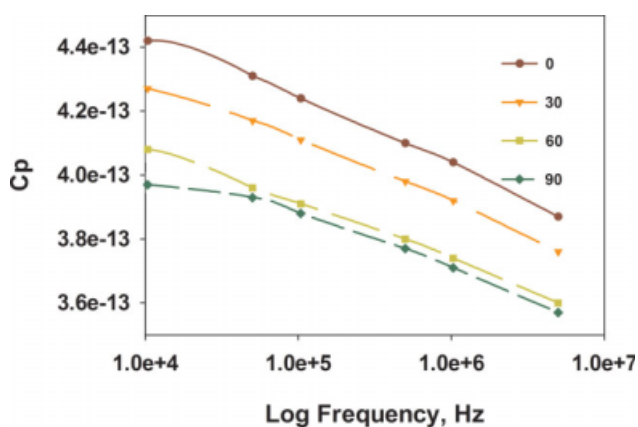a low frequency. With increasing frequency, dipole orientation polarization may not happen because a long time is required to activate it. As a result, E_r decreases with increasing frequency.[11,19–22] Besides, the polymer system contains discrete networks, and these are interpenetrated with one another in the cured resin structure. Such a polymer structure effectively restricts the orientation and relaxation of dipoles in some polar groups of BMI, EP, and VE resins and reduces E_r and the dissipation factor.[6,7,31] In the low temperature range, for fully cured resin systems, the polar groups of the polymer are difficult to orient and relax in the applied electric field because of the frozen molecular chain segments in the glassy state. With increasing temperature, the chain-segment mobility increases. When the temperature approaches T_g, E_r increases dramatically[22] as the dipoles attached rigidly to the polymer backbone gain sufficient mobility and become free to orient in an electric field.[19–26] The BMI, EP, and VE resins were heated far above their T_g's (348, 101, and 127°C for BMI, VE, and EP, respectively). The time dependence (at the fixed frequency of 1 MHz) of E_r for the cured EP, BMI, and VE systems exposed for different times to decomposition temperatures is presented in Table I. With increasing time at the decomposition temperature, the chain-segment mobility increased, and chain fragmentation occurred. The bond breakage was ongoing with increasing time of exposure.[19–26] The number of molecular segments decreased because of the decomposition of the molecule, and that was confirmed by TGA weight-loss measurements.
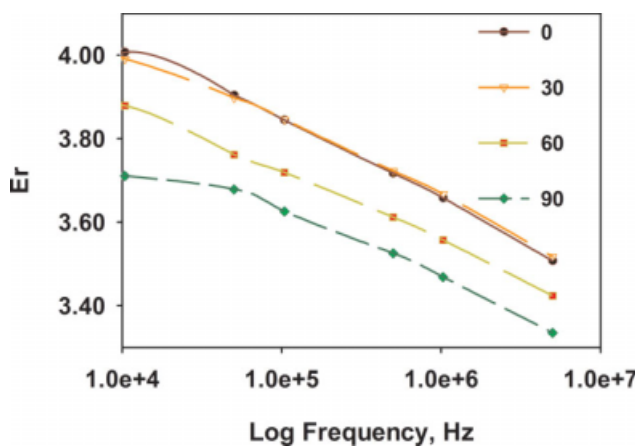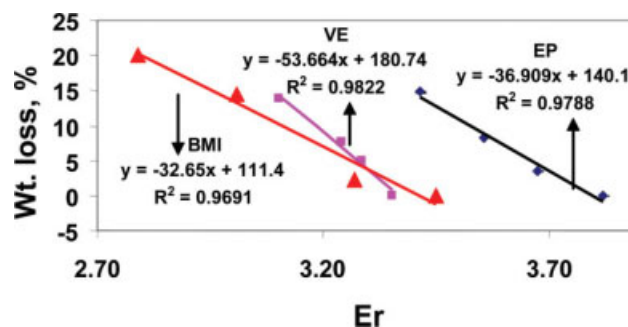
Figure 6 Variation of E_r with the frequency for the EP system for different exposure times. The exposure conditions are given in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 8 Correlation between the weight loss (%) and E_r for the BMI, EP, and VE systems. The heat-exposure conditions are given in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Therefore, the number of polar groups decreased with the exposure time, and this reduced the orientation polarization and E_r of the polymers.[6,7,19–20,31] Figures 6 and 7 show the decreasing trend of E_r with increasing frequency. It indicates that DEA scanning at a lower frequency produced enhanced sensitivity to the time effects. The dipoles in the viscoelastic polymers could get more time to align according to the direction of the applied electric field at a low frequency; therefore, dipole orientation polarization was a major contributing factor for E_r.[19–22] However, the noise was too high to get reliable results at very low frequencies.

E_r values plummeted with the exposure time for the BMI, EP, and VE systems, as shown in Table I. The repeatability was calculated with three different measurements taken on the same day and was within 6.52%. Day-to-day reproducibility was 7.93% (three

samples were measured on three different days). The rate of decomposition was linear for all the systems, and R^2 was 0.96–0.99. An increase in the exposure time decreased E_r. However, the relative standard deviation (RSD) increased (Table I).

The correlation potentials between E_r, E', T_g, the exposure time, and the weight loss of the three different resin systems (EP, VE, and BMI resins) are tabulated in Table II. E_r decreased with decreasing T_g, and they were interrelated linearly. R^2 was between 0.97 and 0.99. A linear relationship was observed for E' with E_r as well (Table II). The weight-loss percentage with E_r is also plotted for the three different systems (Fig. 8). Correlation equations were developed between these two properties. A linear correlation was observed (Table II). R^2 was in the range of 0.97–0.98 for the three systems (Fig. 8). The reduction percentages of T_g and E' with the reduction percentage of E_r are plotted (Figs. 9 and 10). They were linearly associated with one another.
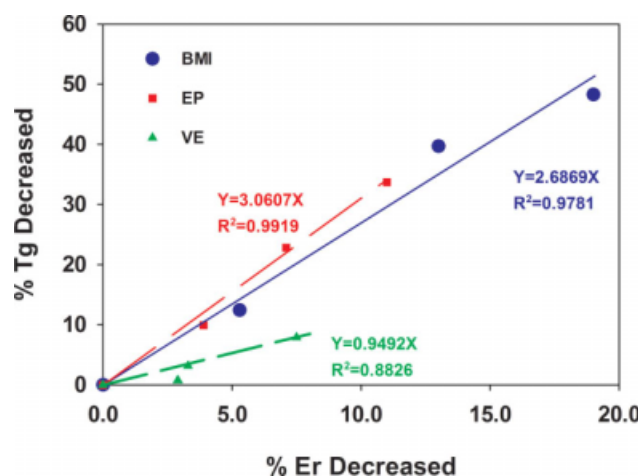

Figure 7 Variation of C_p with the frequency for the EP system for different exposure times. The exposure conditions are given in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 9 Correlation between the decrease in T_g (%) and the decrease in E_r (%) for the BMI, EP, and VE systems. The heat-exposure conditions are given in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
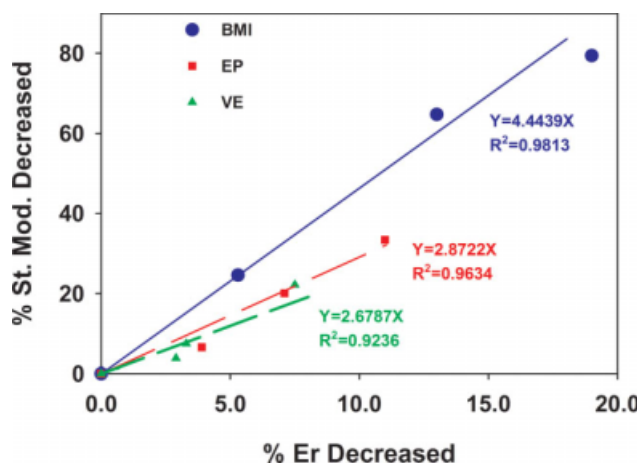
Figure 10 Correlation between the decrease in E' (%) and the decrease in E_r (%) for the BMI, EP, and VE systems. The heat-exposure conditions are given in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Linear correlation equations were developed. The straight line passed through the origin and followed zero-order kinetics. The direct correlation between E_r and the mechanical properties of the heat-exposed resins could be used to predict T_g, E', and the weight loss of the heat-exposed resin systems. Well-established DMA and TGA measurements showed a relationship with E_r. Therefore, the generated equations could be used to predict the viscoelastic properties of the heat-exposed resins. However, DMA and TGA measurements are destructive in nature. A sample once exposed to the machine is fully damaged. DEA is a nondestructive process, and the mechanical properties for any heat-exposed portion of a resin and composite can be assessed with this technique. However, DEA is moisture-sensitive,[19–22] so moisture should be removed from the surface of the sample before any DEA measurements are taken.

It has been reported that at room temperature within the frequency range of analysis,[19] only sub-T_g relaxations play a role. The measured dielectric characteristics of thermosets are governed by short dipolar groups. However, the dielectric properties are almost unaffected by thermal stresses.[19] No effect of thermal aging has been observed on the resistivity even after exposure to 400°C. However, these results appear quite surprising and disagree with reported results.[19] At 400°C, thermal decomposition, as measured by mass loss, usually proceeds at a quite high rate in pure EP and its composite.[22] This is the result of bond scission and chemical transformations within the bulk of the resin, as described previously. As the electrical properties are very sensitive to bulk modifications, the appearance of such defects, if any, will strongly influence the electrical response. The same trend of changes in the dielectric properties

has been observed in this study,[6,7] and that agrees well with the reported results.[22] All the previous studies were conducted with free resin surfaces. This means that a material's surface has been exposed to the surrounding atmosphere. Surface and bulk degradation is observed through the investigation of T_g, the modulus, and the weight loss. In this study, the whole thickness of a sample was probed between the parallel plates, and the bulk governed the electrical response. E_r decreased with decomposition, that is, exposure time. Hence, any thermal degradation, either thermal aging or thermooxidation, was easily seen, and that was detected by the DEA method. Through the thickness, XPS analysis was performed to measure the depth of the thermooxidative process.[31] It was found that the thermooxidation process and thermal degradation process decreased with increasing thickness, and this tallies well with reported results.[17,19–24,31] However, these results disagree with previously reported results[24] in which samples were protected from direct oxidation by avoidance of exposure to the surrounding atmosphere. With the existence of nonnegligible conductivity, the low-frequency relaxation could be related to electrode polarization.[28] Electrode polarization usually leads to a very large (several decades) increase in E_r when it is moving toward low frequencies.[28] Something similar was observed for all three thermoset systems.[6,7,29] The developed DEA measurements were used to characterize (in a preliminary investigation) an EP composite (an EP–S$_2$–glass composite) exposed to a high temperature (330°C) with the exposure time. The results illustrated the same decreasing trends with increasing exposure time that were observed for the pure EP systems.[31]

CONCLUSIONS

A dielectric measurement method was developed for BMI, EP, and VE resin systems to determine the sensitivity of the dielectric properties to heat-induced changes in the resins. The decomposition temperature of the resins was determined with TGA for each system. The fully cured BMI, EP, and VE resin samples were exposed to resin decomposition temperatures of 400, 270, and 330°C, respectively, for a period of time. E_r decreased linearly with heat exposure for all the resin systems. The thermomechanical properties (T_g, weight loss, and modulus) were measured by DMA and TGA and were correlated with the dielectric properties of the three resin systems. These three parameters were linearly correlated with the dielectric properties of the resins for the selected exposure conditions. This dielectric technique reveals a nondestructive tool for evaluating heat-exposed polymer properties.

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