Consistent Model Predictions for Isothermal Cure Kinetics Investigation of High Performance Epoxy Prepregs

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ABSTRACT: An accurate kinetics model is essential for understanding the curing mechanism and predicting the end properties of polymer materials. Graphite/epoxy AS4/8552 prepreg is a recent high-performance thermosetting composite modified with thermoplastic, which is being used in the manufacture of aircraft and military structures. The isothermal cures of this system along with another thermoplastic toughened high-performance prepreg, the T800H/3900-2 system, were investigated by real-time Fourier transform infrared (FTIR) spectroscopy. The cure rate was quantitatively analyzed based on the concentration profiles of both the epoxy and primary amine groups. Three autocatalytic models were used to determine kinetics parameters for both composite systems. The model which utilizes an empirical term, the final relative conversion (at different isothermal curing temperatures), describes the experimental data of both systems more satisfactorily than the model which applies a diffusion factor. The modeling results suggest that the curing of epoxy within both prepregs can be assumed to be a second order process. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2231–2237, 2008

Key words: composites; diffusion; FTIR; high performance polymers; kinetics

INTRODUCTION

Pre-impregnated fiber reinforced composites (prepregs) have been widely used in aerospace industry for fabricating high-performance composite components nowadays. Kinetics modeling of fiber reinforced epoxy composites has been very challenging due to the following factors: the simultaneous presence of several comonomers, the number and type of initiators, the multiplicity of polymerization mechanisms, the insoluble nature of prepregs and the susceptibility of the network to hydrolysis and other types of chemical attacks.[1,2]

Most of the previous studies were performed for the cure kinetics of pure resins; there are only a few works for kinetics study of fiber reinforced composites: Fiberdux 6376,[3] AS4/3502,[4] AS4/3501-6,[5] etc. It was pointed out that the presence of reinforcement restricts the flowability and molecular mobility of the epoxy and amine groups resulting in a lower maximum reaction rate.[6] The reaction rate of reinforced epoxies decreases faster than that of neat epoxies when the reaction is mainly diffusion controlled.[6]

In this work, isothermal kinetics data based on FTIR spectra were analyzed for simulation of the AS4/8552 and T800H/3900-2 aerospace prepregs. AS4/8552 is a recent thermoplastic toughened epoxy system, which has wide applications including Airbus wing sandwich structures and Sikorsky helicopter components.[7,8] T800H/3900-2 is also a thermoplastic toughened tetrafunctional epoxy system, which is extensively used in Boeing structures including the Boeing 777 empennage and floor beams. Both composites are composed of the most widely used tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM)/4,4′-diaminodiphenyl sulfone (DDS) system exhibiting high glass transition temperature, high elastic modulus, and good thermal stability.

The isothermal cure data were obtained from the FTIR spectra in this work. By implementing temperature control, real-time FTIR is capable of investigating the cure kinetics of epoxy-amine reactions by monitoring time-resolved concentration profiles of various functional groups.[9] After the original data curves were smoothed by an MMF function within the sigmoidal regression models' family, autocatalytic models with and without diffusion control were applied to the experimental data.
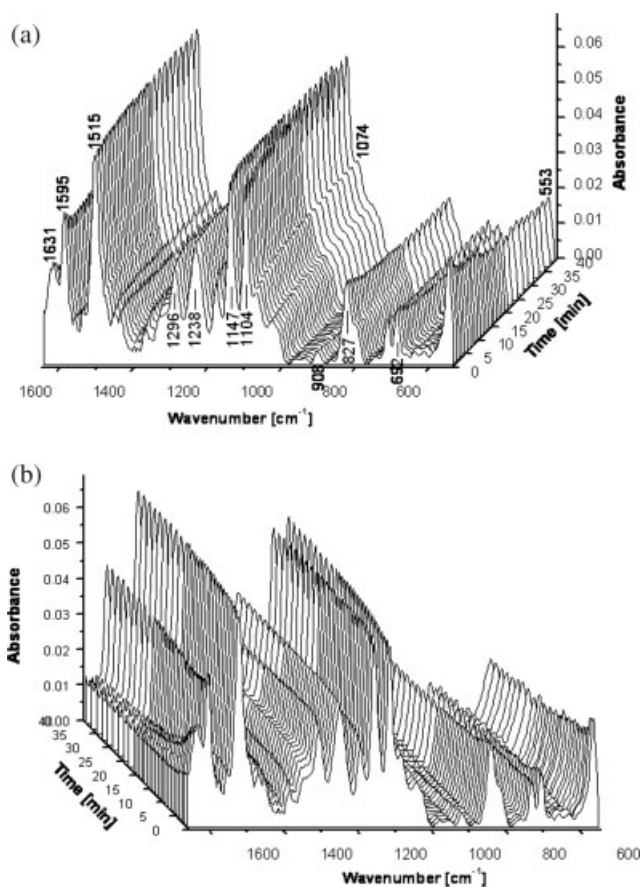
Figure 1 FTIR spectrum changes of the T800H/3900-2 prepreg with isoconversion time at 160°C. (a) and (b) were plotted from different orientation for clear indication of intensity changes.

EXPERIMENTAL

Materials

The basic formulation of the T800H/3900-2 prepreg contains the 177°C curable TGDDM/DDS resin/hardener system with 145 g/m² areal fiber weight and 35 wt % resin content.[10,11] Amorphous polyamide particles are selectively distributed onto the surface of the prepreg for improving the fracture toughness and processability. The 180°C curable AS4/8552 matrix resin consists of both TGDDM and triglycidylaminophenol (TGAP) epoxy monomers and DDS hardeners according to the FTIR analysis performed by Bondzic et al.[8] The areal fiber weight is 268 g/m² and the resin content is 34 wt %. The chemical formulas of the components are reported herein.

Real-time FTIR measurements

Firstly, the prepreg materials were ground into KBr disks excluding carbon fibers (only with small amount of fiber residue in). Then the KBr disk was installed into a Specac 20600 solid holder inside of

an electrical heating jacket Specac 20730. This heating jacket was driven by a Specac 4000 series high stability temperature controller and was directly mounted into the BIO-RAD (excalibur series) spectrometer. FTIR spectra were obtained at a resolution of 4 cm⁻¹ with 32 scans. Thirty-eight seconds were required to complete the collection of one spectrum under the selected instrumental conditions. The spectra were collected with a delay time which was dependent on the rate of cure. Isothermal curing was performed at the temperature of 140, 150, and 160°C for both prepreg systems. The sample holder was preheated to the isothermal curing temperature before the installation of KBr disks.

The relative conversion (α) of the epoxy groups at different isothermal curing temperature was determined as usual:

$$\alpha = 1 - \frac{(A_{\text{reactive peak}}/A_{\text{reference peak}})_{T,t}}{(A_{\text{reactive peak}}/A_{\text{reference peak}})_{T,t=0}} \quad (1)$$

where A is the absorbance, T is the curing temperature and t is the curing time.

RESULTS AND DISCUSSION

Isothermal curing of the T800H/3900-2 prepreg system

FTIR spectroscopy

Figure 1 shows a series of FTIR spectra collected during the first 40 min when the T800H/3900-2 prepreg was isothermally cured at 160°C. Differential spectra for the cure up to 120 min are presented in Figure 2.

The cure of epoxy-amine systems is governed by an autocatalytic reaction. When a reaction is catalyzed by a proton donor already present or one that is produced during cure, the reaction mechanism is said to be autocatalytic.[12] The epoxy group that
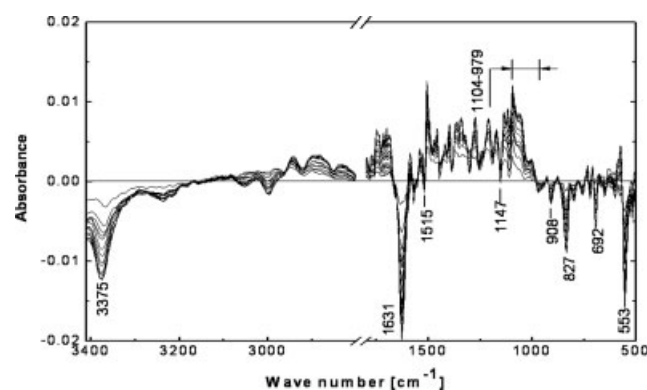

Figure 2 Differential spectra of the T800H/3900-2 prepreg isothermally cured at 160°C over 120 min.
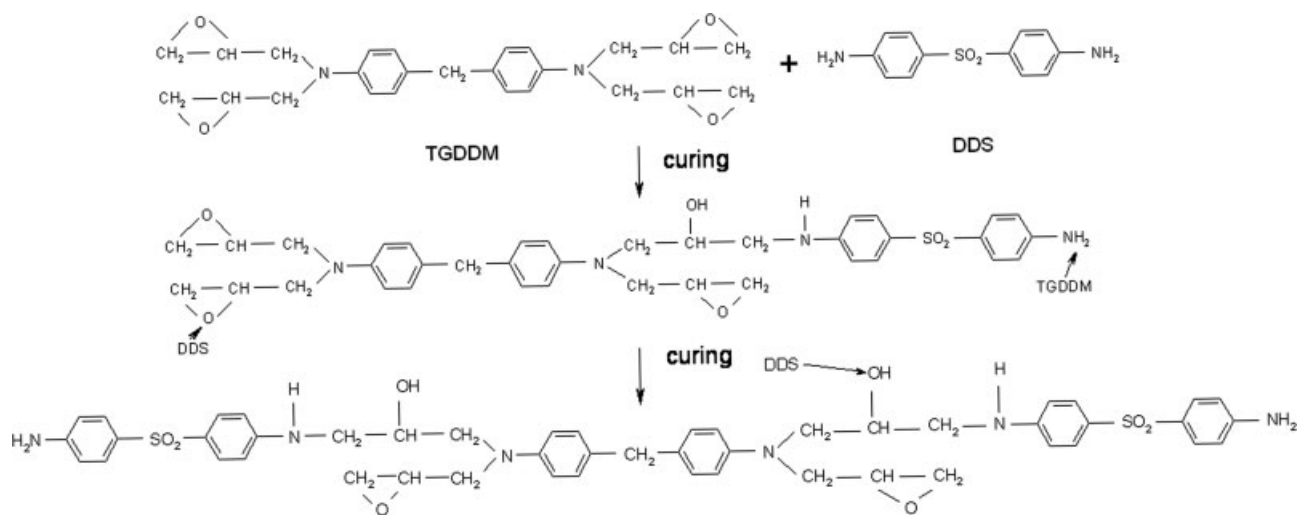
Figure 3 Schematic representation of the cure reactions of the TGDDM/DDS system.

reacts with a primary amine produces secondary amine and then forms the tertiary amine.[5] The addition of the primary and secondary amine groups to the oxirane ring is accelerated by the hydroxyl groups either presented in the accelerators or formed as by-products from the epoxy-amine reaction. It was found that the presence of fibers does not change the reaction mechanisms or the net structure although notable difference was detected in reaction rates.[13] The cure reactions of the TGDDM/DDS system in the presence of glass and carbon fibers are shown in Figure 3.[13]

The absorption at 3375, 1631, 692, and 553 cm^{-1} are related to amine consumption. The conversion of the amine groups can be evaluated by the intensity decrease in these peaks. The broad absorption at around 3375 cm^{-1} covers an overlap of primary amine $\nu(NH_2)$ and secondary amine $\nu(N—H)$ groups. The 1631 cm^{-1} peak [$\delta(NH_2)$] decreases gradually with time up to complete disappearance. The decrease in the 692 cm^{-1} peak related with the $\nu(N—H)$ develops gradually until the intensity reaches a steady value. Because of a possible overlap of $\delta(SO_2)$ and an aromatic ring quadrant vibration, the 553 cm^{-1} peak shows irregularity in intensity changes.[14] The former vibration remains unchanged with time and the latter is associated with the substitution on the aromatic ring. The 1631 cm^{-1} peak was used for quantitative analysis of the primary amine conversion.

The epoxy group consumption was analyzed by the intensity changes of the well-resolved oxirane ring stretching mode at 908 cm^{-1}.[15–17] The 1515 cm^{-1} peak (a ring semi-circle stretching mode of TGDDM) has been widely used as reference peak for normalization in TGDDM/DDS resin systems.[14,18] However, it can be seen from Figure 3 that the 1147 cm^{-1} peak [$\nu_{sym}(SO_2)$] is a better choice for

normalization due to its invariant nature during curing. Therefore, the intensity of the 1631 cm^{-1} and the 908 cm^{-1} peaks was normalized using the 1147 cm^{-1} peak for α calculation.

Quantitative analysis

To avoid excessive error in derivative curves, the relative conversion (α) versus time (t) data were smoothed by using an MMF function within the sigmoidal regression models' family. The function can be expressed as follows:

$$y = \frac{ab + cx^d}{b + x^d} \qquad (2)$$

where a, b, c, and d are fitting parameters. The R^2 values for the nonlinear regression fitting were
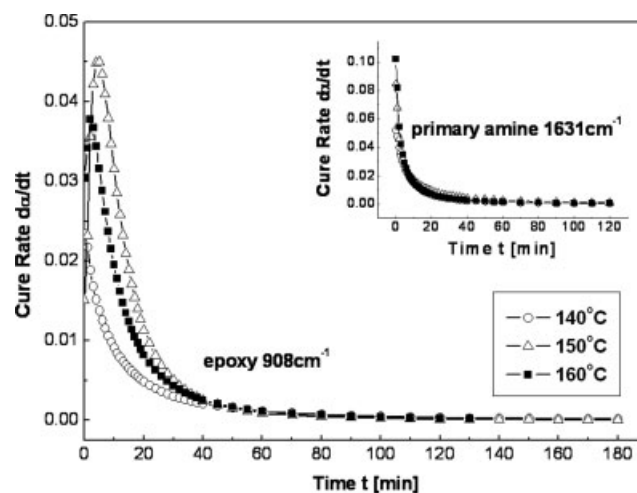

Figure 4 Cure rate as a function of time at different isothermal temperatures for the primary amine and epoxy groups within the T800H/3900-2 prepreg.
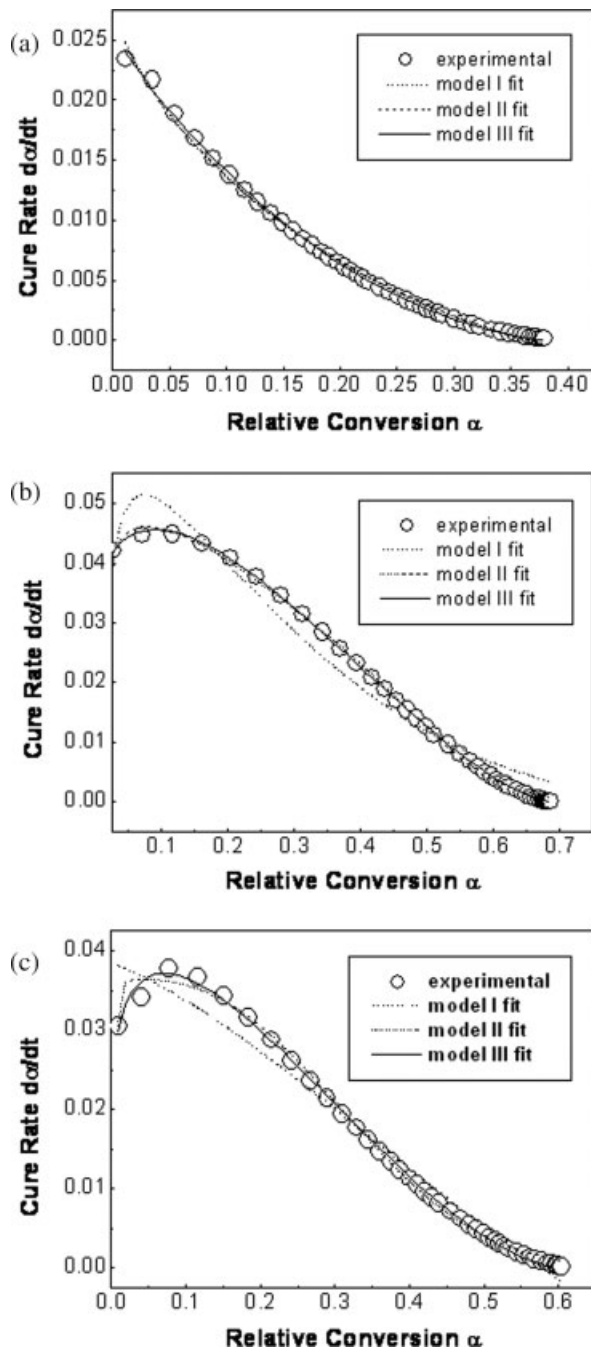
Figure 5 Comparison among the experimental data and different model predictions for the T800H/3900-2 prepreg isothermally cured at (a) 140, (b) 150, and (c) 160°C.

between 0.978 and 0.997, so the MMF model gave a satisfactory fit of the experimental data. Then the derivative of the smoothed α–t curves, i.e. the $d\alpha/dt$ versus t curves, were produced.

Figure 4 shows the $d\alpha/dt$ versus t data for both the primary amine and epoxy groups within the T800H/3900-2 prepreg cured at 140, 150 and 160°C. The primary amine and the epoxy groups exhibit different reaction mechanisms. The cure rate of the primary amine decreases significantly within the first 5 min. In contrast, the reaction of the epoxy group is clearly autocatalytic in nature when the temperature is higher than 140°C, indicated by the positive curvature in the initial stages.

Because of the autocatalytic nature of the epoxy-amine curing process, the following phenomenological model has been widely used for kinetics study (firstly derived by Horie et al.[19]).

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{3}$$

where k_1 and k_2 are reaction rate constants, and m and n are empirical power-law exponents, whose sum represents the overall reaction order. Assuming that the curing of epoxy resin is a second order process, that is, $m+n = 2$, then eq. (3) can be expressed as

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^{2-n})(1 - \alpha)^n \tag{4}$$

To take into account of the diffusion control mechanism at later stage of epoxy conversion, Chern and Poehlein[20] proposed a diffusion factor which is expressed as

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{5}$$

where C and α_c are two empirical constants which are temperature dependent.

Combining eqs. (4) and (5), eq. (4) with diffusion control changes to

$$\frac{d\alpha}{dt} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]}(k_1 + k_2\alpha^{2-n})(1 - \alpha)^n \tag{6}$$

Another approach to consider the diffusion-controlled mechanism was proposed by Musto et al.,[18]

TABLE I
Kinetic Parameters Derived from the Autocatalytic Model III Fitting for Isothermal Cure Process of the T800H/3900-2 Prepreg

Temperature (°C)	k_1 ($\times 10^{-2}$ min^{-1})	k_1 ($\times 10^{-1}$ min^{-1})	n	α_{max} ($\times 10^{-1}$ min^{-1})	R^2	χ^2
140	7.34	1.37	1.09	3.79	0.9992	2.95E−8
150	5.30	1.52	1.51	6.79	0.9999	2.20E−8
160	3.83	1.67	1.66	6.04	0.9986	2.14E−7

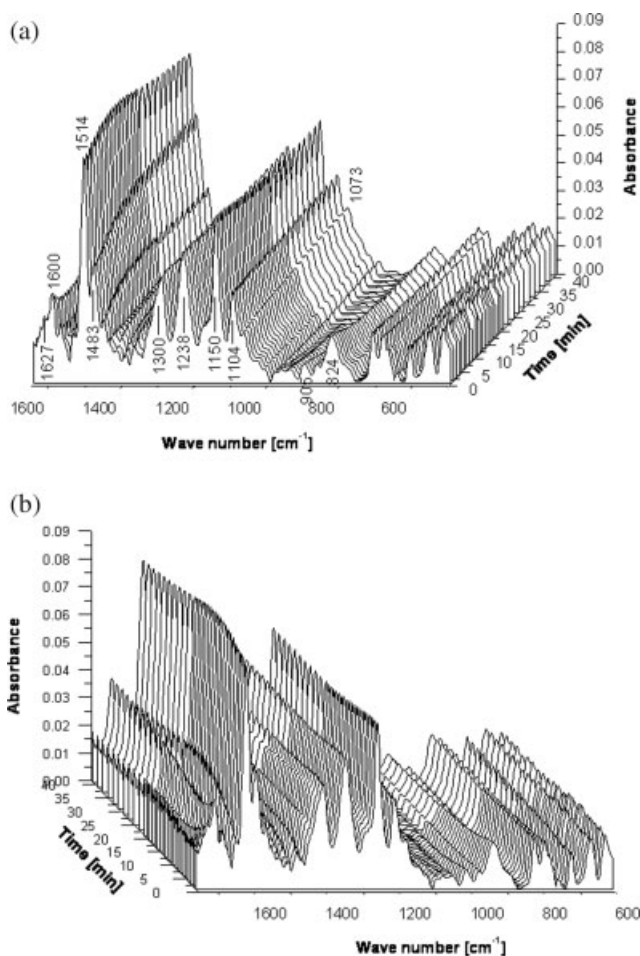R^2 and χ^2 are statistics parameters.

Figure 6 FTIR spectrum changes of the AS4/8552 prepreg with isoconversion time at 160°C. (a) and (b) were plotted from different orientation for clear indication of intensity changes.

which utilizes an empirical term (α_{max}) substituting the term ($1-\alpha$) in eq. (4). α_{max} represents the final relative conversion at different isothermal curing temperatures.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^{2-n})(\alpha_{max} - \alpha)^n \qquad (7)$$

In this work, the ($d\alpha/dt$) versus α plots were simulated by three models to compare the accuracy of various prediction approaches. Kinetics models I, II, and III are based on eqs. (4), (6), and (7), respectively.

Figure 5 shows the experimental ($d\alpha/dt$) versus α data, along with the prediction curves from three models for the T800H/3900-2 prepreg cured at different temperatures. The difference in α_{max} between 150 and 160°C isothermal temperatures is minor, however, when the isothermal temperature drops to 140°C, the conversion of the epoxy group reduces from 67.9, 60.4 to 37.9%. As the curing temperature
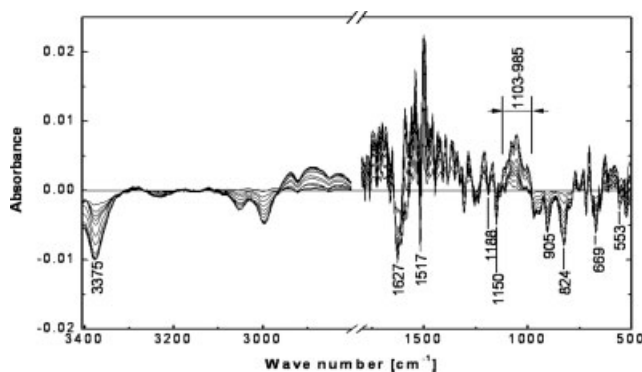

Figure 7 Differential spectra of the AS4/8552 prepreg isothermally cured at 160°C over 120 min.

rises, the when the maximum $d\alpha/dt$ occurs becomes higher. For the 140°C specimen, the cure rate is the highest at the beginning of the cure; for the 150°C specimen, the maximum $d\alpha/dt$ occurs when α is 0.078; at 160°C isothermal curing temperature, the $d\alpha/dt$ reaches its maximum value when the relative conversion is 0.11. Model I gave a relatively poor fit to the experimental data. After the diffusion factor was considered, model II showed a closer fit especially after the relative conversion α reached 0.15. Model III gave a very satisfactory prediction of the real curing data of T800H/3900-2 prepreg, which can be seen in Figure 5(c). The kinetic parameters evaluated by model III for the T800H/3900-2 prepreg isothermally cured at 140, 150, and 160°C are presented in Table I. Model III (the solid line) predicted the experimental data at a very satisfactory level reflected from the high R^2 values which were between 0.9986 and 0.9999.
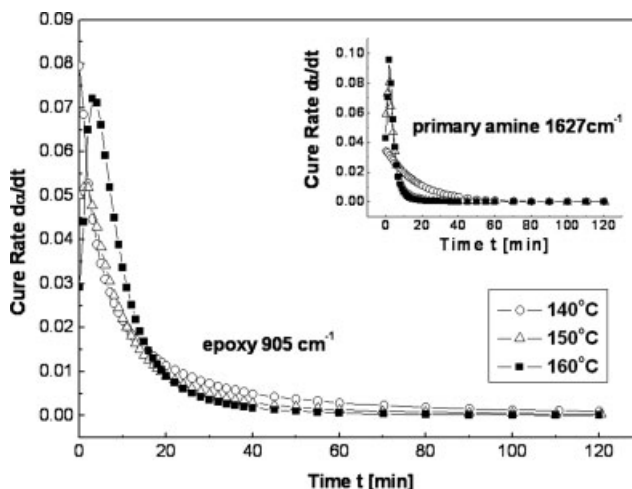

Figure 8 Cure rate as a function of time at different isothermal temperatures for the primary amine and epoxy groups within the AS4/8552 prepreg.
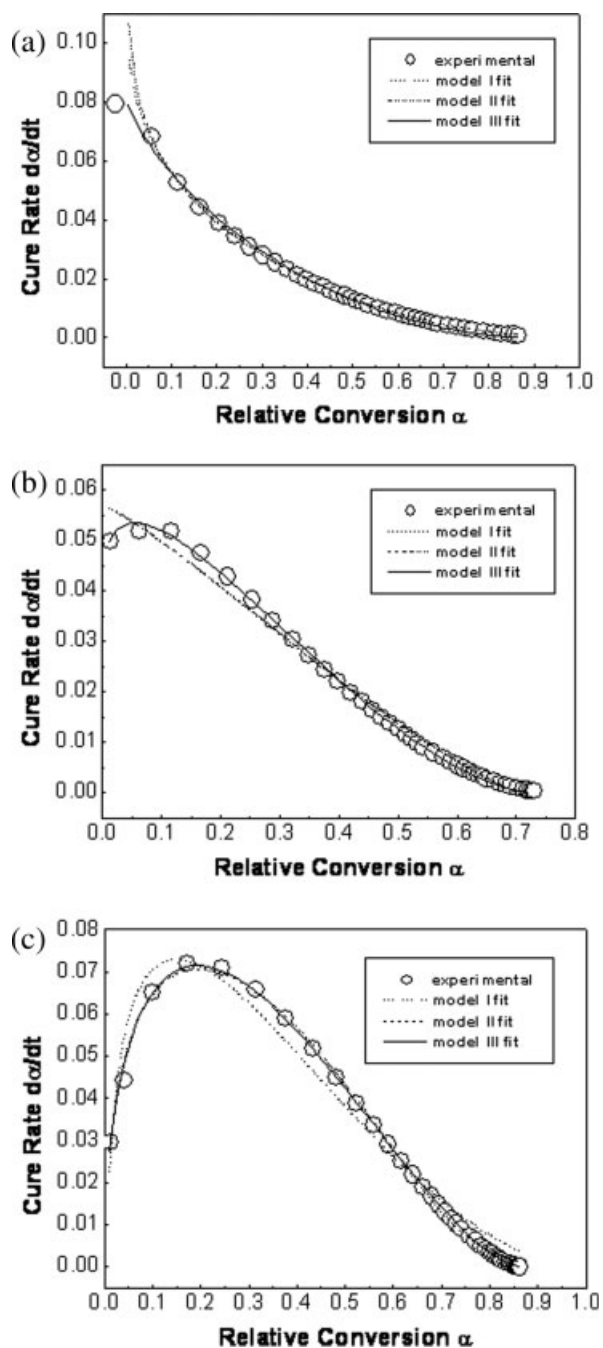
Figure 9 Comparison among the experimental data and different model predictions for the AS4/8552 prepreg isothermally cured at (a) 140, (b) 150, and (c) 160°C.

Isothermal curing of the AS4/8552 prepreg system

FTIR spectroscopy

Figure 6 shows a stack of FTIR spectra collected during the first 40 min when the AS4/8552 prepreg was isothermally cured at 160°C. Differential spectra for the cure up to 120 min are presented in Figure 7. Similar to the T800H/3900-2 prepreg, the absorbance at 1627 cm^{-1} [δ(NH$_2$)] and 905 cm^{-1} [v(C—O—C)] were used for quantitative analysis for the consumption of primary amine and epoxy groups, respectively. The most commonly used reference peak 1514 cm^{-1} (the ring stretching mode of TGDDM) shows great variation with time, therefore it is not suitable for normalization. As seen from Figure 7, the absorbance at 1188 cm^{-1} [v(Ar—C—Ar)][21] is the least variant peak. Therefore, it was chosen as the reference peak for normalization.

Quantitative analysis

The $d\alpha/dt$ versus α data for both the primary amine and epoxy groups within the AS4/8552 prepreg resin are shown in Figure 8. Comparing with the T800H/3900-2 prepreg, not only the epoxy group shows autocatalytic empirical rate curves but also the primary amine group exhibits autocatalytic nature. The primary amine reactions are catalyzed by species capable of hydrogen bonding either from the original hydroxyl groups from impurities presented in the commercial resin or hydroxyl groups produced in the addition reaction.

Figure 9 presents the experimental ($d\alpha/dt$) versus α data, along with the prediction curves from three models for the AS4/8552 prepreg cured at 140, 150, and 160°C. Similar to the results for the T800H/3900-2 prepreg, the higher the curing temperature, the higher the α when the maximum $d\alpha/dt$ occurs. Comparing the three prediction approaches, model III gave the most satisfactory fitting to the experimental data. The kinetic parameters derived from model III for the AS4/8552 prepreg isothermally cured at different temperatures are presented in Table II. The R^2 values for the fitting of model III were between 0.9944 and 0.9990 indicating satisfactory predictions.

TABLE II
Kinetic Parameters Derived from the Autocatalytic Model III Fitting for Isothermal Cure Process of the AS4/8552 Prepreg

Temperature (°C)	k_1 ($\times 10^{-2}$ min^{-1})	k_2 ($\times 10^{-1}$ min^{-1})	n	α_{max} ($\times 10^{-1}$ min^{-1})	R^2	χ^2
140	10.36	0.66	1.48	8.65	0.9944	1.38E−6
150	6.05	1.10	1.67	7.30	0.9990	2.66E−7
160	0.23	2.85	1.55	8.61	0.9990	5.69E−7

R^2 and χ^2 are statistics parameters.

CONCLUSIONS

This work has investigated the isothermal cure of two aerospace prepregs, T800H/3900-2 and AS4/8552, based on the FTIR spectroscopy data. Autocatalytic models were applied to simulate the cure conversion of reacting epoxy bands. Good agreement has been found between experimental data and the model predictions for these two systems when the epoxy-amine reaction was assumed to be a second order autocatalytic process. The model which takes into account both the second order autocatalytic nature and an empirical term, the final relative conversion at different isothermal temperature, gives the best simulation of the experimental data for both systems.

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