

Behavior of Volatile Depletion for LaRCTM-PETI-5 Amide Acid/*N*-Methylpyrrolidinone Solution

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Received 19 February 2002; accepted 26 February 2003

ABSTRACT: The fabrication of composites from polyimide precursors (polyamide acids) that involve condensation reactions requires the removal of volatiles (solvent and reaction by-products) prior to consolidation in order to achieve a void-free laminate. Volatile removal is commonly accomplished with a B-stage processing step. In this study, a PETAA/NMP (phenylethynyl terminated amide acid in *N*-methylpyrrolidinone) solution and prepreg were characterized using thermogravimetric analysis (TGA) and microdielectrometry. A master weight loss profile was constructed by superimposing measurements at various heating rates. The TGA results correlated well with the dielectric ionic conductivities. Under the same thermal conditions, volatiles were depleted at slower rates from the wet prepreg than the neat

resin solution. Dielectric properties were more sensitive to the residual volatile contents than the TGA measurements in both the neat resin and wet prepreg. Dielectric sensing technology was demonstrated to be a feasible tool for future volatile management in the fabrication of PETI composites. This study demonstrates that the combination of TGA and dielectrometry provides useful information to develop proper processing conditions for composite fabrication from prepreps containing volatiles. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1906–1916, 2003

Key words: polyimide; polyimide composite; volatile management; LaRCTM-PETI-5

INTRODUCTION

Polyimides¹ based on phenylethynyl-terminated imides (PETI) have been studied in various applications in recent years.^{1–6} The phenylethynyl endcap offers distinct advantages over the simple ethynyl endcap. The phenylethynyl group is chemically and thermally more stable than the ethynyl group, which allows it to remain unchanged during harsh synthetic conditions and affords oligomers with greater processing windows.

In the synthesis of phenylethynyl amide acid (PETAA), solutions were prepared in *N*-methylpyrrolidinone (NMP) at 30% solids content (w/w). The selected stoichiometric imbalance results in a theoretical number average molecular weight (M_n) of ~5000 g/mol. Unidirectional long-fiber-reinforced prepreps are manufactured by impregnating the PETAA/NMP solution onto the IM7 fiber tows. Composite laminates are fabricated by laying prepreg plies to the desired thickness and orientation, and consolidated by press or autoclave.

Volatile removal from the wet prepreps prior to the consolidation is a critical issue in composite fabrica-

tion. Like many polyimides, the PETAA/NMP system releases a reaction by-product (water) during the imidization reaction. In composite fabrication, volatiles (i.e., NMP and water) have to be depleted before applying pressures to achieve void-free quality laminates. The boiling point of NMP (~200°C) falls within the temperature range (150–250°C) of the imidization reaction. Any attempt of depleting the carrier solvents from the composites leads to higher melt viscosity. A molding cycle that includes 250°C/1 h B-stage and 371°C/200 psi consolidation has been successfully designed for the PETI-5. Residual volatiles are <1% w/w after the B-stage and the consolidated laminates (up to 12" × 12" and 24 plies) are void-free and exhibit very good mechanical properties.⁷ For these small parts, the imidization and crosslinking reactions (minimal, if any) occurring in the PETAA/NMP matrix during the 250°C/1 h B-staging period did not compromise matrix resin processability to an unacceptable level.

Fabrication of thick PETI-5 composite parts requires careful control of process conditions. These thick structural components include applications such as face sheets for sandwich structures (1/4"–3/8", 50–75 plies), skins for skin stringer structures (0.3"–0.5", 60–100 plies), and wing box structures (1", 200 plies). The issue of scale-ability of the PETI composites has to be resolved. Larger and thicker parts are difficult to heat up uniformly in an autoclave. A longer hold time (up to several hours) is often needed at the B-stage tem-

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perature. At any given time during the curing, non-uniform part temperature distributions exist, which results in nonuniform distributions of the degrees of imidization and crosslinking reactions in the resin matrix. Consequently, the processability of the matrix resin is compromised, and the volatile depletion mechanism is distorted in these composite parts. However, large void-free laminates of PETI-5 have been successfully fabricated.⁸

One solution to this problem is to implement an intelligent processing methodology or an expert system during composite fabrication. Before implementing this technology, a thorough understanding of the processing and properties of the subject material system must first be acquired. The work reported herein concerns the behavior and the remote sensing for the volatile removal in the PETAA/NMP prepreg.

EXPERIMENTAL[†]

Materials

Monomers used in the synthesis of the PETAA/NMP solution were 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, Ube Industries, Ltd., NY, mp 295–297°C), 3,4'-oxydianiline (3,4'-ODA, Mitsui Toatsu Chemical, Inc., Japan, mp 72–74°C), 1,3-bis(3-aminophenoxy)benzene (APB, Mitsui Toatsu Chemical, Inc., mp 105.5–107°C), and 4-phenylethynylphthalic anhydride (PEPA, Imitec, Inc., NY, mp 151–152.5°C). These monomers were used as received. The synthetic scheme for preparing the LARCTM-PETI-5 has been reported previously.⁸ The PETAA/NMP solution studied (lot no. 050-055) was manufactured by Imitec, Inc., Schenectady, New York, with a solid content of 35% w/w. Unitape wet prepreg (HYE PETI/IM lot no. 80202Q, 24" wide) was manufactured by Fiberite, Inc., Greenville, TX. This batch of prepreg possessed 22.5% w/w volatile at 600°F, 144.5 g/m² fiber area weight (FAW), and 35% w/w resin content.

Thermogravimetric analysis (TGA)

The weight loss behavior for both neat resin/NMP and prepreg were measured using a Seiko TG/DTA 220 thermogravimetric analyzer in a flowing air (40 mL/min) environment. Temperature profile included an initial ramp from 20 to 250°C with 4 h hold, followed by a second ramp from 250 to 371°C and hold for 5 min. Four heating rates at 0.56, 1.1, 2.2, and 4.4°C/min were employed.

[†]Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

Dielectric properties

A Micromet Eumetric[®] System III microdielectrometer⁹ was used with disposable IDEX sensors. Sensors were used as received either coated with the PETAA/NMP solution or imbedded inside a stacked laminate. The temperature was ramped initially from room temperature (RT) to 250°C, held for 2 hs, followed by a ramp to 371°C and a hold for 1 h. A heating rate of 1.1°C/min was employed. Relative permittivity (i.e., dielectric constant), $\epsilon'(t)$, and loss factor, $\epsilon''(t)$, were measured at 5 discrete frequencies ranging from 10 to 100,000 Hz during the temperature ramp.

RESULTS AND DISCUSSION

Volatile depletion behavior of resin solution by TGA

Weight loss measurements for the PETAA/NMP solution at 1.1°C/min are shown in Figure 1. The rates of weight loss (RWL) during measurement are also included in the figure. Two distinct weight loss processes are evident, with double peaks observed in the RWL curve. The first peak occurred at 82.7°C with a residual weight fraction of 75.3% and the second peak occurred at 136°C with a 51.5% residual weight fraction. A majority of weight losses were completed at 250°C during the temperature ramp. Less than 1% of the weight losses occurred during the subsequent 250°C/4 h hold followed by the ramp to 371°C. The solution had a solid content of 31.2% w/w based upon the fully cured imide oligomers as obtained from the measurement (Fig. 1). A value of 35% based upon monomers molar weights ratio was reported by the manufacturer.

Figure 2 illustrates the heating rate dependence of the weight loss behavior. As the heating rate increased, weight loss profiles shifted to the higher temperature regions. Characteristics at which the peaks of the RWL occurred are summarized in Table I. It is evident from Table I that while temperatures at the peaks increased with the increasing heating rate, the residual weight fractions at the two peaks (75 and 51%, respectively) remained approximately the same. This behavior of volatile depletion helps in the autoclave fabrication of composite, especially for complex thick parts in which nonuniform temperature gradients are commonly experienced during the heat-up periods.

Master weight loss curve for the PETAA/NMP solution

The similarity among the weight loss curves in Figure 2 suggests that a master weight loss curve can be constructed. A reference heating rate, $\dot{T}_r = 1.1^\circ\text{C}/\text{min}$, is selected. A time-temperature shift factor is defined as

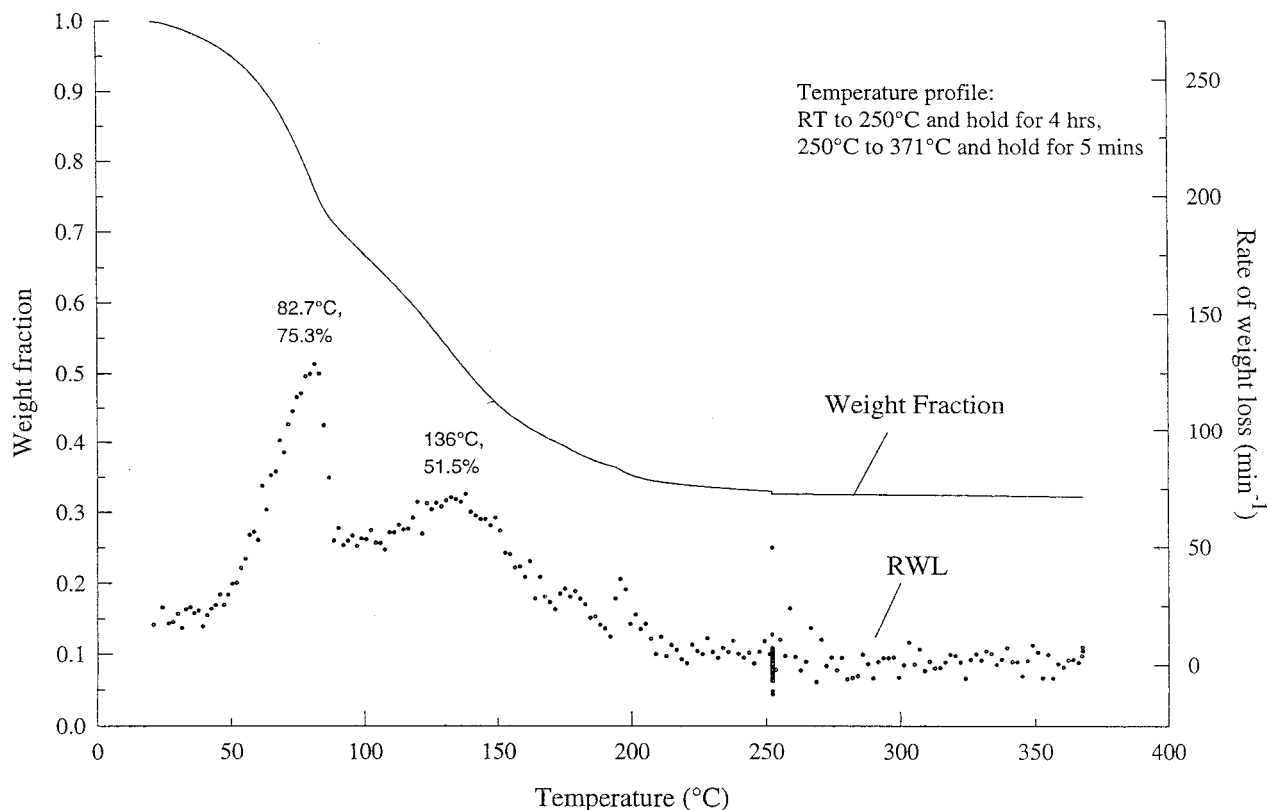


Figure 1 Weight loss profiles of PETI-5/NMP resin at 1.1°C/min determined by TGA.

$$a_T = \frac{T}{T_r} \quad (1)$$

The weight loss curve at 0.56°C/min is shifted on a logarithmic scale to higher temperatures until it is superimposed with the reference weight loss curve at 1.1°C/min. Similarly, the weight loss curves at higher heating rates are shifted to lower temperatures. The resulted values of a_T are shown in Table II. Two sets of a_T are derived that account for the two distinct weight loss processes discussed previously.

For weight fractions ≥ 0.7 , the following equation is obtained by the linear least square regression, which gives a correlation $r^2 = 0.983$:

$$a_T = -0.451 \cdot \log\left(\frac{\dot{T}}{\dot{T}_r}\right) + 1.0 \quad (2a)$$

For weight fractions < 0.7 , the following equation is obtained similarly with a correlation $r^2 = 0.987$:

$$a_T = -0.313 \cdot \log\left(\frac{\dot{T}}{\dot{T}_r}\right) + 1.009 \quad (2b)$$

The superimposed master curve at the reference heating rate is shown in Figure 3. In an attempt to derive

an analytical formula for the master weight loss curve, we begin by postulating

$$WLF_{volatiles,t} = 1 - \exp(-k_r \cdot \dot{T}_r \cdot t^{n_r}) \quad (3a)$$

where $WLF_{volatiles,t}$ is the weight loss fraction of volatile at time t . The rate constant is k_r , and n_r is the order of weight loss. The subscript r refers to the reference heating rate. We also have

$$WLF_{volatiles,t} = (W_{volatiles,t_0} - W_{volatiles,t}) / W_{volatiles,t_0} = 1 - (W_{resin,t} - W_{solid}) / (W_{resin,t_0} - W_{solid}) \quad (3b)$$

where $W_{volatiles,t}$ is the weight of volatile (NMP + water) at time t , $W_{volatiles,t_0}$ is the initial weight of volatile (NMP + water) at time t_0 , $W_{resin,t}$ is the weight of resin solution (solid + volatile) at time t , W_{resin,t_0} is the initial weight of resin at time t_0 , and W_{solid} is the weight of PETI5 molecules, a constant. Combining eqs. (3a) and (3b), we have

$$WF_{resin,t} = WF_{solid} + (1 - WF_{solid}) \cdot \exp\{-k_r \cdot \dot{T}_r \cdot t^{n_r}\} \quad (3c)$$

in which $WF_{resin,t}$ ($=W_{resin,t}/W_{resin,t_0}$) is the resin weight fraction at t as measured by TGA, and WF_{solid}

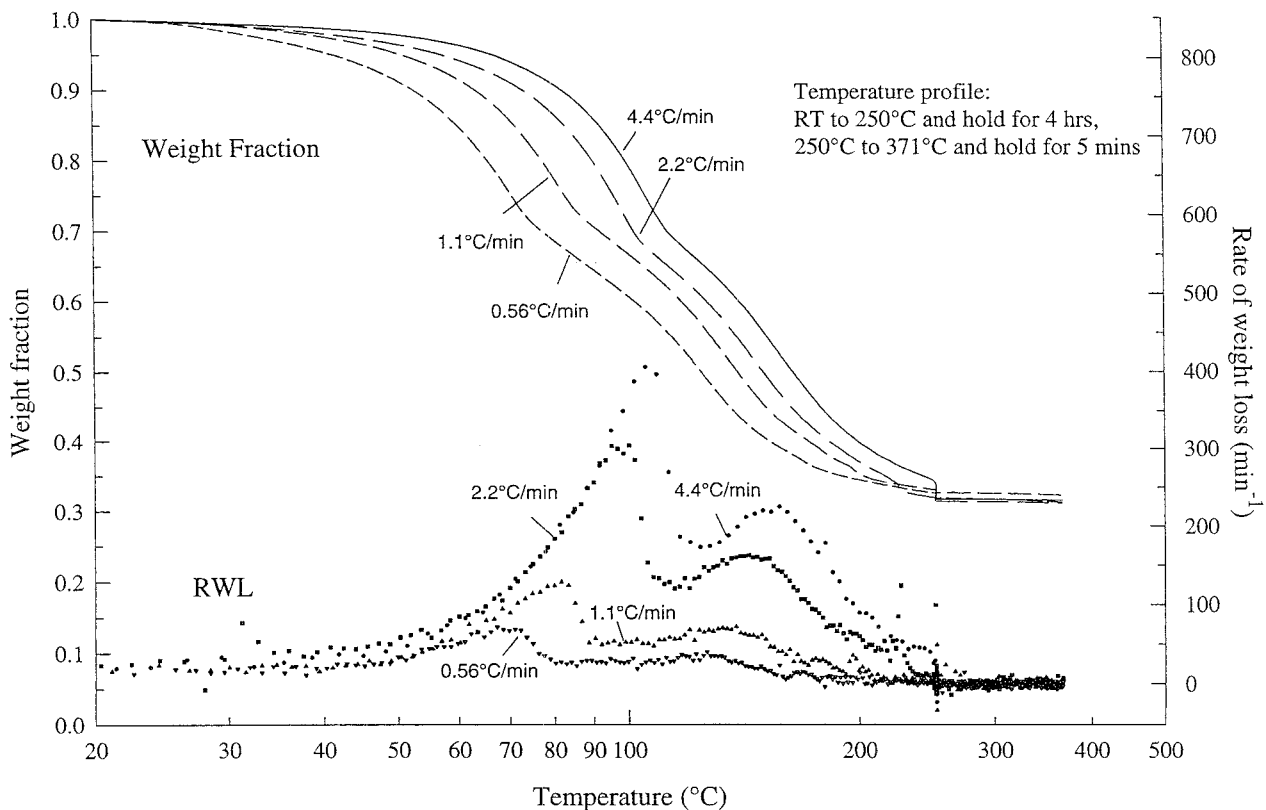


Figure 2 Weight loss profiles of PETI-5/NMP resin at various heating rates determined by TGA.

($=W_{\text{solid}}/W_{\text{resin},t_0} = 0.312$) is the solid weight fraction, also measured by TGA. Considering the existence of two distinct volatile depletion stages in Figure 1, eq. (3c) was generalized to become

$$WF_{\text{resin},t} = 0.312 + m \cdot \exp\{-k_r \cdot \dot{T}_r \cdot (t - t_s)^{n_r}\} \quad (4)$$

where m is the pre-exponential constant and t_s is time shift. Values of m , k_r , t_s , and n_r were determined empirically and are given in Table III. Equation (4) is plotted in Figure 3 by the solid curve. It is evident that agreement between the model and the experimental profile is satisfactory.

Because $T_r = T_0 + \dot{T}_r \cdot t$, where T_0 is the initial temperature of the TGA measurement, we have

$$\dot{T}_r \cdot (t - t_s) = \frac{T}{a_T} - T \quad (5)$$

Substituting eq. (5) into eq. (4), we obtain

$$WF_{\text{resin},t} = 0.312 + m \cdot \exp\left\{-k_r \cdot \left(\frac{T}{a_T} - T_0\right) \cdot (t - t_s)^{n_r-1}\right\} \quad (6)$$

Combined with eqs. (2a) and (2b), eq. (6) can be used to simulate the TGA weight loss profiles at various heating rates.

Volatile depletion behavior of PETAA/NMP prepreg

Weight loss curves for PETAA/NMP prepreg measured by TGA at various heating rates are shown in Figure 4. Prepreg weight loss behavior is also heating rate dependent. The two distinct weight loss processes, observed for the PETAA/NMP resin in Figure

TABLE I
Characteristics of Maximum Rates of Weight Loss at Various Heating Rates for PETI-5/NMP Poly(amide acid) Solution

Heating rate (°C/min)	First peak		Second peak	
	T (°C)	Residual wt fraction (%)	T (°C)	Residual wt fraction (%)
0.56	70.4	75.4	123	50.1
1.1	82.7	75.3	136	51.1
2.2	95.8	75.3	150	50.5
4.4	108.2	72.9	156	53.2

TABLE II
Time-Temperature Shift Factors for the Weight Loss Profiles of PETI-5/NMP Poly(amide acid) Solution

\dot{T} (°C/min)	\dot{T}/\dot{T}_r	a_T	
		wt Fraction ≥ 0.7	wt Fraction < 0.7
0.56	0.509	1.143	1.111
1.1	1.0	1.000	1.000
2.2	2.0	0.833	0.900
4.4	4.0	0.750	0.833

2, were absent in this case. This is attributed to the presence of predominant fiber fraction, which affects the resolution of weight loss measurements by TGA. At the end of the 371°C/5 min hold, the residual weight fractions ranged between 85.1 and 86.3% w/w, which translates into approximately 15% w/w volatile content. This content level is lower than 22.5% w/w reported by the prepreg manufacturer, probably due to the loss of solvent during material handling.

A master weight loss curve for the prepreg at the reference heating rate of 1.1°C/min is shown in Figure 5. The derived shift factors are given in Table IV. From the linear least square regression, we obtain

$$a_T = -0.293 \cdot \log(\dot{T}/\dot{T}_r) + 1.004$$

with a correlation $r^2 = 0.987$.

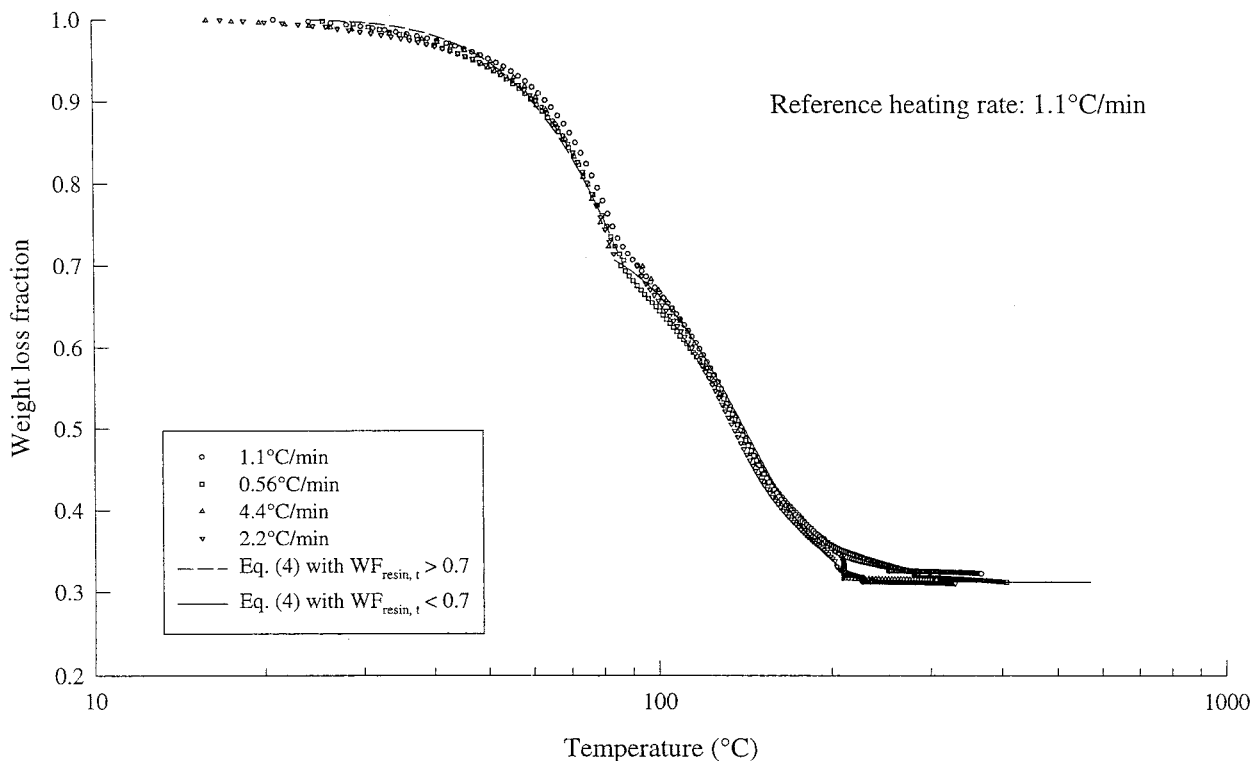


Figure 3 Master weight loss profile for PETI-5/NMP resin determined from time-temperature superposition.

TABLE III
Parameter Values for Equation (4)

	m	t_s	k_r	n_r
$WF_{resin,t} \geq 0.7$	0.688	0	0.000018	2.50
$WF_{resin,t} < 0.7$	0.420	30	0.000018	2.42

Following a similar procedure, an analytical equation is formulated for the master weight loss curve of the prepreg at 1.1°C/min reference heating rate:

$$WF_{prepreg,t} = WF_{solid+fiber} + (1 - WF_{solid+fiber}) \cdot \exp(-k_p \cdot \dot{T}_r \cdot t^{n_p}) \quad (7)$$

in which $WF_{solid+fiber} (=W_{solid+fiber}/W_{prepreg,t_0} = 0.855)$, is obtained from TGA measurement.

Equation (7) is also plotted in Figure 5 with $k_p = 0.000034$ and $n_p = 2.15$. Comparisons between the experimental data and the model predictions appear satisfactory. In composite fabrication such as autoclave processes, master curves of eqs. (6) and (7) are useful in monitoring volatile depletion profiles at various heating rates when an online measuring device, such as microdielectrometer, is implemented.

Correlation between weight losses in PETAA/NMP solution and prepreg

It is interesting to compare the volatile depletion mechanism in the neat resin solution with the fiber

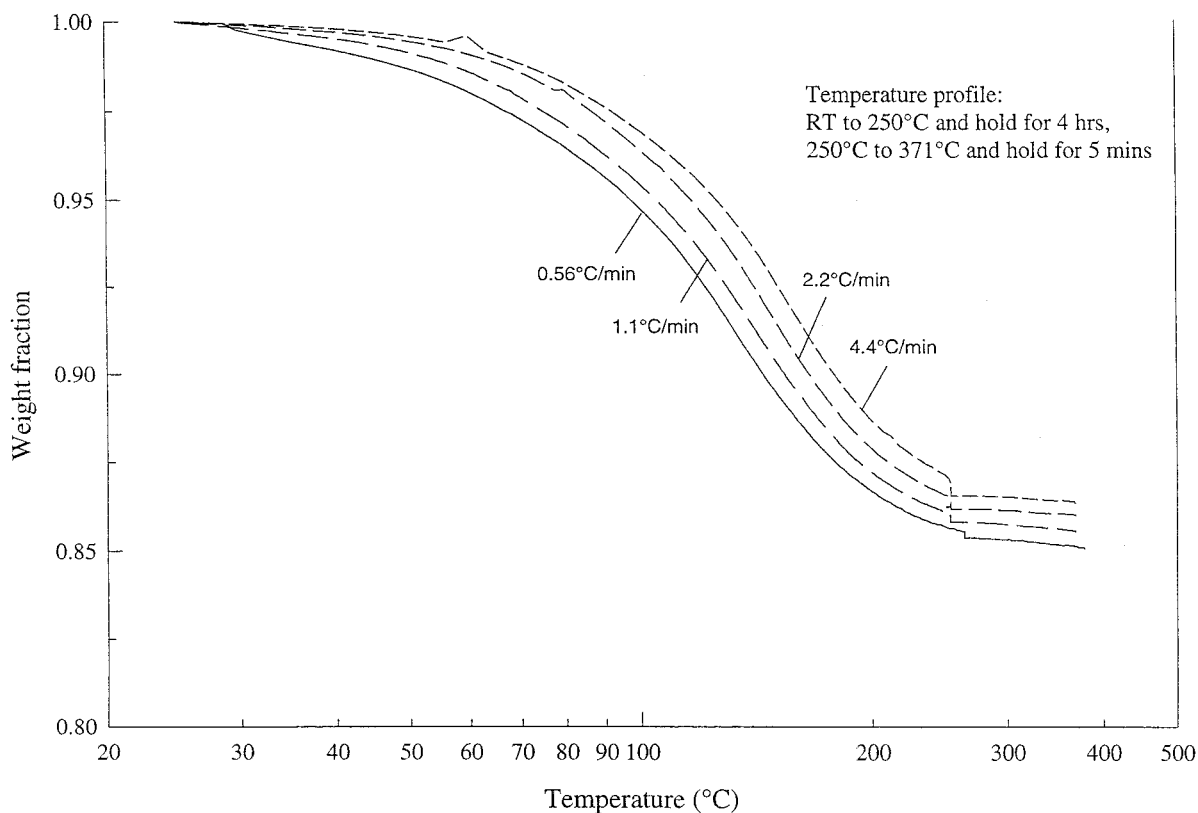


Figure 4 Weight loss profiles of PETI-5/NMP prepreg at various heating rates determined by TGA.

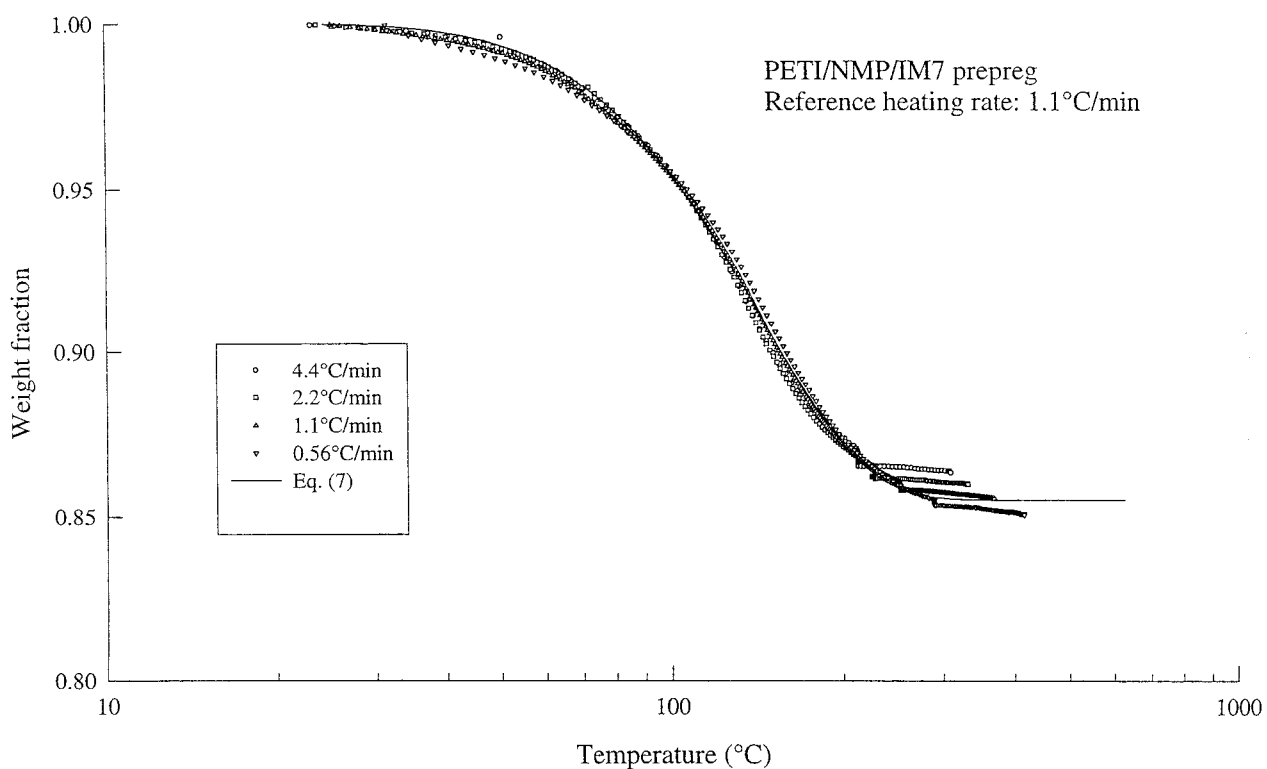


Figure 5 Master weight loss profile for PETI-5/NMP resin determined from time-temperature superposition.

TABLE IV
Time-Temperature Shift Factors for the Weight Loss
Profiles of IM7/PETI-5/NMP Prepreg

\dot{T} (°C/min)	\dot{T}/\dot{T}_r	a_T
0.56	0.509	1.098
1.1	1.0	1.000
2.2	2.0	0.900
4.4	4.0	0.840

reinforced prepreg. We first consider the prepreg material:

$$WF_{\text{prepreg}}(t) = \frac{x + y(t) + z}{x + y_0 + z} \quad (8)$$

where $WF_{\text{prepreg}}(t)$ is the prepreg weight fraction profile measured by TGA, x is the polymer solid weight in prepreg, a constant, $y(t)$ is the volatile (NMP+water) weight in prepreg at time t , y_0 is the initial weight of volatile (NMP+water) in the wet prepreg, and z is the fiber weight in prepreg, a constant.

From TGA measurements in Figure 5, we obtain $WF_{\text{prepreg}}(0) = 1.0$ and $WF_{\text{prepreg}}(\infty) = 0.855$, or $y_0/(x + y_0 + z) = 1 - 0.855 = 0.145$. Equation (8) gives

$$\frac{y(t)}{y_0} = 6.897 \cdot \{WF_{\text{prepreg}}(t) - 0.855\} \quad (9)$$

Next we consider the neat resin/NMP solution. Let

$$WF_{\text{solution}}(t) = \frac{\alpha + \beta(t)}{\alpha + \beta_0} \quad (10)$$

where $WF_{\text{solution}}(t) = WF_{\text{solid} + \text{volatile}}(t)$, the resin/NMP solution weight fraction profile by TGA, α is the polymer solid weight in solution, a constant, $\beta(t)$ is the volatile (NMP+water) weight in solution at time t , and β_0 is the initial weight of volatile (NMP+water) in the solution.

From TGA measurements in Figure 3, we obtain $WF_{\text{solution}}(0) = 1.0$ and $WF_{\text{solution}}(\infty) = 0.312$, or $\beta_0/(\alpha + \beta_0) = 1 - 0.312 = 0.688$. Equation (10) becomes

$$\frac{\beta(t)}{\beta_0} = 1.454 \cdot \{WF_{\text{solution}}(t) - 0.312\} \quad (11)$$

If the rates of volatile depletion in the neat resin solution and the wet prepreg were assumed identical, i.e.,

$$\frac{\beta(t)}{\beta_0} = \frac{y(t)}{y_0} \quad (12)$$

then we have

$$WF_{\text{prepreg}}(t) = 0.855 + 0.211 \cdot \{WF_{\text{solution}}(t) - 0.312\} \quad (13)$$

The calculated $WF_{\text{prepreg}}(t)$ from eq. (13) and the measured profile from TGA are compared in Figure 6. Appreciable differences suggest that under the same thermal conditions, volatiles (NMP and water) were depleted at slower rates from the wet prepreg than the neat resin solution.

Volatile depletion behavior of resin solution by microdielectrometry

A single ramp at 1.1°C/min from RT to 250°C and a hold for 2 h was employed to simulate the B-stage and to study volatile depletion behavior by the microdielectrometer. Dielectric loss factor (ϵ'') and dissipation factor ($\tan\delta = \epsilon''/\epsilon'$) are recorded in Figures 7 and 8. Measurements were conducted at 10, 10², 10³, 10⁴, and 10⁵ Hz. During the temperature ramp, significant changes in the dielectric properties were initially measured at around 125° to 150°C. Beyond this temperature, the loss factors dropped monotonically. This suggests that the imidization reactions started at around 135°C and continued into the 250°C/2 h hold period. Evaporation of NMP and the reaction by-product (water) led to an increase in resin viscosity and consequently a decrease in the dielectric loss factor. The rate of decrease for the loss factors became slower along the temperature ramp-and-hold period, as expected. At the end of 250°C/2 h hold, finite rates of a much slower decrease in the loss factors were still measurable. Under the same thermal history, residual volatiles measured previously by the TGA were less than 0.2% w/w.⁸ This suggests that the dielectric loss factor is a more sensitive property that can be used to monitor volatile depletion in composite fabrication.

For a relaxation process with a single relaxation time, an ideal relationship expressed by the Debye equation¹⁰ is

$$\tan \delta = \frac{(\epsilon_u - \epsilon_r)\omega\tau}{\epsilon_r + \epsilon_u\omega^2\tau^2} \quad (14)$$

where τ is the relaxation time, ω is angular frequency, ϵ_r and ϵ_u are the relaxed and unrelaxed dielectric constants, respectively. Value of τ is a measure of the time required by the dipoles in the polymer chains to orient in response to changes in the applied electrical field. The more the dipoles are constrained, the larger the value of τ . During the ramp-and-hold period, values of τ change (both increasing and decreasing) continuously. By differentiating eq. (14) with respect to τ , we obtain

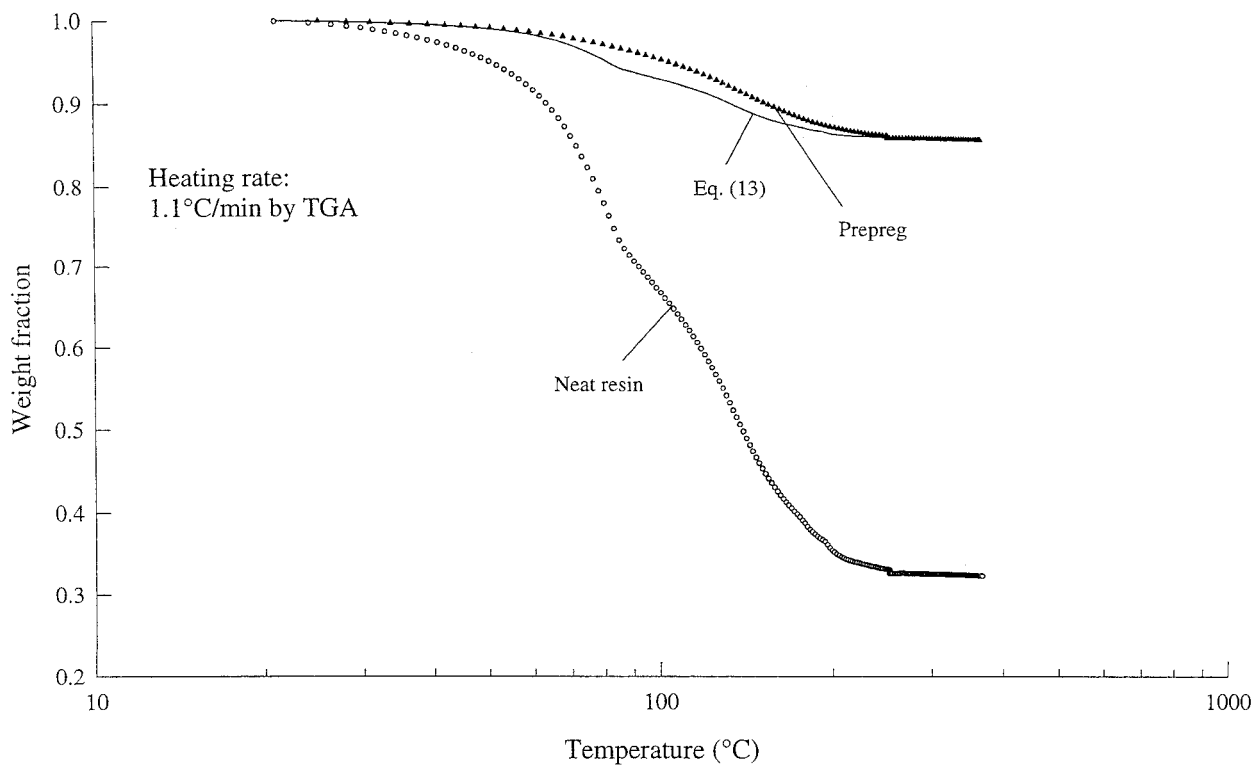


Figure 6 Comparison between measured and calculated weight loss profiles for the PETI-5/NMP system.

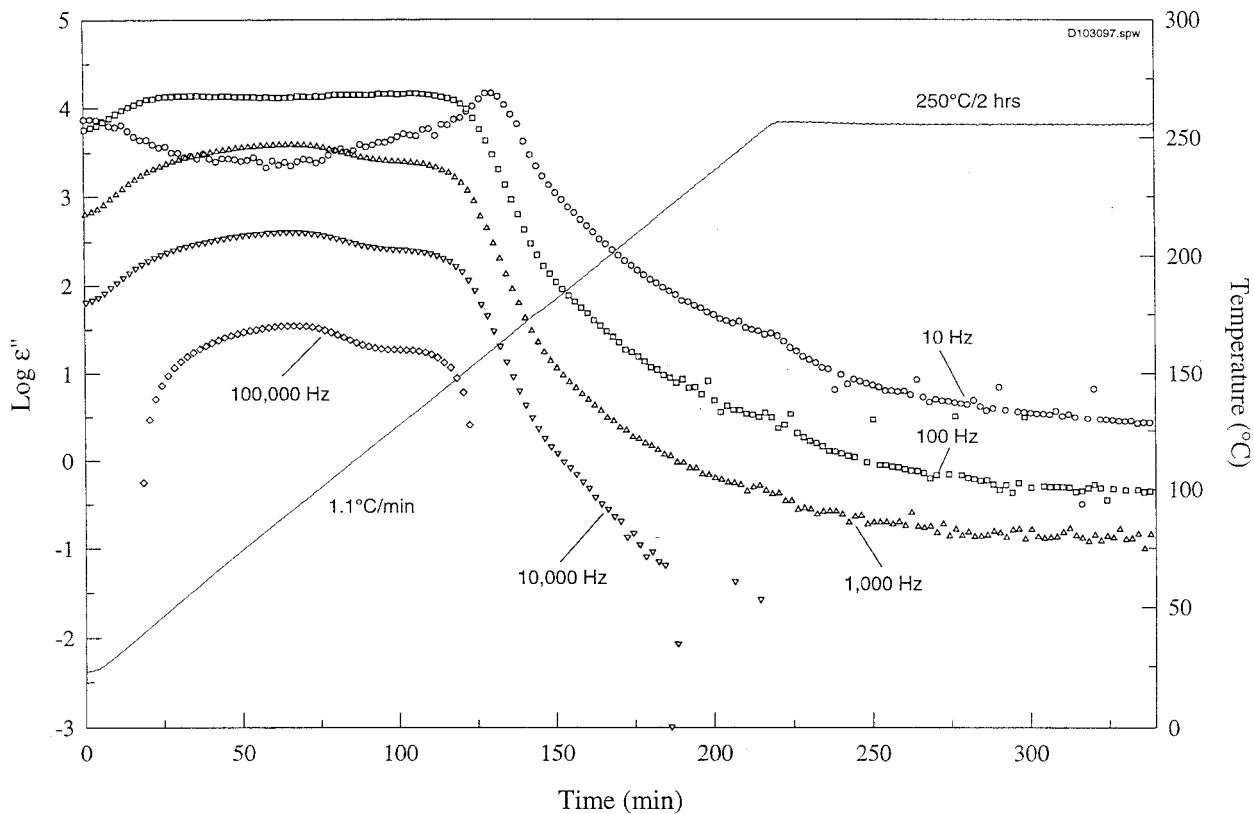


Figure 7 Dielectric loss factor of PETI-5/NMP neat resin during temperature ramp-and-hold.

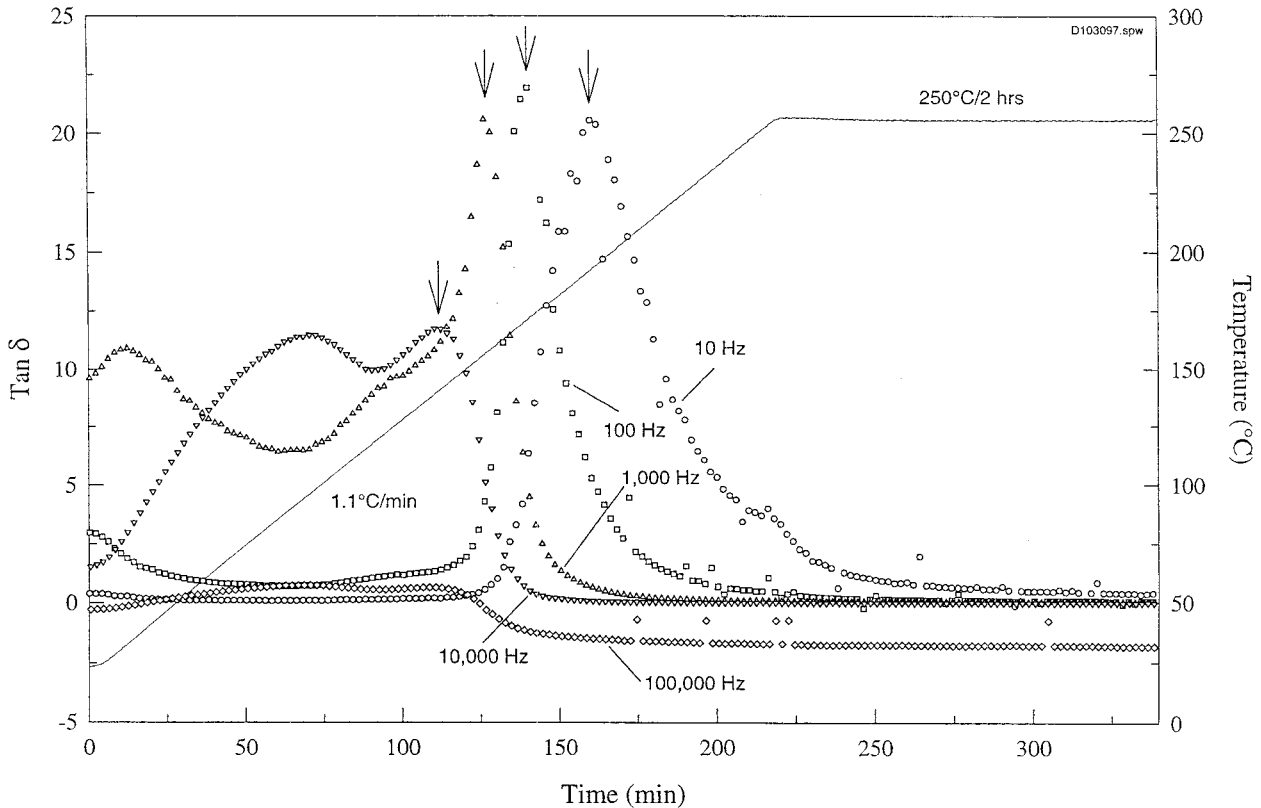


Figure 8 Dielectric dissipation factor of PETI-5/NMP neat resin during temperature ramp-and-hold.

$$\tau_{\max} = \left(\frac{\epsilon_r}{\epsilon_u} \right)^{1/2} \cdot \frac{1}{\omega} \quad (15)$$

where τ_{\max} is the relaxation time at which $\tan \delta$ is a maximum. Values of τ_{\max} are inversely proportional to the measuring frequencies. By substituting eq. (15) into eq. (14), the maximum value of $\tan \delta$ is shown to be a constant and given by

$$\tan \delta_{\max} = \frac{\epsilon_u - \epsilon_r}{2(\epsilon_r \epsilon_u)^{1/2}} \quad (16)$$

Thus, as the temperatures increase during the ramp, values of τ increase (i.e., due to the imidization reaction and the continuous depletion of volatiles, resulting in an increase in the viscosity), and the $\tan \delta$ responses will show a series of maxima (peaks) at succeeding lower frequencies. This behavior can be observed in Figure 8: except for the 10^4 Hz measure-

ment, $(\tan \delta)_{\max} = 20$ are found to be approximately the same for all other frequencies. Equation (16) can be solved for the ratio ϵ_r/ϵ_u :

$$\frac{\epsilon_r}{\epsilon_u} = 1 + 2 \cdot (\tan \delta)_{\max}^2 - 2 \cdot \tan \delta_{\max} \cdot \sqrt{1 + (\tan \delta)_{\max}^2} \quad (17)$$

Values of τ_{\max} , $(\tan \delta)_{\max}$, ϵ_r/ϵ_u , and $\tau_{\max} \omega/2\pi$ are shown in Table V. The $\tau_{\max} \omega/2\pi$ values are found at the order of 10^{-3} , which suggests that the temperature ramp rate is sufficiently low and its effect on the measured relaxation times is negligible.

Frequency independent ionic conductivity (σ) was derived from the loss factor measurements¹¹⁻¹³ and compared to the weight loss profiles in Figure 9. Both measurements were conducted at 1.1°C/min. At temperatures <150°C, the double maximum peaks in the

TABLE V
Change of Relaxation Time During Temperature Ramp at 1.1°C/min

$\omega/2\pi$ (Hz)	$\tan \delta_{\max}$	ϵ_r/ϵ_u	τ_{\max} (s)	$\tau_{\max} \cdot \omega/2\pi$	t_{peak} (min)	T_{peak} (°C)
10,000	11.73	1.81×10^{-3}	6.77×10^{-7}	6.77×10^{-3}	112	141
1,000	20.54	5.92×10^{-3}	3.87×10^{-6}	3.87×10^{-3}	128	158
100	21.91	5.21×10^{-3}	3.63×10^{-5}	3.63×10^{-3}	142	173
10	20.54	5.92×10^{-3}	3.87×10^{-4}	3.87×10^{-3}	160	192

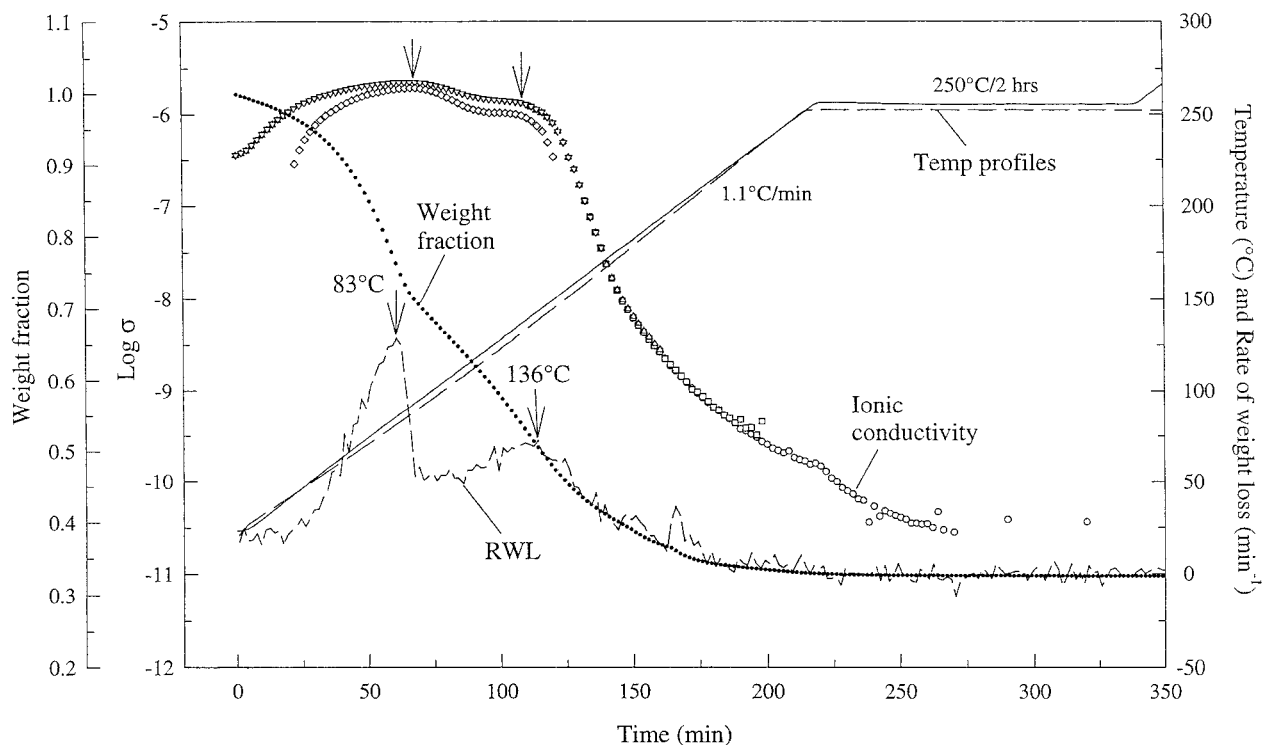


Figure 9 Correlation between weight loss and dielectric ionic conductivity of PETI-5/NMP resin during temperature ramp-and-hold.

$\sigma(t)$ curve coincided approximately with the peaks (at 83 and 136°C, respectively) in the RWL profile, which corresponded to the two distinct weight loss processes during the B-stage period of PETAA/NMP solution discussed before. Values of $\sigma(t)$ remained relatively high at temperatures below 135°C where the residual weight fractions remained >50% w/w. As soon as the temperatures passed 135°C, values of σ dropped sharply, even though the RWL were slowing down as measured by the TGA. When temperature reached 250°C, values of $\sigma(t)$ continued to decrease and the weight losses became no longer detectable. This observation suggests that dielectric measurements are more sensitive to the volatile depletion than TGA.

Volatile depletion behavior of PETAA/NMP prepreg by microdielectrometry

Ionic conductivity vs weight loss for the PETAA/NMP/IM7 prepreg is shown in Figure 10 together with the ramp-and-hold temperature profile. Bare IDEX sensors were initially imbedded in the midplane of a 6" × 6" - [0, 90]_{2s} laminate, which was sealed under a vacuum bag and heated between two hot platens in a molding press. Full vacuum was implemented during the entire cycle but no pressures were applied. It was seen that the sensor was wetted by the resin matrix at around 50°C, where the dielectric properties became measurable. The initial increase in the ionic conductivity was attributed to the softening of

the matrix resin during the temperature ramp. A sharp drop in ionic conductivity occurred at around 135°C, similar to that measured for the PETAA/NMP solution in Figure 9. Values of $\sigma(t)$ decreased approximately five orders of magnitude, followed by a small increase and eventually another decrease as the temperatures continued to rise. The valley and mountain peaks occurred at around 150 and 200°C, respectively. The brief increase in the $\sigma(t)$ profile between 150 and 200°C could be attributed to the melting of the crystalline regions, which were generated during the slow temperature ramp. The formation of crystalline regions has been previously observed in the oligomeric imides during thermal annealing (i.e., 1 h at temperature between 250 and 350°C) following a heating from RT with a much faster heating rate than 1.1°C/min.^{8,14} The presence of fibers may accelerate the formation of crystalline regions in the PETI/IM7 matrix. Similar to the neat resin in Figure 9, when temperature reached 250°C, values of $\sigma(t)$ continued to decrease and the weight losses became no longer detectable, suggesting that dielectric measurements are more sensitive to the volatile depletion than the TGA measurements in the prepreg system. Equation (7) allows the calculation of weight fraction profiles at different heating rates, which can be readily compared with the ionic conductivity measured online under the same condition providing a clear view of the volatile depletion behavior during composite molding process.

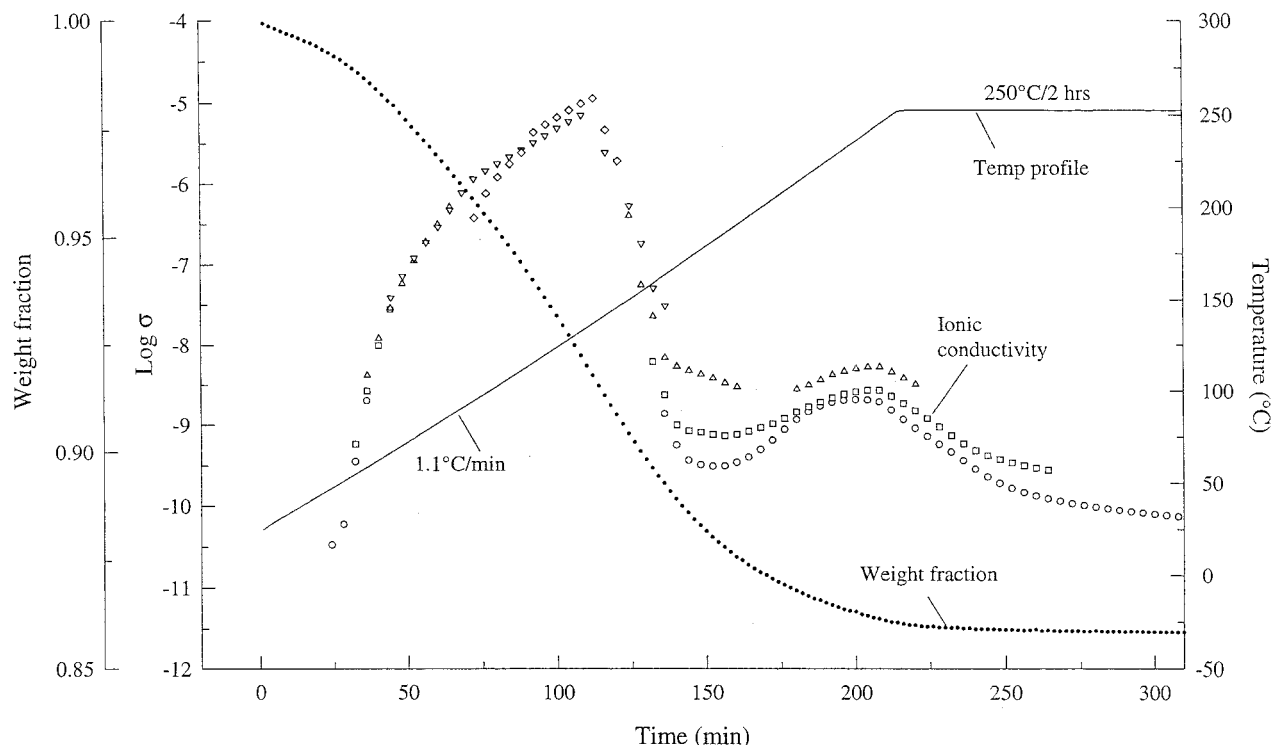


Figure 10 Correlation between weight loss and dielectric ionic conductivity of PETI-5/NMP prepreg during temperature ramp-and-hold.

CONCLUSIONS

Volatile depletion characteristics for PETAA/NMP solution and prepreg were investigated using TGA and microdielectrometry. Four heating rates between 0.56 and 4.4°C/min were employed, which simulated the autoclave processing conditions for composite fabrication. Volatile depletion behavior was found to be heating rate dependent. Using higher heating rates, the same amount of volatile removal was achieved at higher temperatures than that compared with the lower heating rate cases. Weight loss profiles at various heating rates, however, were superimposable to form a master weight loss curve. The time-temperature shift factors were derived, which allowed for the simulation of the weight loss profile at any given heating rate. Under the same thermal conditions, it was found that volatiles (NMP and water) were depleted at slower rates from the wet prepreg than the neat resin solution.

Volatile depletion characteristics as measured by the dielectrometry correlated well with the TGA at various heating rates. The dielectric properties were found to be more sensitive to the residual volatile level than the weight loss measurements. It was demonstrated that composite weight fraction profiles, conveniently calculated from the master curve, can be readily compared with the ionic conductivities measured online, providing a clear view of the volatile

depletion behavior during a composite molding process. It is conceivable that dielectric sensing technology can be applied to future process monitoring and control of PETI/NMP composite fabrication in an autoclave.

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