Characterization, Properties, and Processing of LaRC PETI-5 as a High-Temperature Sizing Material. II. Thermal Characterization

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ABSTRACT: In this publication the glass transition, melting behavior, cure behavior, and thermal stability of LaRC PETI-5 have been extensively studied utilizing differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The material used here was subjected to different thermal history (cumulative cure and individual cure) including an isothermal cure. The extent of cure for the partially cured resin was evaluated taking into account the residual solvent in the resin with the aid of a correction factor. The data show that the thermal history for the imidization reaction may influence the extent of cure for the partially cured LaRC PETI-5. The reaction of the C≡C bonds in the phenylethynyl groups located in the imide polymer chain ends is completed to produce a fully cured LaRC PETI-5 within 1 h at 350°C in air. The result is very consistent with the result obtained using Fourier Transform infrared (FT-IR) spectroscopy in the previous work. This study also demonstrates that no reaction takes place above 350°C prior to degradation. LaRC PETI-5 with a molecular weight of 2500 g/mol has excellent thermal stability up to 550°C as long as it is fully imidized. The result of the isothermal stability suggests that this material may be used without significant loss of its integrity for extended periods of time below 450°C. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1278–1287, 2000

Key words: phenylethynyl terminated imide oligomer, LaRC PETI-5, cure behavior, extent of cure, thermal stability

INTRODUCTION

Excellent high-temperature performance is one of the most desirable advantages of polyimides, especially aromatic polyimides in advanced applications. Polyimides have been extensively used in electronics industry[1] as coatings, films, or adhesives and also in composite industry[2] as a primary or secondary structural material. A potential use may be their application to organic or inorganic fibers, including carbon and glass fibers as a sizing material for high-temperature uses. The thermal characteristics including high-temperature stability and cure behavior are critical to achieve successful processing and properties of the resulting polyimide for these application. Advanced polymers for aerospace and aircraft applications must successfully sustain their properties for long exposures at use temperatures as high as 371°C.[3–5] The important parameters that affect the heat resistance of a material are its glass transition temperature (T_g), melting point (T_m), and thermal stability, which may be dependent on its thermal history. Accordingly, the polymers that are used to fulfill such high-temperature per-

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formance should exhibit a high T_g or T_m and excellent thermal stability. Although many polyimides meet the high-temperature requirement, their use has been limited due to processing difficulties such as poor solubility in common solvents, volatiles releasing during imidization, brittleness, and high processing temperature.[6]

Based upon research[7–11] performed recently at the NASA Langley Research Center, a phenylethynyl terminated polyimide designated as LaRC PETI-5 is of increasing interest for high-temperature applications due to its advantageous processing and properties. LaRC PETI-5 with molecular weight of 2500 g/mol has been shown to possess an excellent combination of processibility, high T_g, high toughness, and mechanical, physical, and chemical properties at elevated temperature, compared with other versions of phenylethynyl terminated polyimides.[12–14] Phenylethynyl terminated polyimides require high-temperature treatment to completely remove solvent and to convert the oligomeric precursor into a cured imide polymer. It has been clearly found from Fourier Transform infrared (FT-IR) spectroscopy studies in the previous paper[15] that the phenylethynyl groups located at the imide polymer chain ends complete their reaction through transformation of the C≡C bond into C═C bond by thermal cure within 1 h at 350°C in air producing a fully cured, three-dimensionally cross-linked structure.

In general, during resin processing the polymer is often exposed to a prescheduled temperature and time cycle. It is important to have information on the best time-temperature conditions for complete solvent removal, imidization, and cure in order to optimize the properties of the polyimide. Hence there are numerous citations about polyimides in the literature.[16–20] However, only a few studies on the thermal behavior of LaRC PETI-5 related materials have been reported,[9,21] but none for the latest version of molecular weight 2500 g/mol. Consequently the primary aim of the present work is to characterize the cure behavior and thermal stability of LaRC PETI-5. In addition, this work provides the foundation for thermal processing of LaRC PETI-5 as a potential future high-temperature sizing material to improve fiber-matrix interfacial properties (i.e., adhesion) in high-performance polymer matrix composites reinforced with carbon fibers or glass fibers.

EXPERIMENTAL

Materials

The phenylethynyl terminated imide oligomer used in the present study was synthesized and supplied in the liquid form of an amide acid from Imitec, Inc. The "as-received" LaRC PETI-5 is a random copolymer with a number average molecular weight of 2500 g/mol, which is prepared from 3,4′-oxydianiline(ODA), 1,3-bis(3-aminophenoxy)-benzene (APB), and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), endcapped with 4-phenylethynylphthalic anhydride (PEPA), as shown in Figure 1. The synthesis of LaRC PETI-5 has been described in detail elsewhere.[7,8] The solids content in *N*-methyl-2-pyrrolidinone (NMP) as solvent is about 35% by weight. The material was used "as-received" throughout this work. The "as-received" solution has been always stored in a refrigerator and only placed at ambient temperature for a couple of hours before use to prevent possible moisture absorption.

Differential Scanning Calorimetric Measurements

Differential scanning calorimetric (DSC) measurements were performed in a standard cell using a Du Pont TA system (2200 DSC) to investigate the effect of cure temperature and time on the dynamic DSC thermogram of LaRC PETI-5. The samples were prepared by heat-treating with two different thermal histories. In one thermal history the sample was cumulatively heated stepwise up to 400°C with an isothermal hold for 1 h each in an air-circulating oven, and in the other thermal history the sample was individually heated at specified temperatures only. Hereinafter, they are simply referred to as cumulative cure and individual cure, respectively. The weight of each sample was about 10 mg. A heating rate of 10°C/min was used with purging N_2 gas of 50 cc/min. The extent of cure at each cure temperature and time was calculated. The variations of glass transition temperature and melting point were also evaluated.

Thermogravimetric Measurements

The thermal stability of LaRC PETI-5 and the extent of solvent depletion remaining in the resin were examined in both dynamic and static modes, using a thermogravimetric analyzer (Du Pont 2200 TGA). The sample weight used was in the range of 20∼30 mg. The heating rate in a dy-

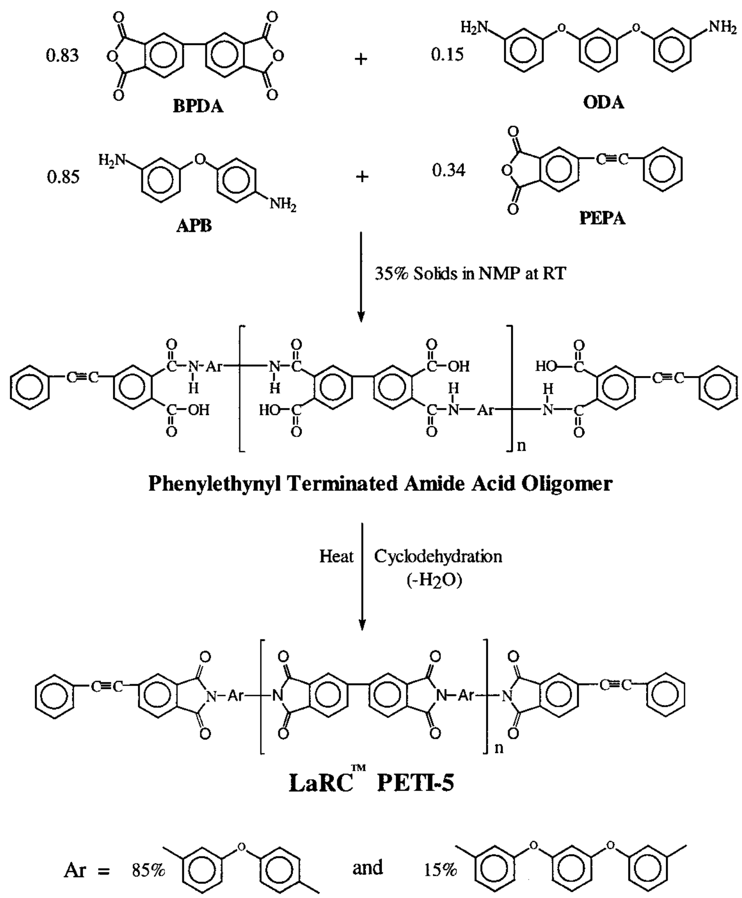

Figure 1 Preparation of LaRC PETI-5 amide acid oligomer (Mn = 2500 g/mol) and the polymer.

namic mode was 10°C/min. In a static mode, the time required to equilibrate at a given isotherm from ambient temperature was about 3–6 min, depending on the set temperature. All experiments were conducted in a N_2 atmosphere.

RESULTS AND DISCUSSION

Cure Temperature Effect on T_g, T_m, and Cure Behavior

Figure 2 shows a DSC thermogram of "as-received" LaRC PETI-5 resin. The strong endothermic peak around 210°C is due to evaporation of NMP solvent near its boiling point. The exothermic peak between 350°C and 400°C is due to the cure reaction in the resin. Because the "as-received" resin is in a solution of NMP at about 65%, the relatively huge endothermic peak predominates compared with the exothermic one.

Figure 3 represents the effect of cure temperature on DSC thermogram of LaRC PETI-5. The temperature increases in 50°C increments up to 400°C. Each sample was exposed cumulatively to

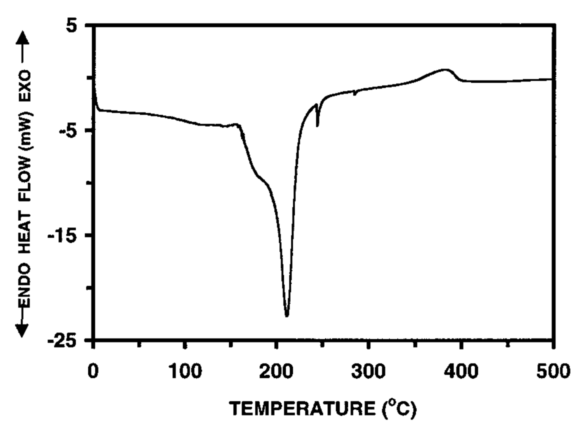

Figure 2 DSC thermogram of "as-received" LaRC PETI-5.

the given temperatures for 1 h each in air. The T_g increases with increasing cure temperature. The T_g is not clearly detected for the sample cured at 200°C and lower because the material may still contain some residual solvent and the structure of LaRC PETI-5 imide polymer is not fully developed with sufficient chain stiffness below 250°C. It has been reported in a previous paper[15] that the structure of the imide polymer is fully developed after heating for 1 h around 250°C.

The melting point was observed to be around 340~350°C. With increasing cure temperature the melting point becomes apparent. It appears that dual melting points around 260°C and 350°C are seen when the cure has been done at 200°C and 250°C, respectively. Also, there are small exothermic peaks at 200°C and 250°C presumably due to melting of crystalline material, depending on curing or annealing temperature. The earlier melting point around 260°C may be ascribed to such crystalline melting behavior. Similar crystallization behavior and dual melting points have been also reported in the earlier work by Hou et al.[9] for an IM7/PETI-5 prepreg system with PETI-5 of a molecular weight of 5000 g/mol. Upon curing at 300°C, dual melting points become closer, as seen in Table I. The melting point is completely gone above 350°C. In fact, no melting was observed for the individually cured samples above 330°C as seen in Table I. Even though the sample cured cumulatively at 330°C was not measured here, it can be concluded that it has no melting, either.

The cure behavior of LaRC PETI-5 can be explained with the variation of the thermograms in the temperature range of 350~460°C in Figure 3. There is a single exothermic peak in the thermograms observed for the neat resins cured at 100°C, 150°C, 200°C, and 250°C. It can be seen that the peak shifts slightly toward higher temperature with increasing cure temperature, especially above 200°C. The (second) peak temperature for the sample cured at 300°C is about 10°C greater than that cured at 200°C. This is because each specimen has been already partially cured as a result of the cumulative cure condition so that the cure reaction of the material exposed to higher temperature proceeds more slowly. In the case of the sample cured at 300°C, another small exothermic peak around 390°C is detected. This additional peak may be explained by an exothermic reaction occurring at the stage at which C≡C bonds in the phenylethynyl group located at the LaRC PETI-5 imide polymer chain ends are reacted and converted into double bonds. Above 350°C, there is no exothermic reaction at all. This means that there is no further reaction above this temperature and the reaction of the C≡C bonds that results in cross-linking and chain extension is completed at this stage. This result agrees well with the result found in the previous study using FT-IR spectroscopy.[15]

Table I A Summary of Melting Temperatures Observed for the LaRC PETI-5s Cured Cumulatively and Individually at Different Temperatures

Cure Temperature (°C)	T_m (°C)	
	Cumulative Cure	Individual Cure
"As-received"	Not observed	Not observed
100	350	Not available
150	340	Not available
200	269/341	261/342
250	266/346	268/340
300	329/342	335/346
330	Not available	No melting
350	No melting	No melting
400	No melting	Not available

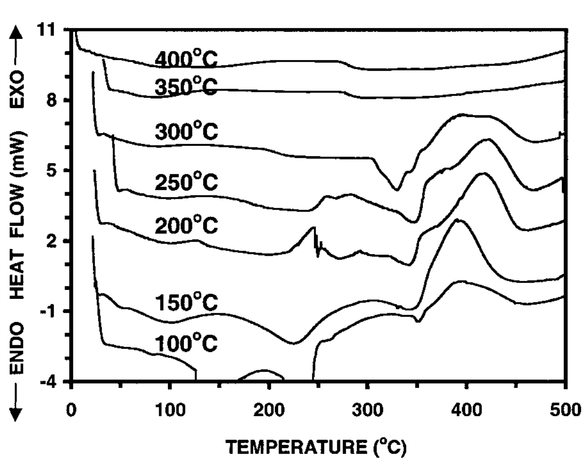

Figure 3 Effect of cure temperature on the DSC thermogram of LaRC PETI-5.

The exothermic reaction of the phenylethynyl end group, of course, takes place around 350°C as a dynamic scan of DSC is performed for the samples heat-treated below 350°C. In the samples exposed to lower temperature, the cure reaction can occur primarily by the phenylethynyl groups that have not been involved in the reaction during heat-treatment. As heat-treatment temperature increases, the extent of reaction increases with the larger participation of the phenylethynyl

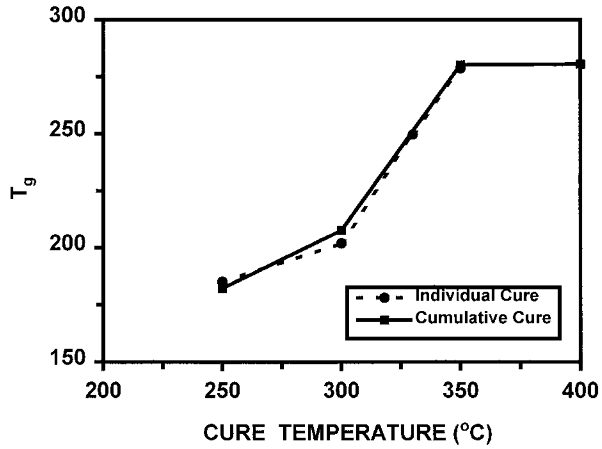

Figure 4 The change of glass transition temperature as a function of cure temperature for LaRC PETI-5 with different cure histories.

group to the cure reaction, reflecting that the degree or extent of cure increases. As the result, the exothermic peak becomes smaller. An upward tendency of the exothermic curvature near 500°C indicates that degradation of LaRC PETI-5 may begin.

Figure 4 shows the change of the glass transition temperature as a function of cure temperature. The difference in the T_g between cumulative cure and individual cure is not significant. As seen in Figure 3, the T_g can be identified clearly above 250°C. It has been reported earlier[15] that the imidization reaction of LaRC PETI-5 is complete around 250°C with a fully developed imide polymer structure. The fully imidized polymer has sufficient chain stiffness to produce a T_g. With increasing cure temperature the chain stiffness increases resulting in a higher T_g. In Figure 4, the T_g slowly increases up to 300°C and there is a large increase in the T_g between 300°C and 350°C. Although the reaction of the phenylethynyl end group in the imide polymer chain is not complete even after curing for several hours at 300°C, the reaction of the end group proceeds slowly at 300°C. Accordingly, it may contribute to some extent to rising the extent of cure and forming the cross-linking structure.

The rate of cure reaction in general increases with increasing temperature and time. As cure temperature exceeds imidization temperature with an increase of the extent of imidization, the formation of three dimensionally cross-linked structure in the imide polymer chain proceeds causing a large restriction of chain flexibility until the network is complete. The constant value of the T_g above 350°C is attributed to a completed network structure in the fully cured LaRC PETI-5 resin with a T_g of about 280°C.

The Extent of Cure

The extent of cure of thermosetting resins can be determined by calculation of the heat of reaction using the DSC data. Table II summarizes the heat of reaction calculated at different cure temperatures before and after considering the presence of residual solvent in the uncured or partially cured resin. The weight percent of the residual solvent in the third column was collected from the samples with the same thermal history as used in Figure 3, using a TGA. The correction factor in the fourth column was calculated from the ratio of pure resin weight percent in the absence of solvent to measuring resin weight percent in the presence of residual solvent [i.e.,

Table II Heat of Reaction at Different Cure Temperatures Before and After Considering the Presence of Residual Solvent in the Uncured and Partially Cured Resins

Cure Temp. (°C)	ΔH (J/g) Measured	Residual Solvent (%)	Correction Factor	ΔH (J/g) Corrected
"As-received"	24.54	67.0	3.03	74.36
100	40.58	44.3	1.80	73.04
150	61.61	13.2	1.15	70.85
200	62.48	0	1	62.48
250	41.06	0	1	41.06
300	50.01	0	1	50.01
350	0.33	0	1	0.33
400	0.32	0	1	0.32

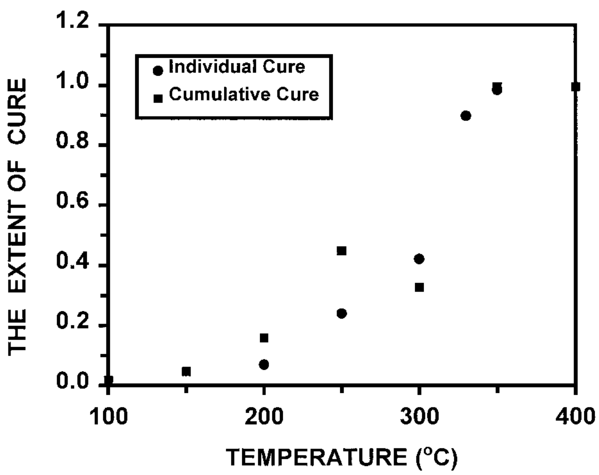

Figure 5 Variations of the extent of cure as a function of temperature for LaRC PETI-5 with different cure histories.

100%/(100−RS)%, where RS is the residual solvent weight percent.]. A product of the "measured ΔH" in the second column obtained directly from the DSC measurement and the correction factor at each cure temperature gives the "corrected ΔH" tabulated in the last column.

Figure 5 exhibits the variation of the extent of cure of LaRC PETI-5 exposed to individual and cumulative cure conditions as a function of temperature, respectively. The extent of cure (X) was calculated from the changes of the exothermic areas representing the heat of reaction by the following equation.[22–24]

$$X = 1 - (\Delta H_r/\Delta H_t)$$

where ΔH_r is the residual heat of exothermic reaction obtained from the partially cured sample and ΔH_t is the total heat of exothermic reaction for an initially uncured sample. As expected, the cumulatively cured material exhibits the higher extent of cure than the one cured individually over the entire temperature range up to complete cure with the exception of 300°C. Such a deviation at 300°C in the case of cumulative cure is probably a complex result of the doublet exothermic reaction, described earlier and in Figure 3. The additional small exothermic peak around 390°C contributes effectively to an increase of the exothermic area in the thermogram. This leads to an increase of the heat of the cure reaction and consequently a decrease of X.

It should also be noted that the material used here starts to cure slowly and partially at lower temperature than the imidization temperature, as found earlier.[15] The cure accelerates around the imidization temperature. The extent of cure of the cumulatively cured sample in the imidization temperature region (200∼250°C) is about twice that of the individually cured sample. This suggests that the thermal history of the imidization reaction may significantly influence the extent of cure of the partially cured resin. The extent of cure increases the greatest in the range of 300∼350°C, where the reaction of the phenylethynyl end group predominates. The extent of cure reaches a plateau region above 350°C as a consequence of the absence of the exothermic reaction, as seen in Figure 3.

Isothermal Effect on Cure Behavior

Figure 6 represents DSC thermograms of LaRC PETI-5 cured isothermally at 300°C, 330°C, and 350°C, respectively. The duration of the cure at fixed temperature has been varied, depending on the cure temperature. In Figure 6a there exist dual melting points at 335°C and 355°C, as similarly found in the cumulatively cured sample. The peak at 355°C diminishes with increasing time, becoming a shoulder at 90 min. Finally, the dual melting points change into a single melting point after 120 min. There was no melting point observed in Figures 6b and 6c. The result of the melting behavior is also summarized in Table I.

At 300°C, the cure reaction has not been completed even after curing for 120 min or longer, as indicated from the occurrence of exothermic reaction in the range of 360∼420°C of Figure 6a. It can be said that the cure reaction does not occur remarkably during the extended period of time at 300°C. However, the cure reaction of LaRC PETI-5 at both 330°C and 350°C proceeds markedly faster, as seen in Figure 6b and 6c. The exothermic peak that is responsible for the cure reaction of the phenylethynyl end group in the imide polymer decreases significantly after curing for 60 min at 330°C and almost disappears after 90 min at 330°C. Also, the peak significantly decreases after curing for 15 min at 350°C and completely disappears after 60 min at 350°C. This behavior points out that the complete cure reaction of LaRC PETI-5 may be achieved by curing for 1 h at 350°C or for a longer period of time than 90 min at 330°C. This result agrees quite well with the results obtained examining the disappearance of C≡C absorption band at 2213 cm^{-1} by means of FT-IR spectroscopy cited in previous work.[15]

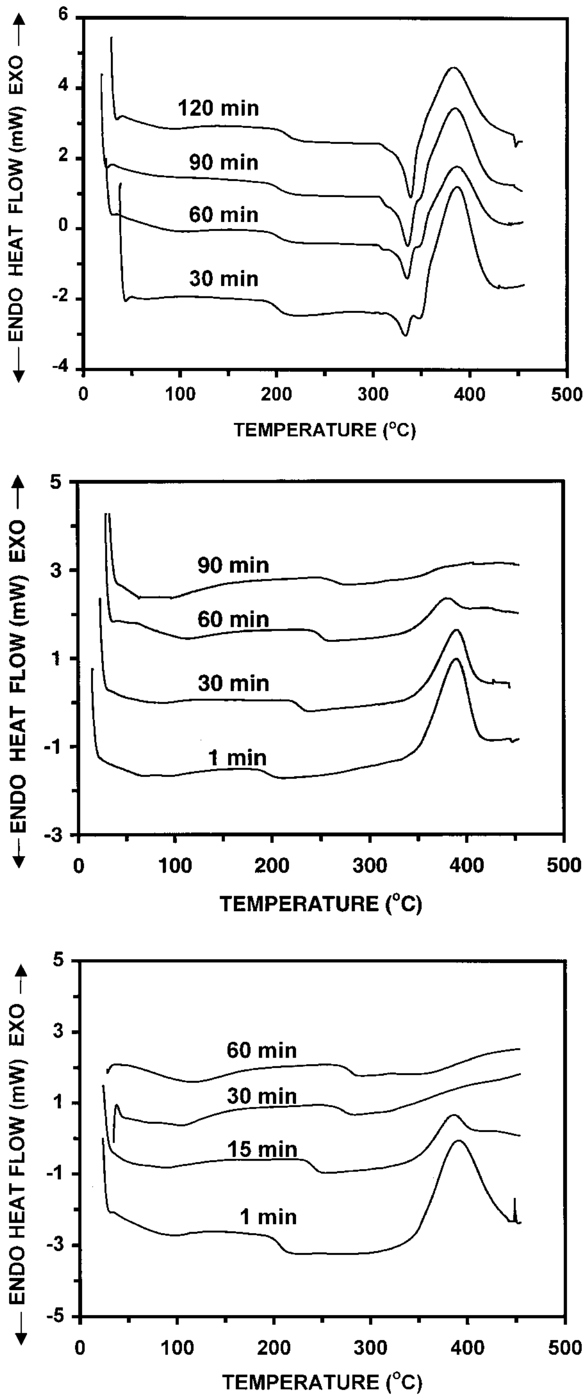

Figure 6 DSC thermograms of the LaRC PETI-5 cured isothermally at 300°C (a), at 330°C (b), and at 350°C (c).

Isothermal Effect on T_g and the Extent of Cure

Figure 7 shows the variations of the T_g of LaRC PETI-5 with time at five different isotherms. The T_g increases very slowly with increasing cure time below 300°C. This indicates that such tem-

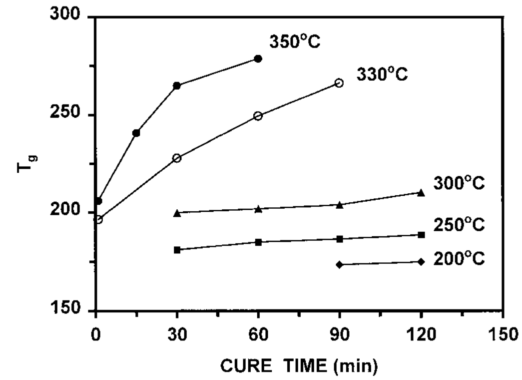

Figure 7 Effect of the isothermal cure at different temperatures on the glass transition temperature.

peratures do not significantly influence the chain stiffness of the polymer even after an extended period of time. However, the T_g increases rapidly with time above 330°C, showing that the T_g already has reached a higher temperature than the temperature required for full imidization.

The variation of the extent of cure with time at various cure temperatures is shown in Figure 8. Similar to the trends seen in the T_g change, the extent of cure increases gradually with temperature up to 300°C; the extent of cure increases by 0.2 for an increment of 50°C after 60 min isothermal cure. At a fixed temperature, the cure proceeds slowly with time. It is noted that there is a big increase in the extent of cure at 350°C, approaching to a value of 1 after 60 min. Such a large increase between 300°C and 350°C in the isothermally cured sample is consistent with the result obtained from the cumulatively cured sample. Upon thermal cure, temperatures greater than the imidization temperature lead to a higher T_g and extent of cure. Therefore, it can be con-

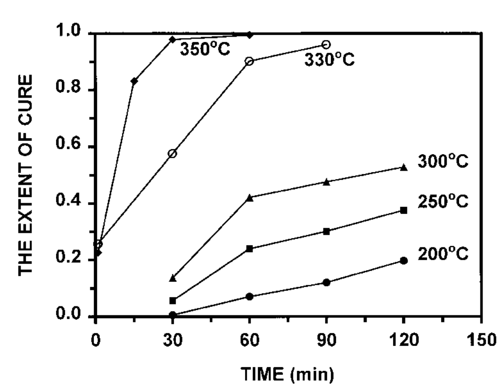

Figure 8 Effect of the isothermal cure at different temperatures on the extent of cure.

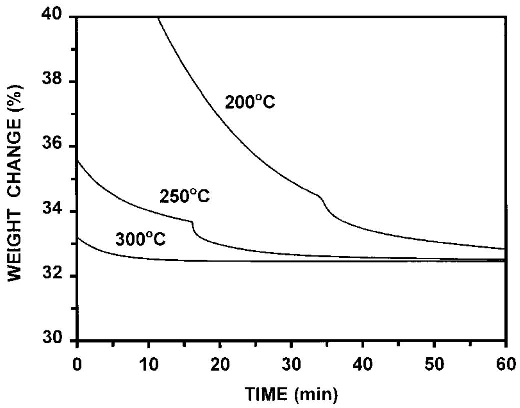

Figure 9 Weight changes in the LaRC PETI-5 resin due to imidization reaction during isothermal heating at 200°C, 250°C, and 300°C.

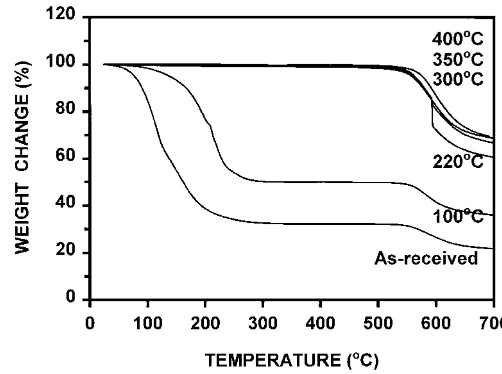

Figure 10 Thermal stability of the LaRC PETI-5 cured at different temperatures.

cluded that a cure temperature around 350°C in air produces a fully cured LaRC PETI-5 within an hour, supporting the conclusions from the previous study using FT-IR spectroscopy.

Weight Change by Imidization

Figure 9 shows the weight change of LaRC PETI-5 during isothermal cure at 200°C, 250°C, and 300°C for 60 min. Note that there are small weight drops in the resin between 30 min and 40 min at 200°C and between 10 min and 20 min at 250°C, respectively. This drop occurs when the residual weight of the resin is lower than 35%, which is the approximate solids content of the "as-received" resin. The small weight loss is attributed to the imidization reaction that generates a very small amount of water as a by-product when the cyclodehydration takes place between the amide and carboxylic acid groups. Such a drop is not seen at 300°C because the cyclodehydration is probably completed prior to reaching at the isothermal equilibrium temperature. This result has been also demonstrated by FT-IR studies[15] for LaRC PETI-5 resin prepared under the similar isothermal cure condition.

Thermal Stability

Figure 10 shows the thermal stability of LaRC PETI-5 cured cumulatively at different temperatures for 1 h each in air. Note that "as-received" resin has the solids content of about 33~35% in NMP. The thermal stability of all the resins cured above 220°C was excellent up to 550°C where the material starts to degrade. The initial weight loss at which the equilibrium temperature for an isothermal treatment is reached (that is, time equals zero) and the time necessary for complete removal of the solvent NMP under the given isothermal condition were examined and summarized in Table III. It is not possible to completely remove all of the NMP solvent by heating at 100°C for several hours and not all but most of the solvent can be removed at 150°C. There is no residual solvent remaining in the imidized resin heat-treated over 1 h above 200°C. Therefore, the thermal stability of LaRC PETI-5 for the samples above 220°C in Figure 10 is for polymer obtained after complete depletion of the solvent involving the imidization reaction during thermal heating. Accordingly, this result suggests that the cure reaction of the resin involving the reaction of the phenylethynyl end group in the imide polymer may not play an important role in enhancing the thermal stability of the resin as long as the material is fully imidized.

Table III Initial Weight Loss at Which Time Is Zero and the Time Needed to Completely Remove the Solvent NMP from the Resin

Isotherms (°C)	Initial Weight Loss (%)	Time
100	12	Not completely removed even after several hours
150	46	Not all but most removed even after several hours
200	48	30–40 min
250	65	10–20 min
300	67	Within 10 min

Table IV Result of the Temperature at a 5% Loss of the Original Weight for the LaRC PETI-5s Cured at Different Temperatures

Cure Temperature (°C)	5% Weight Loss Temperature (°C)
"As-received"	82
100	134
220	555
300	561
350	557
400	574

The stability of polymers for high-temperature applications is often assessed in terms of ability to retain their original weight at elevated temperature. If a material keeps 95% of its original weight at high temperatures, it is known that the material would usually exhibit enough integrity to be suitable for most non-load-bearing applications.[3] Table IV represents the maximum temperature at which LaRC PETI-5 cured at different temperatures retains 95% of its original weight in N_2. The result indicates that this material has excellent high temperature stability in the range of 555~574°C when the resin is cured above 220°C.

The effect of isothermal aging on the thermal stability of the resin cured at 350°C for 1 h is shown in Figure 11. There is no significant weight loss even after isothermal aging at 450°C for 5 h but weight loss at the initial stage of aging becomes more pronounced with increasing temperature. From this result, LaRC PETI-5 may be used successfully without significant loss of its integrity for extended periods of time below 450°C.

CONCLUSIONS

The glass transition temperature, melting behavior, and cure behavior of the LaRC PETI-5 cured cumulatively or individually at various temperatures have been analyzed with the aid of DSC thermograms. The melting point of LaRC PETI-5 is in the range of 340~350°C. The endothermic melting peak completely disappears as the resin is cured above 350°C. Dual melting points are also observed depending on the cure temperature.

There is no significant difference in the T_g of the polymer between cumulative cure and individual cure cycles. With increasing cure temperature the T_g and the extent of cure become higher, especially above 300°C, as a result of an increase in the chain stiffness of the imide polymer. The extent of cure for the partially cured resin has been determined from the heat of cure reaction after taking into account the residual solvent in the resin. It was also noted that the thermal history for imidization reaction may influence the extent of cure of the partially cured resin. The T_g and the extent of cure increase markedly as the T_g exceeds the temperature required for full imidization.

There is no detectable exothermic reaction after curing for 1 h above 350°C. This demonstrates that the cross-linking and chain extension reaction due to C≡C bonds is completed at this stage. Consequently, a cure temperature of around 350°C for 1 h in air produces a fully cured LaRC PETI-5. This result agrees with the result of the disappearance of the FT-IR absorption bands at 2213 cm^{-1} due to C≡C bonds in the phenylethynyl end groups in the previous study. A small weight drop detected by TGA around 200~250°C is consistent with the change in the FT-IR absorption band due to formation of typical polyimide structure involving the cyclodehydration.

All the resins cured above 220°C shows the excellent thermal stability up to 550°C. The TGA study suggests that LaRC PETI-5 may serve successfully without significant loss of its integrity for 5 h below 450°C.

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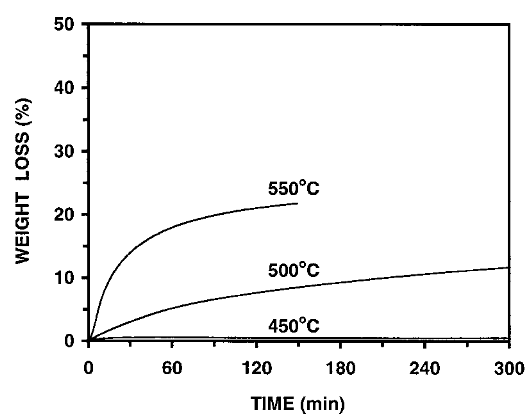

Figure 11 Isothermal stability of the LaRC PETI-5 cured at 350°C.

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