THERMAL CHARACTERIZATION OF LaRC™ PETI-5 AS A POTENTIAL HIGH TEMPERATURE SIZING MATERIAL

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SUMMARY: 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) in this publication. 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 one hour at 350°C in air. 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 and no significant loss of its integrity for extended periods of time below 450°C as long as it is fully imidized. Microscopic observations suggest that LaRC™ PETI-5 resin is useful as a high temperature sizing material, providing uniform fiber surface and good wettability to carbon fiber.

KEYWORDS: 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. 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[1]. 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.

Based upon research[2-5] 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 to other versions of phenylethynyl terminated polyimides[6].

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[7-9]. However, only a few studies on the thermal behavior of LaRC™ PETI-5 related materials have been reported[4,10], 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

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 synthesis of LaRC™ PETI-5 has been described in detail elsewhere[2,3].

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 hour 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 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). All experiments were conducted using a heating rate of 10°C/min in a N_2 atmosphere.

RESULTS AND DISCUSSION

Cure Temperature Effect on T_g, T_m and Cure Behavior

Figure 1 represents the effect of cure temperature on DSC thermogram of LaRC™ PETI-5. Each sample was exposed cumulatively to the given temperatures for 1 hour each in air. The glass transition temperature (T_g) increases with increasing cure temperature. The glass transition temperature 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 another paper[11] of this proceeding that the structure of the imide polymer is fully developed after heating for 1 hour 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. The melting point is completely gone above 350°C. In fact, no melting was observed for the individually cured samples above 330°C.

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 1. 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 which results in crosslinking and chain extension is completed at this stage.

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 group to the cure reaction, reflecting that the 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.

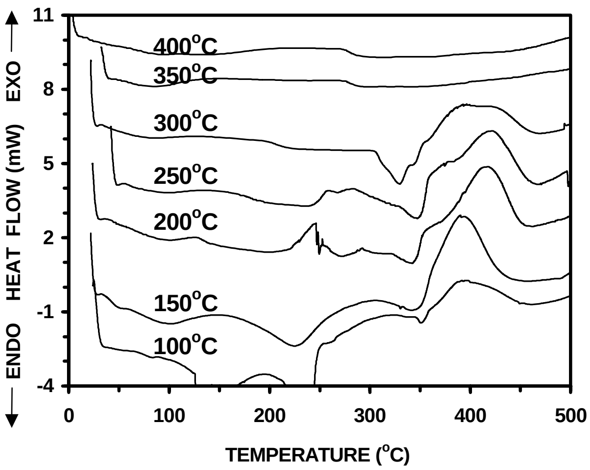

Fig. 1. Effect of cure temperature on the DSC thermogram of LaRC™ PETI-5.

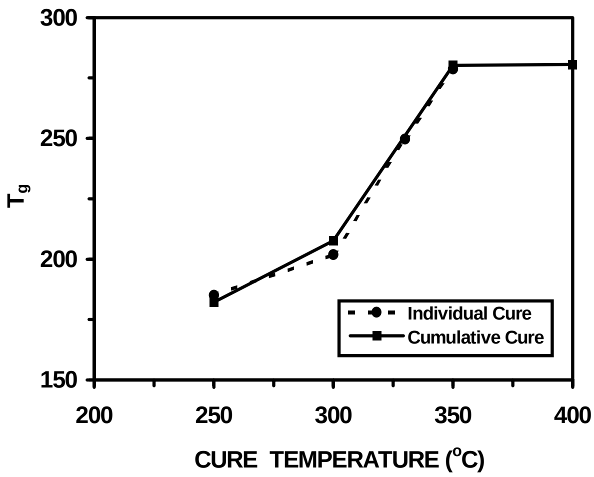

Fig. 2: Glass transition temperature versus cure temperature for two thermal histories.

Figure 2 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 1, the T_g can be identified clearly above 250°C. It has been reported earlier[11] 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 2, 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.

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 crosslinked 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. Figure 3 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.

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

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 1. 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.

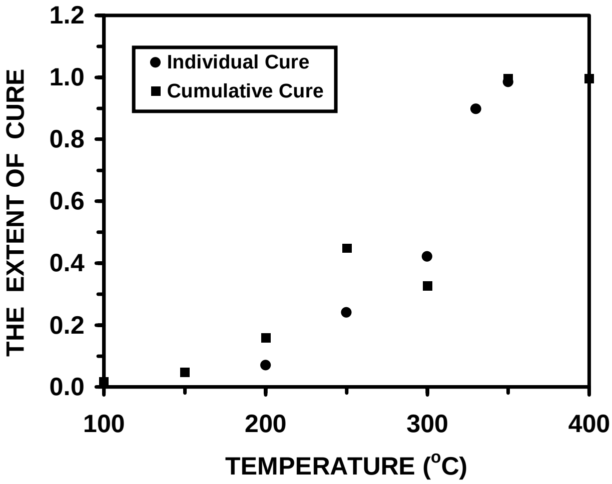

Fig. 3: Variations of the extent of cure against temperature for different thermal histories.

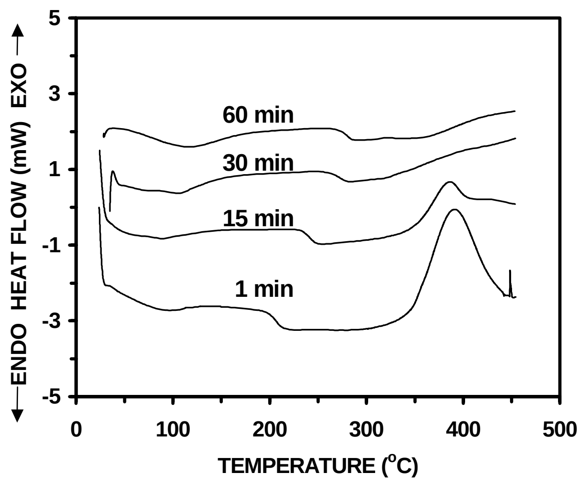

Fig. 4: DSC thermograms of the LaRC™ PETI-5 cured isothermally at 350°C.

It should also be noted that the material used here starts to cure slowly and partially at lower temperature than the imidization temperature. The cure accelerates around the imidization temperature. The extent of cure of the cumulatively cured sample in the imidization temperature region (200~250^{o}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^{o}C, where the reaction of the phenylethynyl end group predominates. The extent of cure reaches a plateau region above 350^{o}C as a consequence of the absence of the exothermic reaction, as seen in Figure 1.

Isothermal Effect on Cure Behavior

Figure 4 represents DSC thermograms of LaRC™ PETI-5 cured isothermally at 350^{o}C. The cure reaction does not occur remarkably during the extended period of time at 300^{o}C. However, the cure reaction of LaRC™ PETI-5 proceeds faster at 330^{o}C and markedly faster at 350^{o}C, as seen in Figure 4. The exothermic peak which is responsible for the cure reaction of the phenylethynyl end group in the imide polymer decreases significantly after curing for 60 min at 330^{o}C and almost disappears after 90 min at 330^{o}C. Also, the peak significantly decreases after curing for 15 min at 350^{o}C and completely disappears after 60 min at 350^{o}C. This behavior points out that the complete cure reaction of LaRC™ PETI-5 may be achieved by curing for one hour at 350^{o}C or for a longer period of time than 90 min at 330^{o}C.

Isothermal Effect on T_g and the Extent of Cure

Figure 5 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^{o}C. This indicates that such temperatures 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^{o}C, showing that the T_g already has reached a higher temperature than the temperature required for full imidization.

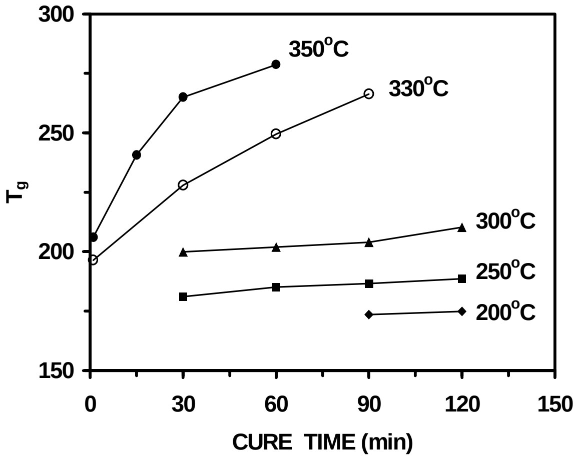

Fig. 5: Effect of the isothermal cure at different temperatures on the glass transition temperature.

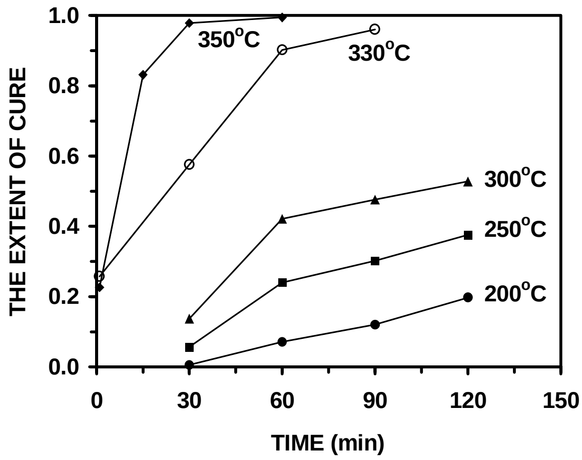

Fig. 6: Effect of the isothermal cure at different temperatures on the extent of cure.

The variation of the extent of cure with time at various cure temperatures is shown in Figure 6. 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 concluded 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.

Thermal Stability

Figure 7 shows the thermal stability of LaRC™ PETI-5 cured cumulatively at different temperatures for 1 hour 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 1. 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 one hour 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.

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.

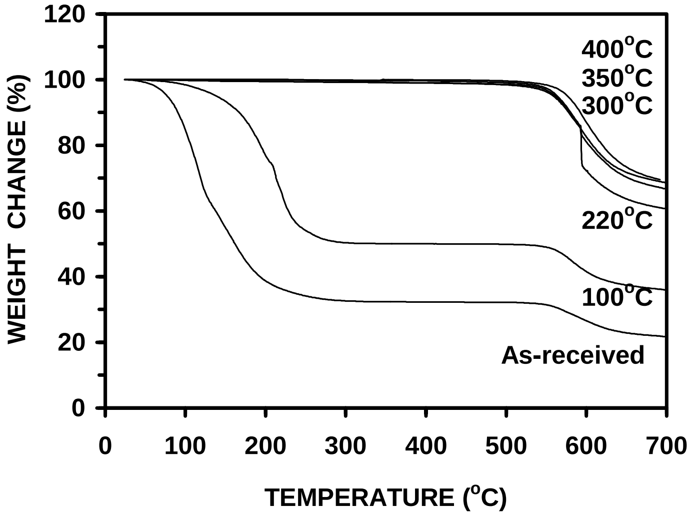

Fig. 7: Thermal stability of the LaRC™ PETI-5 cured at different temperatures.

Table 1. Initial weight loss at which time is zero and the time needed to completely remove the solvent NMP from the resin.

Isotherms (^oC)	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

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^oC. The endothermic melting peak completely disappears as the resin is cured above 350^oC. 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^oC, as a result of an increase in the chain stiffness of the imide polymer. 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 one hour above 350^oC. This demonstrates that the crosslinking and chain extension reaction due to C≡C bonds is completed at this stage. Consequently, a cure temperature of around 350^oC for 1 hour 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.

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

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