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Simultaneous monitoring of the imidization and cure reactions of LaRC PETI-5 sized on a braided glass fabric substrate by dynamic mechanical analysis

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Abstract

The imidization and cure reactions of a thin film of phenylethynyl imide oligomer (LaRC PETI-5, $M_n = 2500$ g/mol) applied to a glass fabric and processed under cumulative and isothermal heat-treatment conditions have been measured. Three distinguishable peaks were detected in the tan δ curves, which give useful information on the glass transition temperature, imidization temperature, and cure reaction temperature. The degree of imidization or cure reaction occurring during the cumulative and isothermal cure processes is related to the presence and size of the imidization peak and the cure reaction peak. The rate of cure increases substantially above 250°C. The T_g of the fully cured LaRC PETI-5 was measured as 287°C. The maximum in the tan δ curve transformed with increasing cure temperature from a triplet due to completion of imidization above 250°C to a singlet after completion of the cure reaction. The maximum of the singlet tan δ curve at 287°C is identified as the T_g of the LaRC PETI-5 polyimide. It is concluded that the dynamic mechanical behavior of LaRC PETI-5 strongly depends on thermal history, especially above 300°C. This result also confirms that after cumulative or isothermal processing, LaRC PETI-5 can be fully cured at 350°C for 1 h. These results agree well with the Fourier Transform infrared spectroscopy and differential scanning calorimetry results reported earlier. © 2001 Published by Elsevier Science Ltd.

Keywords: Phenylethynyl imide oligomer; Dynamic mechanical behavior; Glass transition

1. Introduction

Since acetylene-terminated imide oligomers were first reported in 1974 [1], they have attracted attention as potential candidates for advanced adhesives and composite matrix resins in aerospace and electronics because of their high temperature performance and ease of processing. During the last several years, the attraction has grown as a result of the availability of phenylethynyl-terminated imide oligomers (LaRC PETI-5), which have been developed at the NASA Langley Research Center [2–4]. It has been shown that phenylethynyl-terminated imide polymers have very favorable combinations of chemical, physical, thermal, and mechanical properties that make them suitable as potential candidates for coatings, adhesives, films, and composite matrix resins [6–8]. One possible application under investigation is the use of LaRC PETI-5 as a sizing material for inorganic fiber surfaces, such as carbon fibers and glass fibers, for high temperature applications. In order to be successful as a sizing agent, the polyimide must be applied in the correct thickness and with the proper degree of cure so that it can adhere to the carbon fiber surface, interdiffuse to some degree with the bulk matrix, and produce an interphase with the requisite level of modulus and toughness [9–11]. A sizing that has been advanced by thermal treatment to the point where it is insoluble in the matrix will not be useful, whereas one that can fully dissolve in the matrix under normal processing conditions will have little effect on creating a beneficial interphase. This study is directed at identifying the proper combination of heat-treatment conditions that will result in the LaRC PETI-5 functioning as a sizing that can produce a beneficial interphase in composite materials.

Although much research has been published on the imidization and cure behavior of thermosetting polyimides, only a few studies have been reported for the LaRC PETI-5 version with a number average molecular weight of 2500 g/mol. Cho and Drzal investigated the imidization

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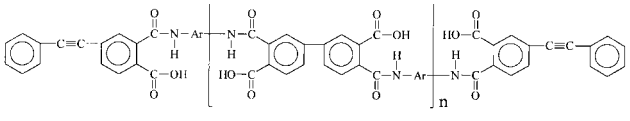
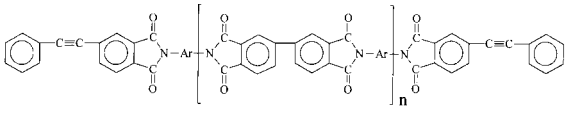


Phenylethynyl Terminated Amic Acid Oligomer



LaRC™ PETI-5

Fig. 1. Chemical structure of an LaRC PETI-5 amic acid oligomer and the corresponding imide oligomer.

and phenylethynyl end group reaction behavior of LaRC PETI-5 (2500 g/mol) using Fourier Transform infrared (FT-IR) spectroscopy [12]. The dynamic and isothermal effects on cure behavior and thermal stability of the material using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) [13] were also reported. Some fundamental studies on the cure of LaRC PETI-5 materials ($M_n = 5000$ g/mol [14,15] and other similar phenylethynyl-terminated imide compounds can be found elsewhere [16,17].

In general, when such polyimides are thermally imidized and cured for use as a composite matrix resin, it is known that the temperature and time profile is a critical factor that influences the thermal and mechanical properties of the final polymer. Thus, it is important to have detailed information on the best time–temperature conditions for solvent removal, imidization, and cure in order to optimize the processing and properties of this polyimide as a fiber sizing agent in high temperature matrix composites. Therefore, it is critical to develop an understanding of the role of thermal parameters such as imidization temperature, glass transition temperature, and cure temperature at the partially or fully imidized and cured stages and their effect on the polyimide mechanical properties and adhesion.

Many investigators have utilized a variety of analytical methods to examine the imidization and/or cure of ethynyl- or phenylethynyl-terminated imide polymers: for example, FT-IR [5,12,18], DSC [5,13,14], TGA [13], HPLC [16] and solid-state ^{13}C NMR [19]. However, FT-IR measurement may be of limited use above the full imidization temperature even though the presence or absence of an FT-IR absorption band of the phenylethynyl end group can be successfully detected. The reason for this is that the glass transition temperature and chain stiffness of the imide polymer increase with increasing degree of cure and the local mobility of the chain segments is largely restricted while being consolidated [12]. DSC may also be of limited use for understanding the imidization behavior occurring at the early stage during consolidation even though it provides useful information on cure behavior [13]. Solid-state ^{13}C NMR can give chemical identification of the molecular structure of cured polyimides but it cannot give detailed information on monitoring imidization and cure [19].

Dynamic mechanical analysis (DMA) is a very powerful technique capable of providing information on the thermal mechanical behavior of a polymer due to the temperature dependence of the storage modulus, loss modulus and tan δ. The glass transition temperature and other physical transition temperatures can be determined from the peak of tan δ or the loss modulus, which is sensitive to molecular mobility, stiffness behavior, phase transformation and morphological change [17]. As a result, the DMA technique has been widely used to explore the thermal mechanical behavior not only of viscoelastic polymer materials [21], blends [22], and polymeric composites [23,24], but also of the interphase [25–27] between the fiber and matrix in a composite system. The reaction behavior can be observed using this method because changing the thermal conditions can change the molecular state during a transformation from amic acid to the fully cured polyimide. Gillham [28] and co-workers have made great contributions to characterizing and understanding the dynamic mechanical behavior of thermosetting polymeric systems using a torsional braid analysis (TBA) technique, which is similar in concept to DMA although relatively different in its instrumental and experimental methodology.

The overall research objective is ultimately to improve fiber–matrix interfacial properties in carbon fiber- or glass fiber-reinforced polymer composites by introducing an LaRC PETI-5 interphase as a high temperature sizing material. Here, we mimic a fiber/interphase/matrix system utilizing a braided glass fabric substrate sized with an LaRC PETI-5 amic acid oligomer. Consequently, the goal of the present study is primarily to simultaneously obtain information about the imidization and cure reactions behavior through dynamical mechanical analysis of a reinforcement of braided glass fabric sized with the LaRC PETI-5 so that suitable sizing process conditions can be developed.

2. Experimental

2.1. Materials

The LaRC PETI-5 used in this work was synthesized and supplied as a liquid amic acid from Imitec, Inc. The LaRC PETI-5 oligomer is a random copolymer with a number average molecular weight of 2500 g/mol, which is prepared from 3,4′-oxydianiline, 1,3-bis(3-aminophenoxy)benzene, and 3,3′,4,4′-biphenyltetracarboxylic dianhydride, endcapped with 4-phenylethynylphthalic anhydride. The synthesis and chemistry of LaRC PETI-5 have been described in detail elsewhere [2,3]. Fig. 1 represents the chemical structure of a phenylethynyl-terminated amic acid oligomer with a solids content of about 35 wt% in *N*-methyl-2-pyrrolidinone

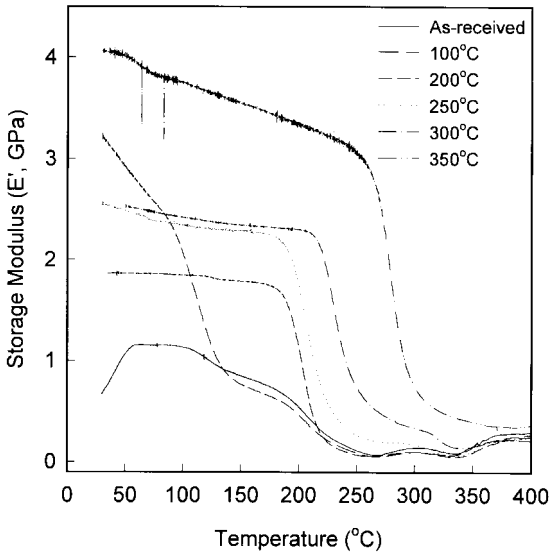


Fig. 2. Variation of storage modulus as a function of temperature in the LaRC PETI-5/braided glass fabric specimens cured at different temperatures.

(NMP) solution. The amic acid oligomer is thermally cyclodehydrated to the phenylethynyl-terminated imide oligomer. The LaRC PETI-5 amic acid oligomer was used 'as-received' without any modification before thermal treatment for imidization and cure throughout this work. The 'as-received' oligomer was stored in a freezer prior to use and warmed to ambient temperature for only a couple of hours immediately prior to use.

2.2. Sample preparation

Each specimen consists of a single ply of the braided glass fabric. The dimensions of the braided glass fabric substrate are 40 mm × 12.8 mm. The thickness was measured to be about 0.08 mm. This commercial substrate was supplied in roll form from the Du Pont Co. with the DMA instrument. Three drops (ca. 51 mg) of 'as-received' LaRC PETI-5 resin were placed on a braided glass fabric substrate. The resin was uniformly distributed, and impregnated through the substrate by manually spreading and pressing the resin with a glass rod. The weight ratio of the resin to the braided glass fabric was 0.44, which resulted in a film of oligomer ~0.5 μm thick. The braided glass fabric substrates sized with the LaRC PETI-5 were cumulatively heated stepwise up to 350°C with an isothermal hold for 1 h in the DMA furnace in an air atmosphere to more accurately control temperature and time. The temperatures used were 100, 200, 220, 250, 300, 330 and 350°C to examine the effect of dynamic heating on the imidization and cure reactions. In a second set of experiments, samples were isothermally heated in a DMA furnace at 220, 230, 240 and 250°C to explore the isothermal effect on imidization and at 300 and 350°C to examine the isothermal response to the cure reaction.

2.3. Dynamic mechanical analysis

The imidization and cure reaction behavior were investigated by means of dynamic mechanical analysis (TA Instruments DMA 983, Du Pont). The impregnated glass fabric specimens were deformed in a single cantilever bending mode. A fixed frequency mode in which the frequency was held constant at 1 Hz during measurement was used. The oscillation amplitude used was 0.15 mm. All the samples after both cumulative and isothermal processing were dynamically scanned from ambient temperature to 400°C at a heating rate of 2°C/min in air, which was expected to be slow enough to thermally equilibrate each specimen in the furnace.

3. Results and discussion

In the present study, the parameters of interest are the glass transition temperature (T_g), imidization temperature (T_i), and cure reaction temperature (T_c) that depend on the (dynamic or isothermal) thermal history of the specimen. The imidization and cure reaction behavior will be explained by variations of storage modulus and tan δ for the LaRC PETI-5 cured at different thermal conditions. Also, the degree of cure may be determined by finding the T_g of the LaRC PETI-5 reacted for various temperatures and times [21].

3.1. Storage modulus

Fig. 2 represents the storage modulus as a function of temperature for the LaRC PETI-5/braided glass fabric specimens heat-treated at six different temperatures. The term 'heat-treated' will be used because the LaRC PETI-5 can only be fully 'cured' at temperatures above 350°C and is only partially cured below this temperature [12,13]. The initial storage modulus for the 'as-received' sample and the sample heat-treated at 100°C is not observed due to the NMP solvent remaining in the specimens.

In general, the storage modulus is very sensitive to changes of molecular structure and mobility taking place with increasing cure temperature, such as molecular weight, chain stiffness, degree of cure, and the fiber–matrix interface or interphase, especially in thermosetting polymers. For the samples heat-treated at and above 250°C, an increase of the storage modulus is detected after the solvent is completely removed from the sample. The LaRC PETI-5 amic acid oligomer becomes partially imidized around 200°C. Solvent desorption and partial imidization take place competitively below 200°C, as demonstrated in earlier studies using FT-IR [12], DSC and TGA [13]. The chain stiffness increases somewhat with temperature as the amic acid transforms into a corresponding imide oligomer. It was found from the earlier work [13] that DSC thermograms showed some crystalline melting of LaRC PETI-5 when it was cumulatively heat-treated at 200 and 250°C. Such

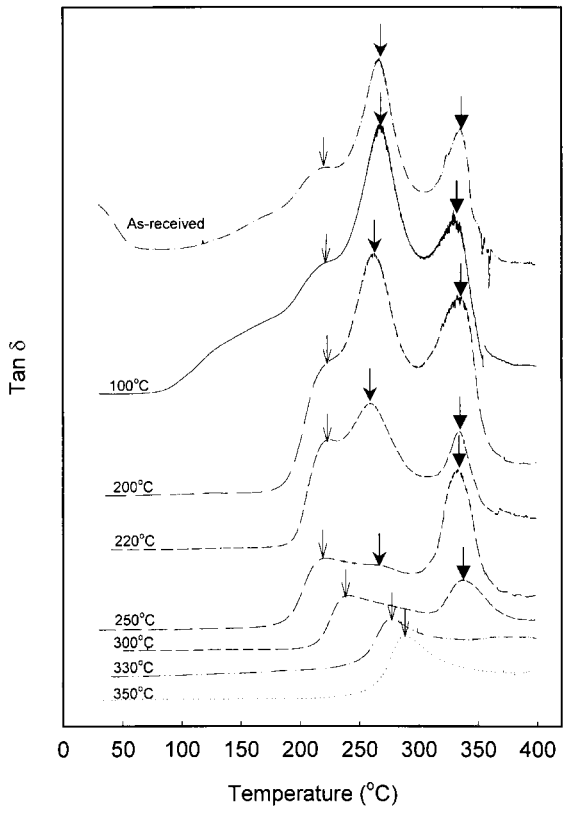


Fig. 3. Variation of tan δ as a function of temperature in the LaRC PETI-5/braided glass fabric specimens cured at different temperatures. The arrows in the left designate glass transition peaks, the arrows in the middle designate imidization peaks, and the arrows in the right designate cure reaction peaks.

crystalline melting behavior may be the cause of the increase in chain stiffness of LaRC PETI-5 resin, which then increases the storage modulus of the braided glass fabric sample.

A large increase in the storage modulus in the temperature range from 300 to 350°C is observed because the LaRC PETI-5 polymer is fully cured. There is also a large increase in glass transition temperature and an increase in the extent of cure in this temperature range. This result suggests that a very small amount of the LaRC PETI-5 sizing material can be differentiated from the glass fabric due to the influence on the dynamic mechanical properties.

3.2. Variations of the peak temperatures determined from tan δ

Fig. 3 shows the variations of tan δ peaks as a function of temperature in the LaRC PETI-5/braided glass fabric specimens cumulatively heat-treated at different temperatures for 1 h each. It is noted that there are three distinguishable peaks in the tan δ curves, as indicated by the arrows. The storage modulus decreases when main chain molecular motion begins; at the same time, tan δ is maximized when the frequency of the forced oscillation coincides with the frequency of the molecular motion of the main chain. The first peaks seen as a shoulder at lower cure temperatures indicate the change of glass transition temperature with increasing cure temperature. The second peaks around 260°C are due to the imidization in converting the amic acid oligomer into the imide oligomer. The third peaks around 330°C are due to the cure reaction of the imide oligomer. Therefore, it is appropriate to explain the tan δ behavior in terms of the T_g from the first peak, imidization temperature T_i from the second peak, and the cure reaction temperature T_c from the third peak, respectively.

T_i is defined as a maximum temperature at which the imidization takes place. The disappearance of this peak demonstrates that the imidization reaction has been completed. The T_c is defined as a maximum temperature produced by an exothermic peak at which the formation of the crosslinked network structure proceeds. The disappearance of the T_c peak also demonstrates the absence of further-cure reaction, which means that the polymer has been fully cured. T_c is differentiated from the 'heat-treatment temperature' used to prepare the specimens with different thermal histories. Interestingly, there is a transition from a triplet pattern of the tan δ peak to a doublet pattern due to completion of the imidization reaction above 250°C and finally to a singlet shape due to completion of the cure reaction. Therefore, a maximum of the singlet tan δ curve is determined to be a T_g of the cured LaRC PETI-5 polymer.

The variation of the T_g values at different cure temperatures is illustrated in Fig. 4. The peak temperature, which is the T_g, increases with increasing cure temperature. The increase in T_g takes place at a higher rate when the cure temperature exceeds 250°C. The T_g of the fully cured LaRC PETI-5 polyimide is 287°C. This value is quite consistent with a fully cured T_g of about 280°C obtained using the DSC method reported in an earlier paper [13]. There is no significant increase in the T_g of the polymer processed either for longer times or higher temperatures because a three-dimensionally crosslinked structure in the polyimide chain has been sufficiently formed under this thermal processing profile.

Comparing the average T_g values for partially cured polymer obtained by DMA with those obtained by DSC, the difference in the T_g is about 30°C at 250°C, about 25°C at 300°C and about 20°C at 330°C. These T_g values are higher by about 30–40°C than the values obtained from the DSC measurement [13] at the corresponding heat-treatment temperature for the LaRC PETI-5 with the same thermal history. The main reason for this is that the specimens consist of a very thin layer of LaRC PETI-5 and a single layer of braided glass fabric. The braided glass fabric makes the LaRC PETI- resin stiffer with increasing cure temperature. As the result, the T_g is observed to be higher in comparison with the neat LaRC PETI-5 sample investigated with the DSC method. Another reason may also be the difference in the instrumental methodology used. The tan δ peak obtained with the dynamic DMA method normally appears

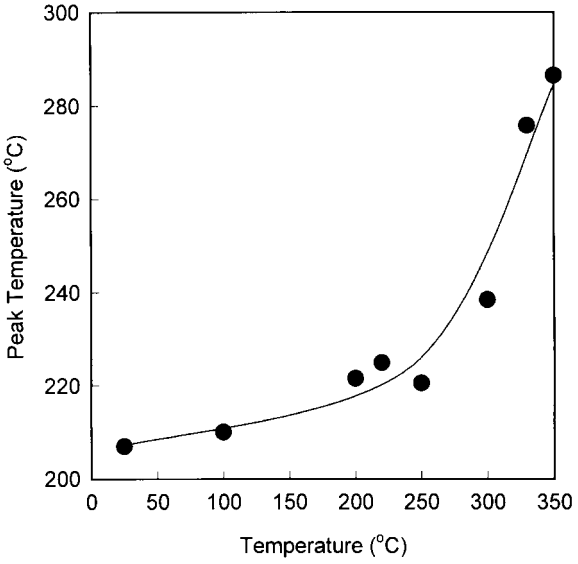


Fig. 4. Variations of the peak temperatures from tan δ with increasing cure temperature for LaRC PETI-5.

at higher temperatures than that with a DSC method, which is a relatively static one. The T_g difference may be in the range of 5 to 20°C depending on the polymer itself, frequency, and other experimental parameters used. The DMA technique is in general more sensitive to large scale molecular motions, even though both techniques are based on the thermal motions of polymer chains [20]. It has been known that a tan δ peak measured at a frequency of 10^{-4} Hz in DMA is relatively consistent with a T_g determined from a DSC for an identical sample [20]. A frequency of 1 Hz has been used in this work and it is known that the tan δ maximum shifts to a higher temperature with increasing frequency. Accordingly, these two reasons are responsible for the higher T_g value of the LaRC PETI-5 investigated in this study.

The T_i values are observed to be 10–20°C higher than as expected from the FT-IR result [12]. This is similarly explained by the additional effect on the increase of stiffness owing to the glass fabric substrate. The imidization peak almost disappears at 250°C for 1 h as seen in Fig. 3. Above 300°C, the second peak in the tan δ curve completely disappears, reflecting that no further imidization reaction occurs. The cure reaction of LaRC PETI-5 takes place rapidly around 330–340°C because the phenylethynyl end groups react at an appreciable rate. The reaction peak is barely detectable for the specimen heat-treated at 330°C and finally it disappears for the specimen processed at 350°C, reflecting that no further reaction occurs. The variation of T_c does not significantly depend on cure temperature. This can be explained by the fact that the polyimide develops higher stiffness in this temperature range, which strongly influences its dynamic mechanical properties.

The degree of cure of the polymeric resin in a fiber-reinforced polymer composite can be determined by finding the

Table 1
Values of the degree of cure obtained for the LaRC PETI-5 cured at different temperatures

Temperature (°C)	100	200	250	300	330	350
X_p	0.02	0.13	0.28	0.58	0.83	1

T_g of samples cured at several temperatures and times using the following equation [29],

$$X_p = (T_g - T_{g0})/(T_{g\infty} - T_{g0})$$

where T_{g0} is the glass transition temperature of the uncrosslinked polymeric resin and $T_g\infty$ is the ultimate glass transition temperature, which does not depend on the heat-treatment temperature. T_g can be easily obtained from the tan δ peak temperature for partially cured LaRC PETI-5 at each processing condition in this DMA experiment. X_p is the degree of cure of partially or fully cured polymer in a fiber-reinforced polymer composite system, which can vary with treatment temperature and time. The values of X_p determined in this work are given in Table 1. The variation of the degree of cure as a function of cure temperature for LaRC PETI-5 was very similar to the trends seen in Fig. 4. The degree of cure slowly increases with increasing cure temperature below 250°C. Above 250°C, the degree of cure increases at a higher rate. This result also agrees with the variations of T_g and the extent of cure for neat LaRC PETI-5 resin found in DSC studies [13].

3.3. Isothermal effect on the imidization and cure reactions

Fig. 5 shows the variation of tan δ peaks including imidization behavior against temperature for samples cured under isothermal conditions at temperatures between 220 and 250°C. With varying isothermal time, the presence and absence of the imidization reaction can be clearly monitored by finding the appearance and disappearance of the second characteristic peak in the tan δ curve. The first and third peaks do not change with the isothermal processing temperatures in either position or height. At 220°C in Fig. 5(a), the tan δ peak around 260°C can be clearly seen even after an isothermal hold of 6 h. This indicates that the imidization reaction is not completed at 220°C after 6 h. Fig. 5(b) shows that imidization occurs at 230°C for 3 h and is almost complete after 6 h. With increasing isothermal temperature, the second peak around 260°C becomes smaller and finally disappears at shorter isothermal times. At 250°C, the peak is detectable at 20 min but it disappears after 100 min. In the previous study using FT-IR [12], the imidization behavior of LaRC PETI-5 has been interpreted in terms of the disappearance and appearance of characteristic absorption peaks. It may be concluded here that the imidization behavior can be more clearly followed by monitoring the change of the tan δ peak for both the cumulatively and isothermally cured specimens.

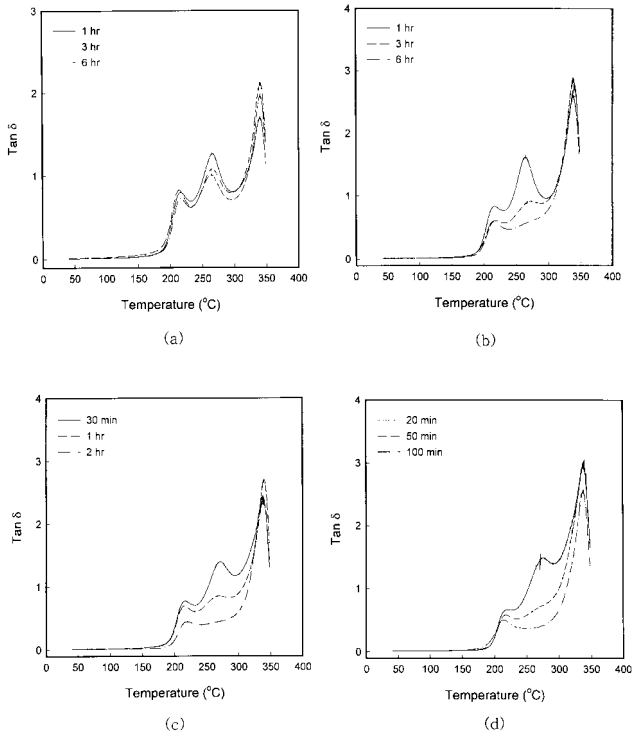


Fig. 5. Changes of tan δ peaks showing imidization behavior against temperature in LaRC PETI-5/braided glass fabric samples cured at different isotherms: (a) 220; (b) 230; (c) 240; and (d) 250°C.

Fig. 6 represents the variation of storage moduli and tan δ peaks as a function of temperature for two different isothermal conditions. At 300 and 350°C, the second peak indicating the imidization reaction is not found. There are only two characteristic tan δ peaks seen at shorter isothermal time. One is an indication of glass transition below 300°C and the other above 300°C is an indication of the cure reaction. The peak around 330°C becomes smaller with increasing time and then disappears after an isothermal hold at 300°C for 3 h. This suggests that no further cure reaction occurs in this system. At 350°C, the tan δ peak or shoulder around 320°C rapidly diminishes after an isothermal hold for a short period of time. The peak finally disappears after 60 min. This result agrees well with the disappearance of the characteristic absorption peak at 2213 cm^{-1} in the reactive phenylethynyl end group at 350°C, as studied using FT-IR spectroscopy [12].

This isothermal study also confirms that the LaRC PETI-5 imide oligomer can be converted to a cured polyimide at 350°C for 1 h. It is observed that the storage modulus slightly increases with increasing cure temperature and isothermal time over the whole temperature range, as seen in Fig. 6(a) and (b).

Fig. 7 shows the effect of an isothermal hold at various temperatures from 220 to 350°C on the tan δ peak temperature as a function of time. Here, the peak temperature indicates the glass transition temperature at each isotherm. The T_g does not strongly depend on the isothermal time when the

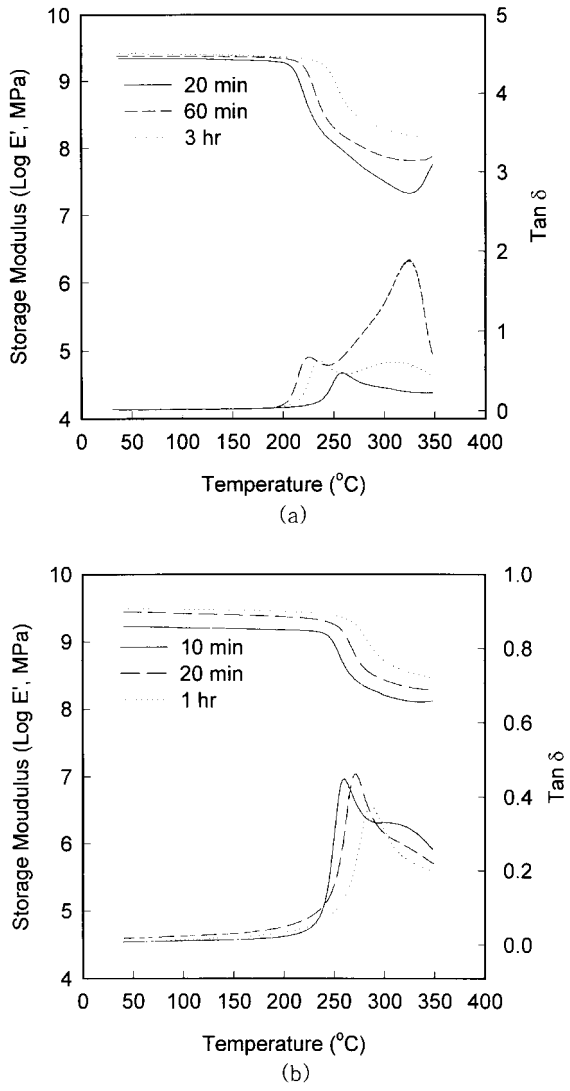


Fig. 6. Changes of storage moduli and tan δ peaks depending on cure reaction against temperature in LaRC PETI-5/braided glass fabric samples at different isotherms: (a) 300; and (b) 350°C.

cure temperature is lower than 300°C. The position of the first peak does not change significantly during the isothermal cure. This indicates that such low temperatures do not significantly influence the chain stiffness even after an extended period of time. For the sample cured at 350°C the peak temperature rapidly increases with increasing isothermal time. This is because the network structure formed in the imide polymer chain causes a large reduction of chain mobility. As the result, the increased chain stiffness leads to a higher T_g. The ultimate T_g of the LaRC PETI-5 polyimide produced by an isothermal cure is observed to be 286°C. This is approximately the same value (287°C) observed in the cumulative cure work. The variation of the peak temperature with time shown in Fig. 7 agrees with the DSC result [13]. Therefore, it can be concluded that processing at temperatures higher than the full imidization temperature leads to a T_g with a large shift of tan δ to

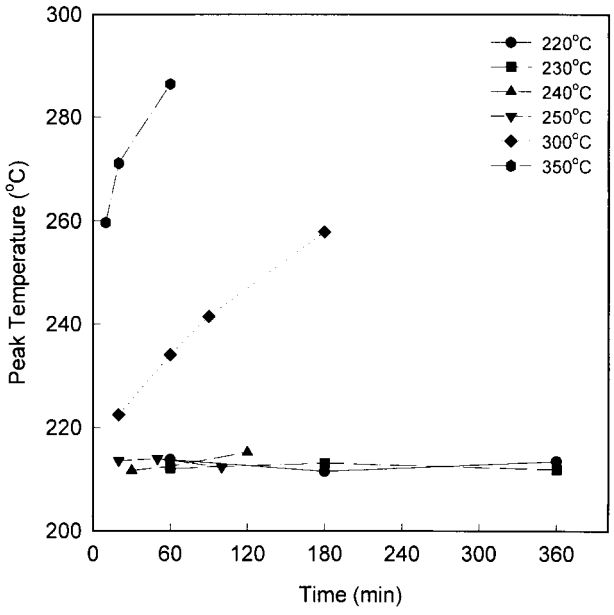


Fig. 7. Effect of the isothermal cure at various temperatures on the tan δ peak temperature as a function of time in LaRC PETI-5/braided glass fabric specimens.

higher temperatures, corresponding to an increase in the degree of cure.

4. Conclusions

The imidization and cure reactions of a LaRC PETI-5/braided glass fabric substrate system have been simultaneously monitored using dynamic mechanical analysis. The chain stiffness and storage modulus increase with increasing cure temperature as the amic acid transforms into an imide oligomer and then a polyimide. The result shows that the dynamic mechanical properties strongly depend on thermal history, especially above 300°C.

Three distinguishable peaks in the tan δ curves are clearly found. The tan δ behavior for the materials cured at different temperatures is explained based upon the variations of glass transition temperature from the first peak in the range of 207–289°C, imidization temperature from the second peak in the range of 260–270°C, and cure reaction temperature from the third peak in the range of 330–340°C, respectively. It has also been noticed that there is a transition from a triplet tan δ peak to a doublet pattern due to completion of imidization above 250°C and finally to a singlet after completion of the cure reaction. The maximum of the singlet tan δ curve at 287°C is identified as the T_g of the LaRC PETI-5 polyimide.

The DMA results also give useful information on the T_g of LaRC PETI-5 heat-treated below 250°C. The degree of cure slowly increases with increasing heat-treatment temperature below the full imidization temperature at 250°C. It increases at a higher rate above 300°C due to fast development of the polyimide network structure. The T_g does not significantly depend on the isothermal processing conditions below 250°C. Thermal processing above 250°C leads to a higher T_g with a large shift of tan δ to higher temperatures. This study confirms that regardless of cumulative or isothermal processing, LaRC PETI-5 can be converted to a fully cured polyimide at 350°C for 1 h.

This study also suggests that a very small amount of LaRC PETI-5 applied as a sizing material to a glass fabric can significantly influence the dynamic mechanical properties in a fiber sizing material system and probably in a fiber-sizing interphase–matrix system. To evaluate the sizing possibilities for a carbon fiber-reinforced polymer composite system, this work will be extended to LaRC PETI-5 with a carbon fabric substrate.

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