

Fluorescence Characterization of LaRC PETI-5, BMI, and LaRC PETI-5/BMI Blends

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Abstract: In the present study, the fluorescence behavior of a phenylethynyl-terminated imide (LaRC PETI-5) resin, a bismaleimide (BMI) resin, and various LaRC PETI-5/BMI blends with different blend compositions has been characterized as a function of heat-treatment temperature, using a steady-state fluorescence technique with a front-face illumination method for solid-state films. It is observed that there are distinguishable changes in the spectral shape, size, and position of fluorescence with varying heat-treatment temperature in the pure and blend samples. The result is qualitatively explained in terms of charge transfer complex formation as well as microenvironmental change with local mobility and viscosity occurring in the LaRC PETI-5, BMI, and their blends during the cure process. The result also implies that a steady-state fluorescence technique may be a useful tool to understand the processing conditions of polyimides and their blends in the film form on the basis of their thermo-photophysical responses.

Keywords: Fluorescence, Phenylethynyl-terminated imide, Bismaleimide, LaRC PETI-5/BMI blend, Cure

Introduction

Phenylethynyl-terminated polyimides (LaRC PETI-5), which have been developed at the NASA Langley Research Center several years ago, and increasingly considered as a new generation of acetylene-terminated thermosetting polyimides, have potential use not only in aerospace and aircraft industries but also as advanced composite matrix resins, adhesives and sizings because of their high temperature and processing performance[1-4]. Bismaleimide (BMI) resin, one of the major types of thermosetting polyimides with reactive end-groups, has received much attention commercially and academically because it can play a role in bridging the gap in temperature, processing performances and various properties between epoxies and polyimides[5,6]. BMI has been widely used as a polymeric matrix in advanced carbon fiber composites for commercial and military aircrafts applications[7-9] since it has unsaturated double bonds in the chain, which can thermally cure without evaporation of volatiles and with reduced shrinkage.

Use of polymer blends is often necessary to combine and enhance the beneficial properties that cannot be successfully achieved only by a single homopolymer component. LaRC PETI-5/BMI blends are of chemical and/or physical incorporation of a tough LaRC PETI-5 polymer and a brittle BMI polymer, depending on their thermal cure profile. Each component can be crosslinked forming a three-dimensional network structure in the polymer chain when processed under proper temperature and time schedules. In LaRC PETI-5, imidization increasingly takes place with temperature to 250 °C via cyclodehydration between the amide and carboxylic acid groups and subsequently cure gradually

takes place with increasing temperature up to 350 °C via crosslinking reaction at the reactive sites in the conjugated polyene and the phenylethynyl end group in the polyimide chain[10,12]. In BMI resin used here, it has been known that 4,4'-bismaleimidodiphenyl methane and *O,O'*-diallyl bisphenol A monomers react via the 'ene' reaction to form the 'ene' prepolymer adduct in the 100-200 °C range and the principle cure reaction takes place in the 200-300 °C range[8,9,13].

Fluorescence techniques have attracted attention as convenient and reliable tools for investigating the cure reaction or crosslinking behavior of thermosetting polymers. This is due to the fact that the fluorescence behavior is sensitive to the microenvironmental change with local viscosity and also the molecular interaction or aggregation, due to a decrease in radiationless deactivation of the excited state[14,15]. Such a photophysical change of fluorescence often allows one to monitor chemical reaction behavior as well as physical behavior occurring during heat-treatment of a thermally curable resin.

A number of publications have been made with the objective of understanding the cure behavior of phenylethynyl-terminated imide oligomers[10-12,16,17] and BMI resins [13,18,19] using analytical methods like differential scanning calorimetry, Fourier Transform infrared spectroscopy, and dynamic mechanical analysis. Also, there have been several literatures reporting the fluorescence behavior of not only some polyimides[20-23] but also polyimide/polyimide blends [24-27] with different monomeric systems resulting in different aromatic polyimide structures. The objective of the present study is to first characterize and qualitatively understand the intrinsic fluorescence behavior of a LaRC PETI-5, a BMI, and various LaRC PETI-5/BMI blends with different blend compositions as a function of heat-treatment or cure temperature, using a steady-state fluorescence

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technique with a front-face illumination method for solid-state films.

Experimental

Materials

The phenylethynyl-terminated imide oligomer used in this work was synthesized and supplied in the liquid form of an amic acid from Imitec, Inc. (Schenectady, NY). 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). The synthesis and chemistry of LaRC PETI-5 have been described in detail elsewhere[4]. The solids content in *N*-methyl-2-pyrrolidinone (NMP) as solvent is about 35 % by weight. The LaRC PETI-5 amic acid oligomer is thermally cyclodehydrated to the LaRC PETI-5 imide oligomer and subsequently transformed into the corresponding polyimide. Figure 1 represents the chemical structures of the components, amic acid and polyimide of LaRC PETI-5. The bismaleimide (BMI) resin used was the Matrimid™ 5292 (Ciba-Geigy, Co.) of a

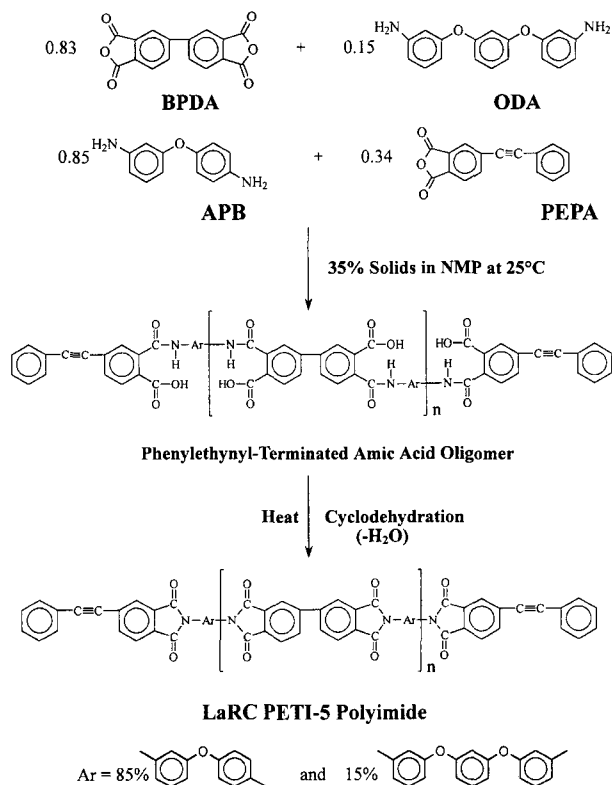


Figure 1. Chemical structures of the components, amic acid oligomers, and polyimide of LaRC PETI-5.

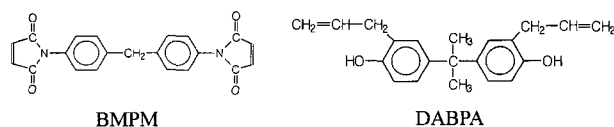


Figure 2. Chemical structures of 4,4'-bismaleimidodiphenyl methane and *O,O'*-diallyl bisphenol A monomers for a bismaleimide resin.

copolymer composed of 4,4'-bismaleimidodiphenyl methane (BMPM) and *O,O'*-diallyl bisphenol A (DABPA) monomers in a 1:1 molar ratio. Figure 2 illustrates the chemical structures of BMPM and DABPA for the BMI resin.

Sample Preparation

The 'as-received' amic acid oligomer with 35 % solids content in NMP was kept in a freezer and warmed to ambient temperature immediately prior to use. The oligomer was diluted to be 10 wt% solids content of LaRC PETI-5 by adding NMP with a magnetic stirrer. The DABPA monomer, an amber viscous liquid, was poured into a beaker with a magnetic stirrer and heated in an oil bath at 130 °C until the viscosity decreased. The BMPM monomer, a yellow crystalline powder, was added slowly and mixed until a homogeneous solution was obtained. The prepolymer solution was then degassed in full vacuum at 130 °C. At room temperature, the solid-state BMI resin was pulverized to be fine powder. The BMI powder was homogeneously mixed to be 10 wt solution by adding NMP with a magnetic stirrer. Thin, uniform films of the LaRC PETI-5 resin and the BMI resin were formed on individual glass plates and subsequently dried at 100 °C for 1 h, respectively. A variety of thin, uniform films of LaRC PETI-5/BMI blends were also prepared by mixing the 10 wt% LaRC PETI-5 solution with the 10 wt% BMI solution with a magnetic stirrer at ambient temperature: BMI:LaRC PETI-5 = 10:90, 30:70, 50:50, 70:30, and 90:10 by weight.

The glass plates with the film samples of the neat resin and the blends were subsequently heated up to 400 °C in steps of 50 °C for 1 h in air. This procedure results in a sample that was exposed to cumulatively greater degree of polymerization at each given heat-treatment temperature prior to each fluorescence measurement. It is noted that each sample must be placed horizontally during the heat-treatment procedure so that it has uniform thickness for acquiring reproducible data of fluorescence.

Fluorescence Measurement

Steady-state fluorescence spectra of each film were observed at ambient temperature in air using an Aminco-Bowman Series 2 Luminescence Spectrometer equipped with a CW xenon lamp as light source. A front-face illumination method with an incident angle of 24° was

utilized. The slit widths were 4 nm for excitation and 8 nm for emission, respectively. The excitation wavelength was 368 nm throughout this work.

Results and Discussion

Phenylethynyl-terminated Imide (LaRC PETI-5) Resin

Figure 3 shows the variations of fluorescence emission spectra as a function of wavelength measured for LaRC PETI-5 at different heat-treatment temperatures. The LaRC PETI-5 amic acid oligomer heat-treated at 100 °C exhibits a structureless broad emission band with a maximum near 458 nm. The size and shape of the spectrum for the 'as-received' oligomer were observed to be almost similar to this band without significant change. It is noted that there are three distinguishable changes in the spectral shape, size and position with varying heat-treatment temperature from 100 °C to 350 °C. The first is a prominent reduction of the fluorescence intensity below 500 nm, the second is a strong enhancement of the intensity near 530 nm, and the third is a large red-shift of the peak to longer wavelength. Such the spectral pattern of fluorescence is quite consistent with the result observed in the previous work[28] on the photophysical behavior of imidization and cure of a phenylethynyl-terminated imide oligomer studied with different types of lamp intensity for fluorescence measurement.

From the earlier work[10-12] it has been found that the reaction rate of LaRC PETI-5 strongly depends on imidization and cure temperatures. The molecular state and mobility of the polyimide chain may alter significantly as consequence. Such molecular changes may play an important role in the fluorescence characterization of interest because fluorescence depends on the changes of molecular environments by physical causes as well as by chemical causes.

The fluorescence spectra observed for the samples heat-

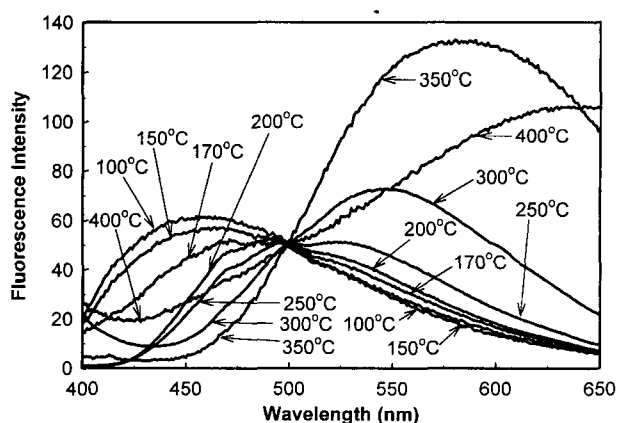


Figure 3. Results of the fluorescence emission spectra obtained for pure LaRC PETI-5 resin as a function of heat-treatment temperature.

treated below 200 °C are largely influenced by NMP solvent in the 'as-received' LaRC PETI-5 amic acid oligomer. It is likely that solvent removal significantly influences the fluorescence emission band below 500 nm, and partial imidization rather influences the band above 500 nm. With the development of the imidized structure in the resin, the fluorescence band at wavelengths above 500 nm is enhanced with a long wavelength tail, especially at 250 °C. As found earlier[9b], the imidization reaction in the LaRC PETI-5 is complete after 1 h at 250 °C. The fluorescence intensity above 500 nm gradually increases with increasing heat-treatment temperature below 250 °C. Such an increase in the fluorescence of LaRC PETI-5 can be explained by the formation of charge transfer complexes occurring during the imidization process. Several publications[14,20,21,29] have reported that the formation of intermolecular charge transfer complexes in aromatic polyimide chains is mainly responsible for the enhancement of fluorescence intensity with heat-treatment or cure. In the LaRC PETI-5 chain, the anhydride moieties in the BPDA and PEPA molecules play a role as electron acceptor and the diamine moieties in the APB and ODA molecules as electron donor. Electron-donor and acceptor molecules can intermolecularly interact each other forming the complexes depending on the molecular environment between two neighboring molecules in the different imide chains during the imidization process.

The large increase of fluorescence intensity at 300 °C is primarily ascribed to cure reaction of LaRC PETI-5 polyimide, which is activated around 300 °C. The intensity is markedly increased at 350 °C. This may be due to the higher concentration of the charge transfer complexes formed at higher heat-treatment temperature, resulting in rigidization of the aromatic polyimide chains. In other sense, the significant enhancement of the fluorescence intensity in the range of 300 °C-350 °C is substantially the result of a micro-environmental change occurring during the cure process. The viscosity and molecular weight of the LaRC PETI-5 significantly increase at this stage. As the cure temperature exceeds the imidization temperature, the formation of a three-dimensionally crosslinked structure between C≡C bonds in the reactive phenylethynyl group located at the imide polymer chain ends proceeds causing a large restriction of chain mobility until the network is complete. An increase in the micro-viscosity in the thermally curable polyimide system results from the large restriction of molecular mobility with further rigidization of the fluorescing imide chains on cure. It has been generally understood that the degree of aggregation and the concentration of intermolecular charge transfer complexes increase with increasing degree of cure and short-range molecular ordering in polyimide[14]. As a result, there is a decrease in the nonradiative decay rate and consequently an increase in the fluorescence quantum yield, reflecting an increase in the fluorescence intensity.

The formation of a well-developed network structure may influence the red-shift of the spectrum as well as the fluorescence intensity. The red-shift of the fluorescence emission peaks, as clearly observed above 300 °C, is due to the development of more ordered stable structure with a lower energy state by the formation of intermolecular charge transfer complexes at higher cure temperature. This result, showing a large enhancement of the fluorescence intensity in the range of 300 °C-350 °C, agrees well with the previous results obtained from differential scanning calorimetry (DSC)[10] and dynamic mechanical analysis (DMA)[12] studies. As found earlier from the thermal studies, the present fluorescence result also shows that in the LaRC PETI-5 the cure largely proceeds in the range of 250 °C-300 °C, occurs with a greater extent in the range of 300 °C-350 °C, and completes at 350 °C. The fluorescence emission band is further red-shifted at 400 °C. This is likely ascribed to an additional red-shift due to a post-curing effect of LaRC PETI-5 polyimide. Charge transfer fluorescence also occurs with a lower energy state, resulting in a shift to longer wavelength.

Bismaleimide (BMI) Resin

Figure 4 shows the variations of the fluorescence emission spectra for BMPM/DABPA bismaleimide resin in the film form heat-treated at different temperatures. As can be seen, there are multiple peaks in the spectral range of 465-500 nm, observed for the samples heat-treated at 100 °C, 150 °C, and 170 °C. The peak intensities decrease with increasing temperature. With increasing the heat-treatment temperature to 170 °C, the characteristic fluorescence band with peaks almost disappears while a broad structureless band is developed with a maximum at about 525 nm, showing the enhanced fluorescence intensity in the higher wavelength range. The disappearance of the fluorescence peak in the

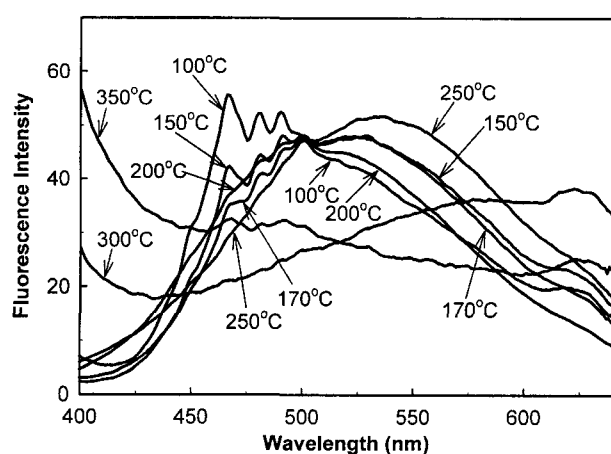


Figure 4. Results of the fluorescence emission spectra obtained for pure bismaleimide resin as a function of heat-treatment temperature.

range of 465-500 nm and the broadening of the spectrum with a maximum at about 530 nm indicate that the phenylmaleimide in the BMPM is consumed to transform it into the phenylsuccinimide structure with a higher possibility at 170 °C, as described in the earlier fluorescence work in solution on the model compounds by Phelan and Sung[30]. A dramatic enhancement of fluorescence intensity on cure, as detected in the LaRC PETI-5, was not observed in the BMI resin because the phenylmaleimide moiety in the BMPM plays a role as a fluorescence quencher of the DABPA in the intermediate stage of cure reaction[30]. The fluorescence intensity for the sample heat-treated at 200 °C is decreased. The reason for this has not been clear. One possible explanation is that fluorescence intensity tends to reduce as a result of low molecular weight charge transfer complex systems[20].

It is generally known that 250 °C is frequently used as the highest resin cure temperature for processing a fiber reinforced BMI composite. The fluorescence intensity with a maximum at about 535 nm is increased at 150 °C and is further increased at 250 °C. The result implies that the cure reaction via the C=C bonds initially takes place around 150 °C and it is apparently completed near 250 °C. It is noted that BMPM and DABPA monomers react via the 'ene' reaction to form the 'ene' prepolymer adduct in the 150 °C-200 °C range. The principle cure reaction to complete the polymerization takes place around 250 °C, as pointed out that most of the C=C bonds in the phenylmaleimide group are consumed to be succinimide moieties by the 'ene' reaction at 250 °C for 3 h[8,9,13].

In the solid state, fluorescing moieties in the molecular chains may be located close enough to each other with high possibility. This is likely to cause charge transfer interactions when molecules are excited. The greatest increase of the fluorescence emission at 250 °C is mainly attributed to crosslinking of the BMI resin, at which the principle cure reaction takes place. At this stage, the highest concentration of the charge transfer complexes may be formed, resulting in rigidization of the cured BMI product with a network structure. The microenvironmental change accompanying the increased local viscosity and the restricted molecular motion during the heat-treatment process also contributes to enhancing the fluorescence intensity, resulting in a decrease in radiationless deactivation of the excited state, as described earlier.

At 300 °C, the fluorescence emission band is shifted to longer wavelength. This is likely ascribed to a thermal aging effect of the BMI resin, as similarly observed for the LaRC PETI-5 polyimide at 400 °C. As a matter of fact, the color of the sample heat-treated at 300 °C was changed to black color indicating the initial loss of integrity of the material. Subsequent heating to 350 °C causes the serious loss of integrity of the cured resin and also its fluorescing moieties in the molecules, leading to an increase of radiationless

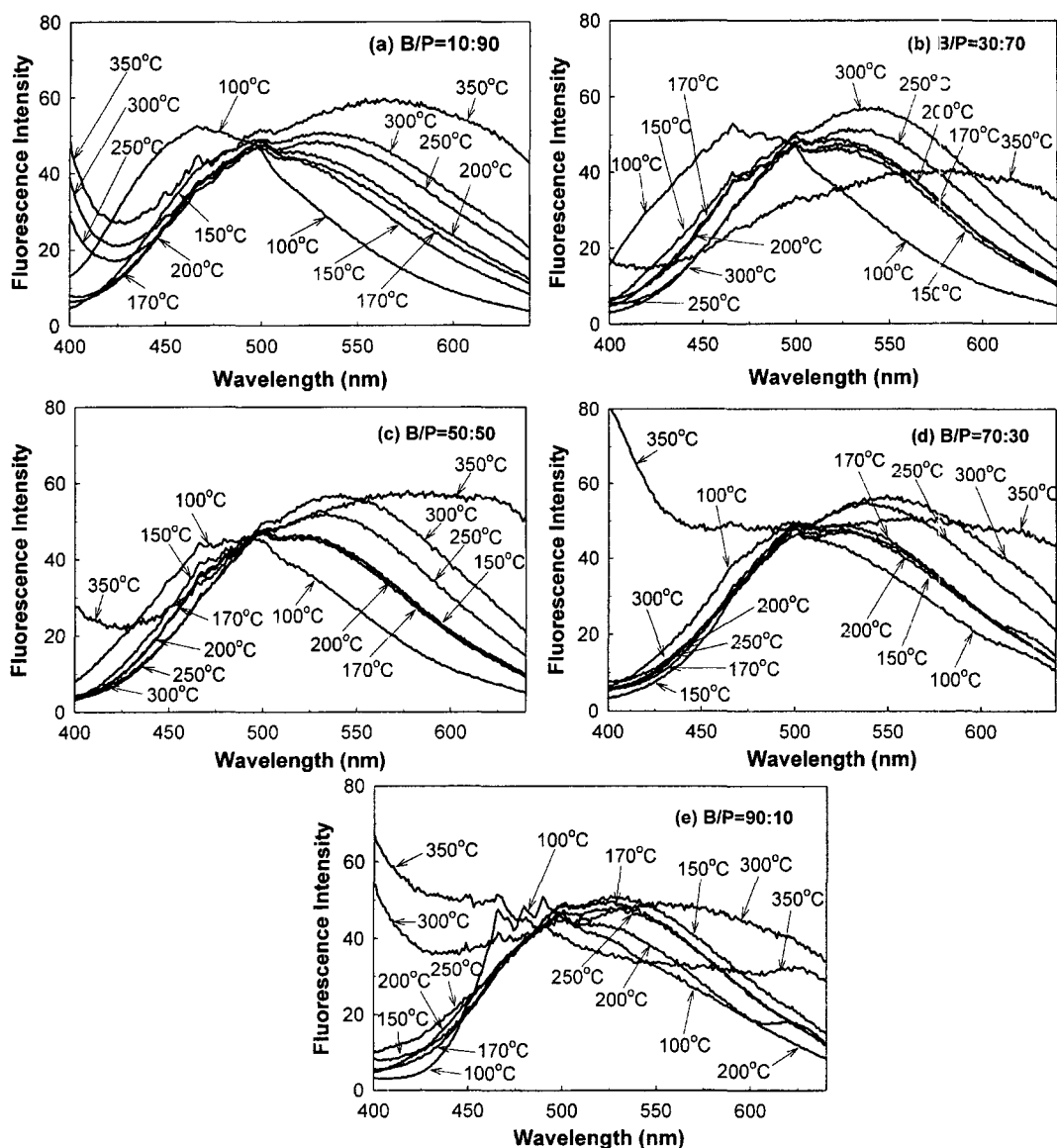


Figure 5. Results of the fluorescence emission spectra obtained for LaRC PETI-5/BMI blends with different compositions as a function of heat-treatment temperature. B and P designate BMI and LaRC PETI-5 components in the blend, respectively.

deactivation.

LaRC PETI-5/BMI Blends

In this work, LaRC PETI-5/BMI blend films for fluorescence measurement were prepared varying heat-treatment temperature of LaRC PETI-5 amic acid oligomer and BMPM/DABPA prepolymer blend films obtained by solution casting at each blend composition. Figure 5 shows the variations of the fluorescence spectra as a function of heat-treatment temperature at different blend compositions. In the figures, B and P designate the BMI and the LaRC PETI-5, respectively. As noted earlier, it is also observed that there are distinguishable changes in the spectral shape, size and

position with varying heat-treatment temperature in each blend sample. The distinct spectral changes are shown above 500 nm as well as below 500 nm, depending on temperature and blend ratio. It is found that the relative fluorescence intensities observed for all the blend samples heat-treated below complete imidization temperature of LaRC PETI-5 are comparable with those observed for pure LaRC PETI-5 and BMI under the identical conditions with the fluorescence measurements used in Figures 3 and 4. However, the fluorescence behavior observed above 500 nm for the samples heat-treated above complete imidization temperature is somewhat different between the blend compositions.

The fluorescence emission bands for the cured blend sample in the wavelength range above 500 nm are less developed than those for the cured LaRC PETI-5 seen in Figure 3. This may be due to an incorporation of the BMI chains into the LaRC PETI-5 polyimide chains during cure process. The fluorescence intensities above 500 nm are relatively greater as the LaRC PETI-5 component predominates (ca. B/P=10:90) in the blend than as the BMI component predominates (ca. B/P=90:10). That is, the enhancement of the fluorescence intensity above 500 nm is decreased with increasing the BMI content in the blend. It may be explained by that the BMI chains composed of non-fluorescent BMPM and fluorescent DABPA[30] may play a role as weak fluorescence quencher of LaRC PETI-5.

With increasing the LaRC PETI-5 composition in the

blends, the spectral pattern of fluorescence measured for the uncured samples is more likely to be that of pure LaRC PETI-5 shown in Figure 3. On the other hand, with increasing the BMI composition, the spectral pattern is more likely to be that of the pure BMI shown in Figure 4. This is probably because there is no significant interaction between the two components in the uncured state. However, the fluorescence behavior is different when the blend sample is cured. If there is some physical and/or chemical interaction between the components of the blend, the spectral shape of the blends and that of pure polyimide should not be identical. When the binary blend is quite miscible, there may be some physical and/or chemical interactions between the components. In the present system, the LaRC PETI-5 and BMI molecular chains may interdiffuse and/or co-cure

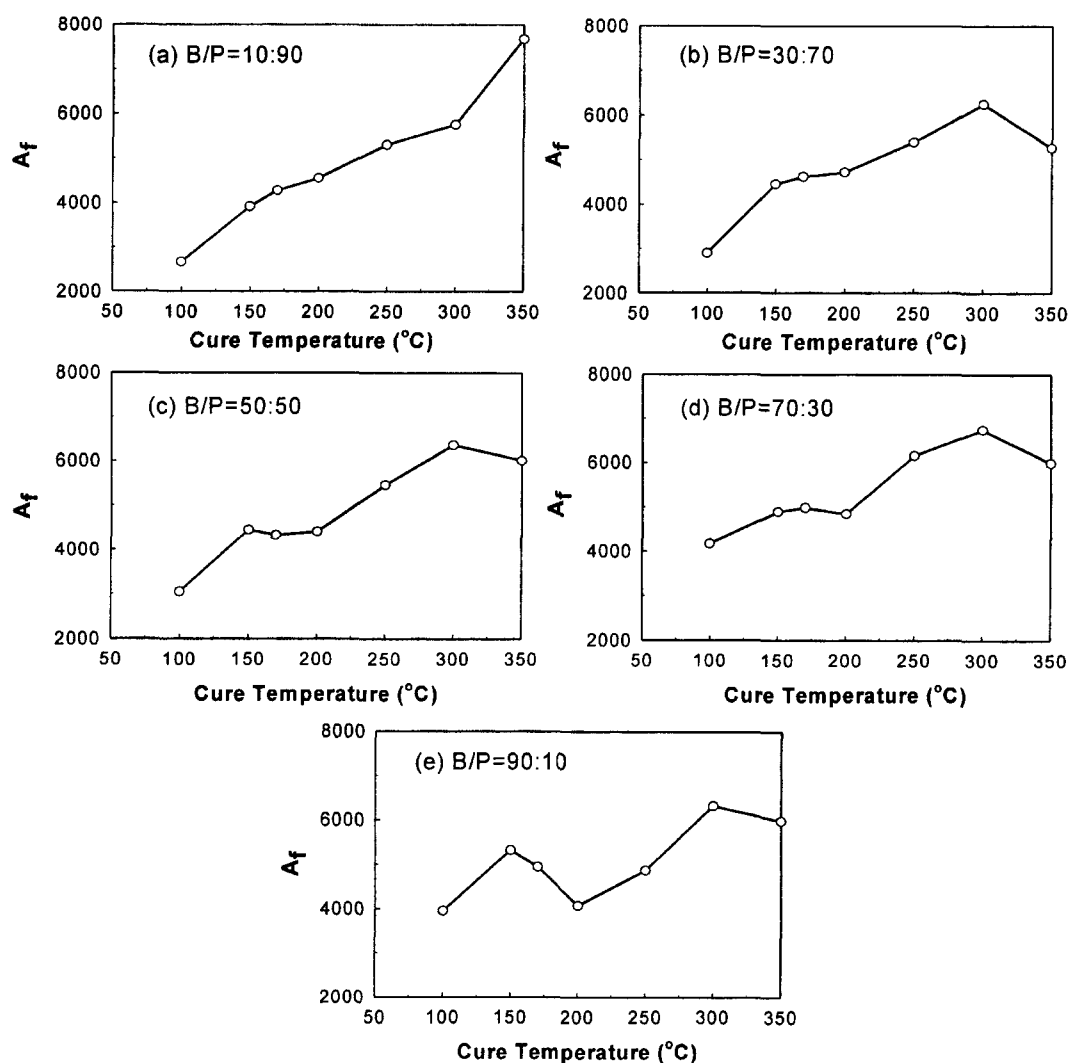


Figure 6. Variations of the spectral area (A_f) of fluorescence measured for LaRC PETI-5/BMI blends with different compositions as a function of cure temperature. The A_f values were calculated based on the wavelength range of 500-640 nm.

because both components are miscible in a common solvent and also thermally curable at common cure temperature in the range of 200 °C-300 °C. If the blend is immiscible or phase-separated during the cure process, the fluorescence of each component in the blend will behave as that of the pure component.

Figure 6 represents the plots of the spectral area of fluorescence (A_f) calculated from 500 nm to 640 nm as a function of cure temperature at five different blend compositions. The reason for a choice of 500-640 nm instead of the whole wavelength range measured is that the fluorescence band significantly changes with cure temperature in the spectral range of 500-640 nm. There are two characteristic features in the plots seen in Figure 6. One is the variation of the spectral area when each blend sample is fully cured. As noted earlier, the principle cure reaction is completed around 350 °C for the pure LaRC PETI-5 and around 250 °C for the pure BMI. As LaRC PETI-5 component predominates in the blend (B/P=10:90), the spectral area is gradually increased between 200 °C-300 °C and is markedly increased between 300 °C-350 °C. The increase of A_f in Figure 6(a) is due mostly to the fluorescence from the LaRC PETI-5 component but it is slightly suppressed by the BMI component.

In Figure 6(b), the increase of the spectral area of fluorescence with increasing cure temperature is more suppressed by the BMI component than in Figure 6(a) due to the increased BMI component in the blend. The change of the fluorescence spectrum at the cure temperature of 350 °C in the blend can be influenced by two reasons. One is due to charge transfer complexes formed increasingly at the final stage of cure of the LaRC PETI-5 component, resulting in the enhancement of fluorescence intensity and the red-shift of the spectrum. The other is because at 350 °C the BMI component may decompose and lose its fluorescing moiety in the molecule, leading to an increase of radiationless deactivation. The two facts may contribute to the fluorescence behavior of the blends. As the result, the fluorescence intensity for the blend sample cured at 350 °C is lower and it is shifted to longer wavelength, as shown in Figure 5(b). The spectral area is rather decreased at 350 °C, as plotted in Figure 6(b). With increasing the amount of the BMI, the radiation deactivation becomes profound. Therefore, the fluorescence at 350 °C cannot be properly detected and analyzed at which the BMI component is equal to or greater than the LaRC PETI-5 component even though the data are included in Figures 6(c), (d), and (e).

When the BMI is a dominant component in the blend, the spectral area around 150 °C is slightly increased in Figure 6(d) and largely increased in Figure 6(e). And then, the A_f is increased again above 200 °C. This is because the BMI component in the blend is initially cured in the range of 150 °C-200 °C and principally cured in the range of 200 °C-250 °C, as described earlier. Combining all the fluorescence

results, processing temperatures for LaRC PETI-5/BMI blends are suggested to be around 150 °C for the primary cure, around 250 °C for the secondary cure, and below 300 °C for the final cure.

Conclusions

The fluorescence behavior of a LaRC PETI-5 resin, a BMI resin, and various LaRC PETI-5/BMI blends with different blend compositions has been characterized as a function of heat-treatment temperature, using a steady-state fluorescence spectrometer equipped with a solid state sample compartment for front-face illumination. Some distinguishable changes in the spectral shape, size, and position of fluorescence are observed depending on heat-treatment or cure temperature of LaRC PETI-5, BMI, and their blends. The result is understood in terms of charge transfer complex formation as well as microenvironmental change with local mobility or viscosity occurring in the LaRC PETI-5, BMI, and their blends during the cure process.

This fluorescence result, showing a change of the fluorescence intensity examined at temperatures for characterizing the reaction of LaRC PETI-5 or BMI between 100 °C and 400 °C, agrees well with the previous results obtained from thermal studies. The fluorescence result suggests that promising processing temperatures for LaRC PETI-5/BMI blends are around 150 °C for the primary cure, around 250 °C for the secondary cure, and below 300 °C for the final cure. The result of the present study also implies that a steady-state fluorescence technique may be a useful tool to understand the processing conditions of polyimides and their blends in the film form on the basis of their thermophysical responses.

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