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The Effect of Cure History on the Fluorescence Behavior of an Unsaturated Polyester Resin with A Fluorescence Probe

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Abstract: Abstract: We have extensively characterized the fluorescence behavior of unsaturated polyester (UP) resin in the absence and presence of a 1,3-bis-(1-pyrenyl)propane (BPP) fluorescent probe at various dynamic and isothermal cure histories by means of a steady-state fluorescence technique using a front-face illumination equipment. In addition, we explored the effect of the fluorescence intensity on the relaxation of the fluorescent probe in the UP resin by resting the dynamically and isothermally cured resin at ambient temperature and pressure for 24 h. The monomer fluorescence intensity, which has two characteristic peaks at 376 and 396 nm, changed noticeably depending on the cure temperature and time and provided important information with respect to the molecular and photophysical responses upon curing. The result of the fluorescence study indicates that the increased local viscosity and restricted molecular mobility of the UP resin surrounding the BPP probe after curing are both responsible for the enhancement of the monomer fluorescence intensity. Our results also demonstrate that once the BPP probe has enough time to rearrange and become isolated prior to fluorescence, a sufficient amount of fluorescence is emitted. Therefore, we note that the fluorescence behavior of this UP resin system is influenced strongly by the relaxation process of the fluorescent probe in the resin as well as process used to cure the resin.

Keywords: steady-state fluorescence, unsaturated polyester, fluorescence probe, dynamic and isothermal cure behavior.

Introduction

Unsaturated polyester (UP) resins have been widely used in versatile industrial and commodity applications, especially as thermosetting matrix resin for glass fiber-reinforced polymer composites, which were manufactured by compression molding in the form of sheet or bulk molding compounds, pultrusion and resin transfer molding.[1,2] This is due to their versatility in properties, processibility, and low cost. The properties of UP resin and the composite strongly depend on the cure behavior.[3,4] Therefore, understanding the cure behavior of UP resin is critical for process control and property optimization of the products.

The UP resin is thermally curable at room temperature or elevated temperature, depending on cure time and temperature, curing agent, and/or accelerator involved.[5-7] The UP resins normally undergo rapid cure accompanying exothermic reaction. However, the cure of UP resin proceeds based upon a free radical reaction mechanism with initiation, propagation, termination, and transformation. Also, physical processes such as gelation, crosslinked network formation, vitrification and infinite molecular weight build-up take place during curing.[8]

There have been a variety of analytical tools[3] to investigate the cure behavior of thermosetting polymers, for example, differential scanning calorimetry (DSC),[6,7] dynamic mechanical analysis (DMA),[4] Fourier transform infrared (FTIR) spectroscopy,[6,7] fluorescence,[9,10] etc. Each analytical method has different instrumental methodologies and its own advantages and limitations in use, depending on the cure characteristics of measuring resins. Among analytical methods, a fluorescence technique is very powerful to explore the cure behavior based upon molecular and photophysical information involved in changes of local viscosity, chain mobility, micro-environment, and complexation between an intrinsic or extrinsic fluorophore and polymer chains, relying on a time/temperature profile during cure process.[11-13] Fluorescence measurement is also relatively simple, highly reliable, and rapid for data acquisition. In addition, this method is non-destructive and possible to on-line monitor the cure process, which is significantly influenced by a temperature/time profile.

A number of papers have been reported that the cure behavior of thermosetting resins such as epoxy,[10,14] polyimide[13,15] and polyurethane[16] can be effectively monitored by means of

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a steady-state fluorescence technique using probed or labeled molecules with fluorescing moieties. This is possible because probed or labeled molecules, which have strong absorption and emission in the ultraviolet region, are very sensitive to the local mobility of molecules that decrease with increasing the degree of cure and viscosity. However, studies on the cure behavior of unsaturated polyester using a fluorescence technique have rarely been found. Recently, Cho *et al.* reported that use of fluorescence spectroscopy can provide useful information on the cure characteristics of an epoxy system with 1,3-bis-(1-pyrene)propane (BPP) probe molecules in the low cure temperature region, where has not been well interpreted by other analytical methods.[10]

This study focuses on monitoring the cure behavior of UP resin, which is not photophysically characteristic, with an aid of BPP probe that fluoresces characteristically and uniquely. Consequently, the objectives of the present work are first to investigate the fluorescence behavior of UP resin, which is dynamically and isothermally cured at different temperature and time, in the absence and presence of a BPP fluorescence probe by means of a steady-state fluorescence technique with a front-face illumination equipment. And, the second objective is to explore the effect of the fluorescence intensity on the relaxation of the fluorescence probe in the UP resin as the dynamically and isothermally cured resin with the probe has been rested at ambient temperature and pressure for 24 hrs.

Experimental

Materials. The orthophthalic-based UP resin (UP-G R235) used in this work was supplied from Sewon Chemical Co., Korea. The commercial resin has the styrene contents of about 35% by weight as crosslinking agent and diluent and also has a very small amount of inhibitor, hydroquinone. Methyl ethyl ketone peroxide (MEKP) was used as the initiator. 1,3-Bis-(1-pyrenyl)propane (BPP), which was purchased from Molecular Probes, Inc., was used without modification as a fluorescence probe. Figure 1 shows the chemical structures of (a) UP resin, (b) MEKP, and (c) BPP used in the present study.

Sample Preparation. First, the BPP probe was well dissolved in MEKP because it was not uniformly dispersed in the UP resin of relatively high viscosity. The solution of MEKP and BPP was homogenously mixed again with the UP resin by mechanically stirring in a 100 ml beaker. The resin sample for fluorescence measurement was prepared to contain the MEKP of 0.2 wt% and the BPP of 1.0×10^{-4} M. The resin mixture was placed in a vacuum oven for a sufficient period of time to completely remove the air bubbles generated during mixing. In this study, the MEKP concentration has been fixed to avoid possible complexity to interpret a number of fluorescence data.

A glass plate and a cover glass slide were sandwiched each other and then three sides of the sandwiched glasses were dammed with small pieces of glass in rectangular shape. All the contacting sides between the glass pieces were adhered with a fast-cure adhesive to avoid possible licking of the resin during fluorescence measurement. Then, a small amount (about 1~2 mg) of the UP mixture resin was carefully inserted in between a glass plate and a cover glass slide. Cure processes of the resin sample containing in the sandwiched glasses were performed under given temperature and time in a dry oven. Each sample was dynamically cured at 50, 70, 90, 100, 110, 120, 150 and 170 °C for 10 min, respectively. Also, samples were isothermally cured at 90 °C for 10, 30, 60, 120 and 150 min, respectively. During the cure process, the BPP segregation in the UP resin was not observed.

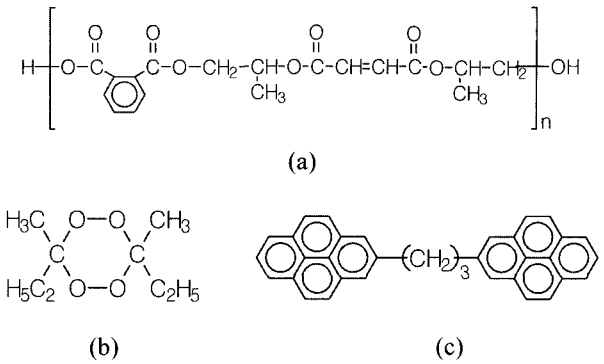

Figure 1. Chemical structures of (a) unsaturated polyester, (b) methyl ethyl ketone peroxide (MEKP) and (c) 1,3-bis-(1-pyrenyl) propane (BPP) used in this work.

Fluorescence Measurement. A steady-state fluorescence spectroscopy (Aminco-Bowman Luminescence Spectrometer Series 2: SLM-AMINCO Spectronic Instruments, Inc.) was used to examine the photophysical responses according to the dynamic and isothermal cure processes of the UP resin containing BPP probe molecules. A 7 watt pulsed xenon lamp was used as the light source. A front-face illumination method with an incident angle of 45°, which is proper for measuring solid samples like resin and film, was applied throughout this work. A slit width of 4 nm was used for both excitation and emission. The excitation wavelength was 358 nm and the emission wavelength was 437 nm. The scanning range of the fluorescence emission was 300 to 600 nm. All the emission spectra were corrected for instrumental response. The background spectrum from the covered glass was subtracted from each fluorescence spectrum obtained from the UP resin sample. To see how the resting time of the UP resin sample after sample preparation influences the fluorescence spectrum with varying cure condition, fluorescence measurements were conducted as soon as each sample was prepared and also after 24 hrs were elapsed in ambient temperature since the sample preparation. All fluorescence measurements for uncured and cured samples were done at ambient tem-

perature and pressure.

Results and Discussion

Dynamic Curing Effect. Figure 2 shows the steady-state fluorescence spectra of UP resin without a BPP probe measured at various cure temperatures from 50 to 170 °C. The fluorescence spectrum of uncured UP resin is also compared with the cured ones. The uncured one exhibits a broad structureless emission band with a maximum at about 440 nm. There is no significant change in the spectra observed for the UP resins cured up to 120 °C, at which the curing process obviously takes place. It is observed that the spectra for the samples cured at 150 and 170 °C, respectively, are shifted to lower wavelengths about 30 nm with slightly higher intensity. A blue-shift in the fluorescence emission band may be because the UP resin with network structure and higher rigidity is obtained as curing process is completed. However, the most prominent stage of curing process in the range of 70~150 °C, as demonstrated with an identical UP/MEKP system using differential scanning calorimetry (DSC) earlier,[17] has not been successfully analyzed with the fluorescence spectra measured in this UP resin system without an introduction of fluorescence probe.

Therefore, a BPP probe with intrinsic fluorescing moieties has been introduced in the present resin system. Figure 3 represents a typical steady-state fluorescence spectrum observed for a BPP probe in NMP solution, showing three characteristic emission peaks at 376, 396, and 418 nm due to monomer fluorescence. The two sharp peaks at 376 and 396 nm are prominently distinguishable, as studied earlier.[10] The monomer fluorescence emission is resulted from the isolated BPP probe with pyrenyl groups in the excited state. The broad peak centered at about 490 nm is due to excimer fluorescence formation[18] between the incorporated probe molecules in dilute solution. It has been studied that the excimer fluorescence emission is generally resulted from the fluorescence emission coming from excimers that have a conformationally sandwiched structure formed between two pyrenyl groups located at the two ends of flexible methylene units in BPP.[10] The excimer fluorescence is normally found at higher wavelengths than the monomer fluorescence.

Figure 4 shows the fluorescence spectra of the UP resin containing a BPP probe of 1.0×10^{-4} M measured at various cure temperatures from 50 to 170 °C. The cure time was 10 min at each cure temperature. Each fluorescence measurement

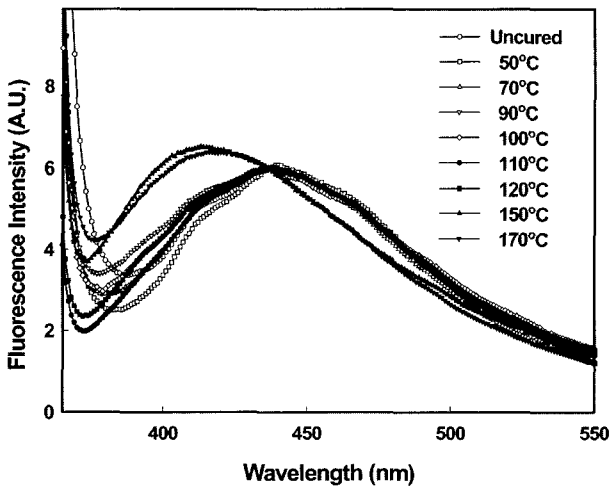

Figure 2. Steady-state fluorescence spectra of unsaturated polyester without a BPP probe measured at various cure temperatures. Cure time was constant to be 10 min at each temperature.

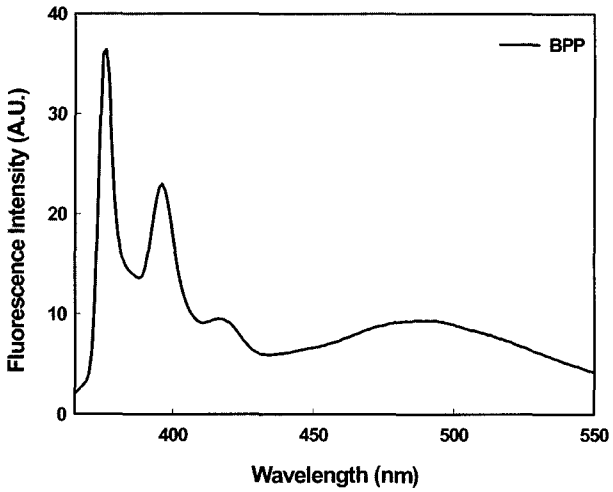

Figure 3. A steady-state fluorescence spectrum of BPP probe dissolved in *N*-methyl-2- pyrrolidinone. λ_{ex} = 358 nm.

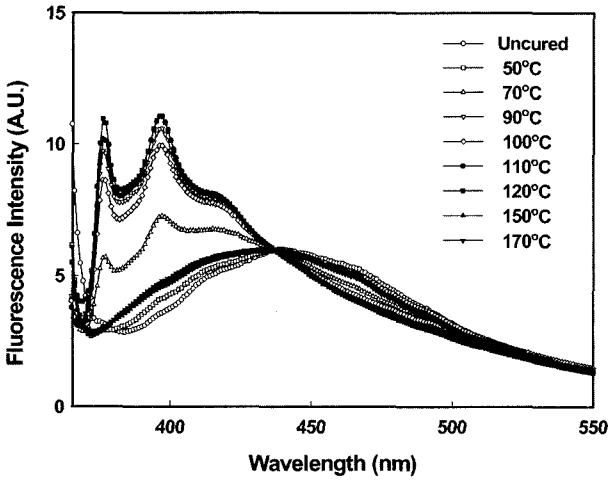

Figure 4. Steady-state fluorescence spectra of unsaturated polyester with a BPP probe measured at various cure temperatures. Cure time was constant to be 10 min at each temperature. Each fluorescence measurement was performed right after the sample preparation.

was performed as soon as each sample was cured at given conditions in an oven and then cooled down to ambient temperature. Both UP resins uncured and heated at 50 °C exhibit a broad structureless fluorescence band with a maximum at about 440 nm, as similarly found in Figure 2. At a cure temperature of 70 °C, the spectrum is markedly changed from a structureless band to a structured band, reflecting the incorporation of BPP probe in the UP resin. The two peaks at 376 and 396 nm have exactly same locations as observed in Figure 3, but with smaller intensity. Such the two peaks due to monomer fluorescence emission are not found in the spectra observed from both resins uncured and heated at 50 °C. It was reported that the UP resin with the same amount of MEKP does not show any exothermic reaction at 50 °C, which means no cure reaction involved at this stage.[17]

Figure 5 depicts the variation of the fluorescence intensity as a function of cure temperature at 376 and 396 nm, respectively. Each data was obtained from the spectra in Figure 4. The fluorescence intensities at the two peaks significantly increase with increasing cure temperature up to 120 °C, with the exception of 100 °C. However, there is no pronounced change in the spectral shape of the fluorescence, indicating that there is no significant specific interaction between the UP resin and the fluorescence probe. The result indicates that the maximum values of the fluorescence intensity at 376 and 396 nm in the present UP resin system are attained in the cure temperature range of 110~120 °C. The increase of the monomer fluorescence intensity is ascribed to an increase of local viscosity of the UP resin surrounding the BPP probe molecules. The molecular mobility of the isolated BPP probe in the excited state is gradually restricted by an increase of local viscosity of the UP resin with increasing the extent of cure. Hence, the molecular energy, which cannot be emitted due to the restricted molecular motion, may

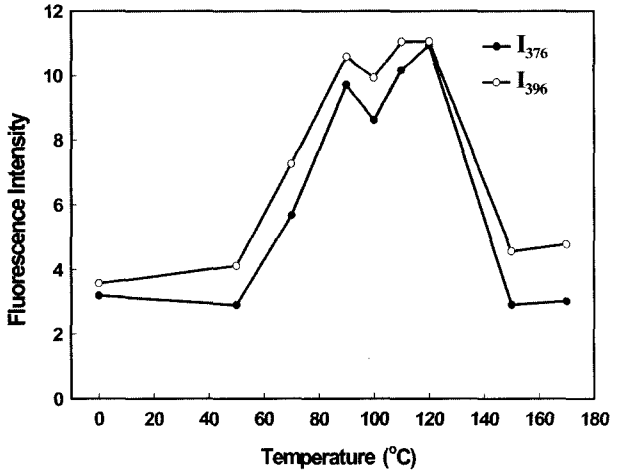

Figure 5. Plots of fluorescence intensity as a function of cure temperature at λ_{em} = 376 nm and λ_{em} = 396 nm, respectively, obtained from the spectra in Figure 4. λ_{ex} = 358 nm

fluoresce with the enhanced intensity, leading to a decrease in the non-radiative decay process. As shown in Figure 4, both fluorescence spectra measured with the samples cured at 150 and 170 °C, respectively, exhibit a broad structureless band without the characteristic peaks in the low wavelength range again, as examined in the uncured resin. A slight spectral shift to lower wavelengths is also observed. The fluorescence intensity largely decreases at these two cure temperatures, as shown in Figure 5. At the final stage of curing process above 150 °C, the resin viscosity ultimately increases and a three-dimensional network structure with infinite molecular weight is formed.[19] The molecular mobility of BPP probe is completely restricted. It is noticeable that the monomer fluorescence emission from the isolated BPP probe disappears. One possible reason for this is that BPP probe is thermally unstable above 150 °C and it may lose its fluorescing moieties so that no more fluorescence emits.

For the case of the sample cured at 100 °C, the slight decrease of the fluorescence intensity at 376 and 396 nm may be resulted from a very small amount of inhibitor contained in the as-received UP resin. Since the cure reaction of UP resin is exothermic, the stated reaction can proceed quite rapidly. The molecules in inhibitor absorb free radicals formed during the reaction and play a role in inhibiting the occurrence of the reaction to some extent. Therefore, the presence of inhibitor results in an increase of fluorescence emission with an increased non-radiative decay process. In an earlier report,[17] the additional exothermic reaction takes place near 105 °C by some unreacted styrene remaining in the resin due to the inhibitor even after the initiator MEKP has been completely consumed at this temperature.

As seen in Figure 4, no excimer fluorescence band was observed unlike the spectrum in Figure 3. This is probably because in the excited state the conformationally sandwiched structure between two pyrenyl groups of the BPP probe cannot be formed spatially in the resin or solid state. The third peak near 418 nm shown like a shoulder is not changed greatly once the resin cure proceeds to a large extent above 90 °C. The lower value of the fluorescence intensity in the UP resin system in Figure 4 than that of BPP seen in Figure 3 may be attributed to the micro-environmental change surrounding the fluorescing BPP probe. It may be deduced from an earlier report[20] that the UP resin may play a role as fluorescence quencher of BPP probe, although the quenching effect may be reduced while the resin cure proceeds with temperature and/or time.

This fluorescence result is quite consistent with the result revealed from a differential scanning calorimetry (DSC) thermogram measured during curing. Based upon the DSC result studied previously,[17] it is expected that the maximum fluorescence intensity may be found at the lower temperature region of 85~95 °C with an increase of MEKP concentration. Even though the same cure time and temperature conditions are utilized, one cannot have absolutely comparable data on

cure between fluorescence and DSC. This is because the two analytical techniques are different in the instrumental methodology and mechanism for data acquisition. However, one may have just a relatively comparable result.

Figure 6 shows the steady-state fluorescence spectra of UP resin with a BPP probe at various cure temperatures. The measurement was conducted after each sample was rested at ambient temperature for a long period of time (24 h) prior to each fluorescence measurement. The only difference of the measuring sample in Figure 6 from the sample used in Figure 4 is the length of time elapsed from sample preparation to fluorescence measurement. It is noticeable that there are three distinguishable changes in the spectral pattern in comparison with the result shown in Figure 4. First, the relative values of the monomer fluorescence intensity at 376 and 396 nm are greater than those in Figure 4 at each cure temperature. The UP resin can be additionally cured with more compact molecular structure at a much slower rate while the prepared samples under the given cure conditions have been rested at ambient temperature for 24 hrs. This turns out that under this condition the BPP probe has enough time to be rearranged and isolated prior to fluorescence so that the BPP monomer fluorescence is sufficiently emitted during measurement.

Second, the monomer fluorescence intensity at 376 and 396 nm gradually decreases with increasing cure temperature, as depicted in Figure 7. This is different from the tendency examined in Figure 5. In Figure 6, the spectra measured for the resins completely cured at 150 and 170 °C is almost similar pattern of the fluorescence with the bands shown in Figure 4. The values of the fluorescence intensity are comparable. The result implies that, in the case of quick measurements without resting the sample, the fluorescence behavior in Figure 4 is mainly governed by the curing process of the UP resin system. On the other hand, in the case of delayed measurements with sufficiently rested samples, the fluorescence behavior is significantly governed by isolation or relaxation process of fluorescence probe molecules as well as cure process. It is also noted that there is a slight drop of the monomer fluorescence intensity at both 376 and 396 nm, as similarly pointed out in Figure 5. This is attributed to the presence of inhibitor remaining in the UP resin during the curing process, as described earlier.

Third, the fluorescence peak height at 376 nm is greater than that at 396 nm. It is likely that the spectral pattern may follow one obtained from BPP probe only in Figure 3. This result also supports that the fluorescence behavior is primarily influenced by the isolated fluorescence probe on cure, showing a greater difference in the peak height at lower cure temperature. In all the cases shown in Figure 6, the excimer fluorescence emission was not also observed even after a long period of resting time of the samples. The peak height at 376 and 396 nm in Figure 4 is not obviously distinguishable like in Figure 7.

Isothermal Curing Effect. Figure 8 shows the steady-state fluorescence spectra of UP resin without a BPP probe isothermally cured at 90 °C for 10, 30, and 60 min, respectively. The overall shape of the spectra looks similar with the result in Figure 2. The fluorescence band is broad and structureless without a characteristic emission peak. As expected, the spectrum for the sample cured isothermally is shifted to lower wavelengths about 30~35 nm with slightly higher intensity. It is said that the fluorescence band is blue-shifted at the early stage of isothermal cure within 30 min at 90 °C. However, the effect of isothermal cure on the fluorescence behavior of UP resin has not been clarified without using a fluorescence

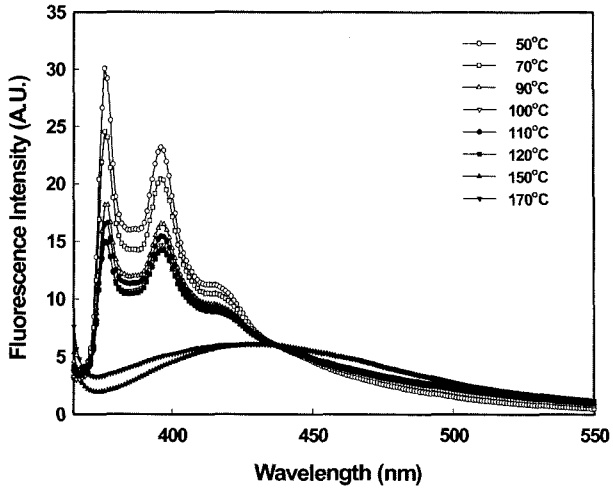

Figure 6. Steady-state fluorescence spectra of unsaturated polyester with a BPP probe measured at various cure temperatures. Cure time was constant to be 10 min at each temperature. Each sample was rested at ambient temperature for 24 hrs prior to each fluorescence measurement.

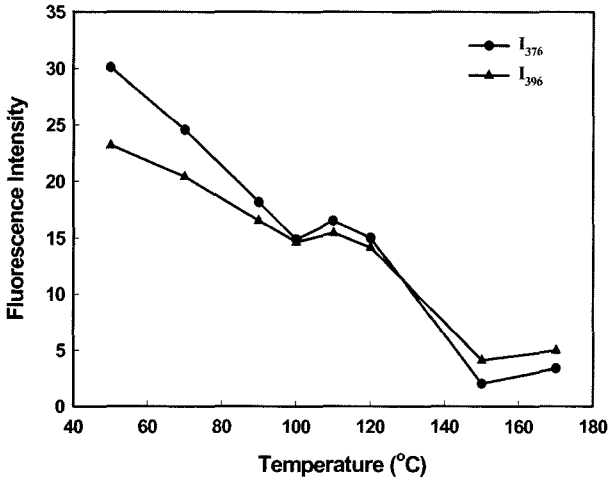

Figure 7. Plots of fluorescence intensity as a function of cure temperature at λ_{em} = 376 nm and λ_{em} = 396 nm, respectively, obtained from the spectra in Figure 5. λ_{ex} = 358 nm

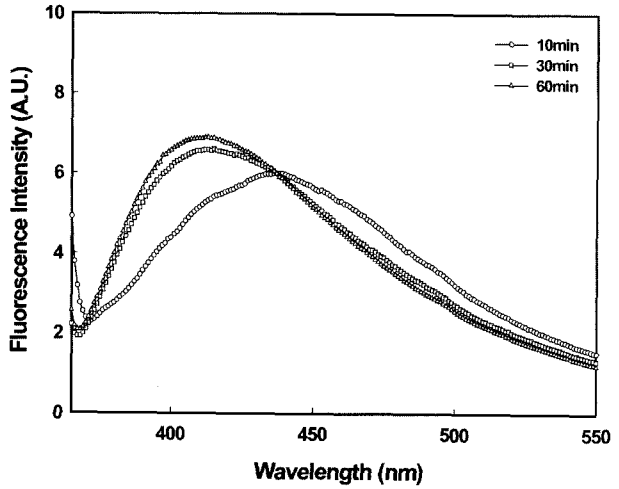

Figure 8. Steady-state fluorescence spectra of unsaturated polyester without a BPP probe isothermally cured at 90 °C for 10, 30 and 60 min, respectively.

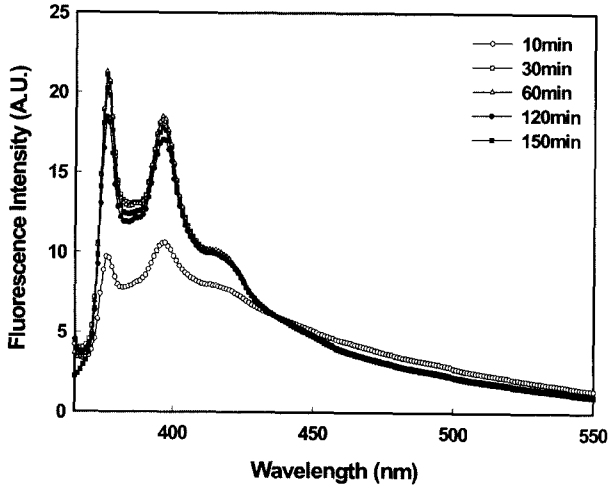

Figure 9. Steady-state fluorescence spectra of unsaturated polyester with a BPP probe cured at 90 °C for different cure times. Each fluorescence measurement was performed right after the sample preparation.

probe. Therefore, the BPP probe used to understand the dynamic curing effect has also been utilized in the isothermal study.

Figure 9 represents the fluorescence spectrum of the UP resin incorporated with a BPP probe measured at various cure times from 10 to 150 min at 90 °C. Each fluorescence measurement was conducted as soon as each sample was isothermally cured at given conditions and then cooled down to ambient temperature. All the spectra observed have a structured emission band with two peaks at 376 and 396 nm, as seen in Figure 4. The fluorescence intensity of the cured UP resin at 90 °C for 30 min or longer is largely enhanced.

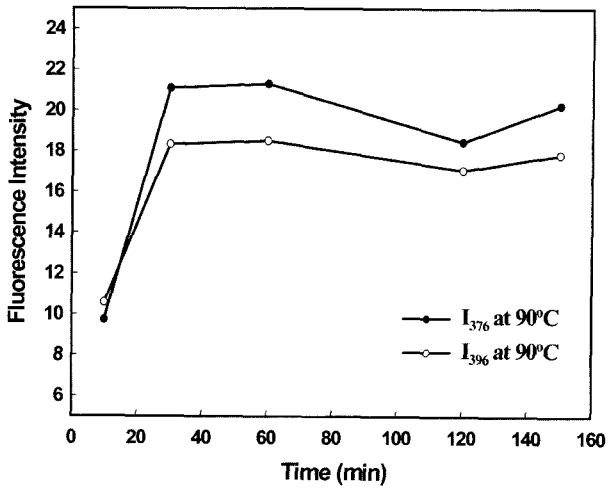

Figure 10. Plots of fluorescence intensity as a function of time at λ_{em} = 376 nm and λ_{em} = 396 nm for unsaturated polyester with a BPP probe, obtained from the result of Figure 9. λ_{ex} = 358 nm

Beyond 30 min, the intensity is not significantly changed. The relative values of the intensity are greater than those measured for the cured samples with a 10 min holding time at each cure temperature in Figure 4. Figure 10 plots the fluorescence intensity as a function of isothermal cure time at 376 and 396 nm, respectively, resulted from the spectra in Figure 9.

The isothermal result indicates that a cure time of 30 min at 90 °C is long enough for the BPP probe in the UP resin to be relaxed and isolated so that the BPP monomer fluorescence effectively emits. It also implies that, on the basis of molecular and photophysical responses, the primary cure process in the present UP/MEKP system is accomplished within 30 min, producing almost saturated fluorescence emission. The small peak at 418 nm as a shoulder is not changed with varying cure time. The excimer fluorescence behavior is not observed in the isothermal study, either, as expected. At the cure time of 10 min, the fluorescence intensities at the two peaks are more or less comparable. However, for 30 min or longer, the fluorescence peak height at 376 nm is greater than that at 396 nm, as investigated with the BPP probe only in Figure 3 and also with the samples rested for a long period of time in Figure 6. As mentioned earlier, this isothermal result also indicates that the fluorescence behavior of the UP resin strongly depends on the relaxation process of the probe incorporated during isothermal cure as well as cure process.

Figure 11 illustrates the fluorescence spectra of UP resin with a BPP probe at various cure times at 90 °C. The measurement was conducted after each sample was rested at ambient temperature for 24 hrs prior to fluorescence measurement. Compared with the result in Figure 9, the most noticeable change in the fluorescence band is the one cured for 10 min. The intensity is greatly enhanced due to the

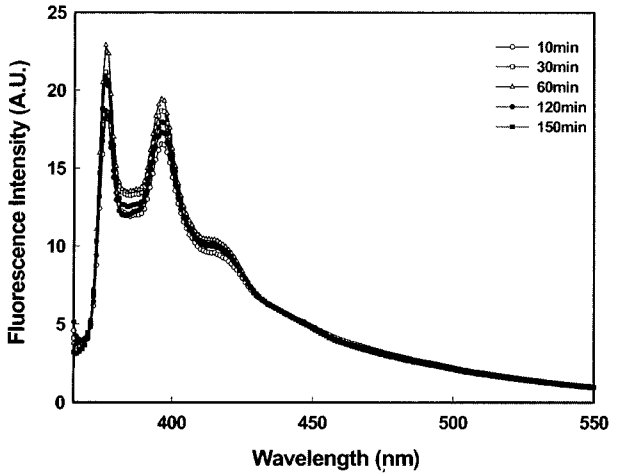

Figure 11. Steady-state fluorescence spectra of unsaturated polyester with a BPP probe cured at 90 °C for different cure times. Each sample was rested at ambient temperature for 24 hrs prior to each fluorescence measurement. In the open marks, cure time increases upwards. With a further increase of cure time, the fluorescence intensity decreases, as indicated with the closed marks.

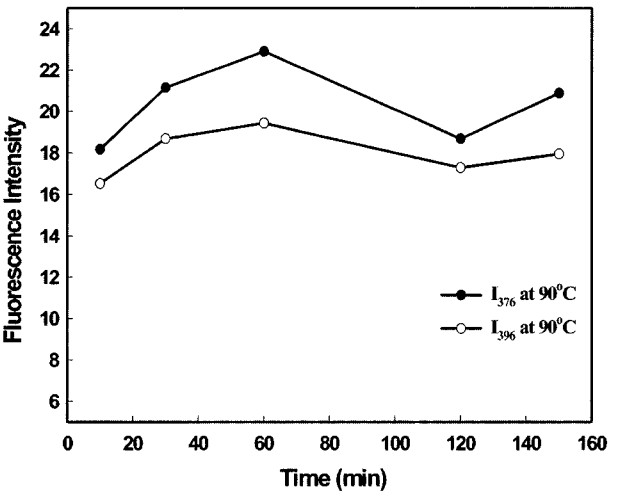

Figure 12. Plots of fluorescence intensity as a function of time at λ_{em} = 376 nm and λ_{em} = 396 nm for unsaturated polyester with a BPP probe, obtained from the result of Figure 11. λ_{ex} = 358 nm

delayed measurement for about 24 hrs after the isothermal curing process. Also, the peak height at 376 nm becomes greater than that at 396 nm. Other samples cured at 90 °C for 30~150 min show a similar spectral pattern with the counterparts in Figure 9, having the slightly enhanced intensity of the fluorescence.

Figure 12 depicts the variation of the fluorescence intensity as a function of cure time. There is an increase of the intensity up to 60 min of cure time. In Figure 12, the enhancement rate of the initial fluorescence intensity at 376 and 396 nm is lower than in Figure 10. This is because the UP resin with the probe has additionally cured slowly for a long period of time at ambient temperature prior to fluorescence measurement. The intensity measured for the sample cured at 90 °C for 120 min is rather decreased. This may be due to the inhibitor effect, as discussed earlier.

Conclusions

The steady-state fluorescence behavior of unsaturated polyester resin with a 1,3-bis-(1-pyrenyl)propane fluorescence probe of very low concentration has first been successfully characterized under both dynamic and isothermal cure histories. The following conclusions are noted.

The results suggest that a steady-state fluorescence technique is also useful to explore the dynamic and isothermal cure behavior and relaxation process in the UP resin system in the presence of BPP probe, providing molecular and photophysical information in terms of local viscosity, chain mobility, and micro-environment, depending on a time/temperature profile during cure process.

Near a cure temperature of 70 °C, the fluorescence spectrum of the UP resin is distinguishably changed from a structureless band to a structured one with two characteristic peaks at 376 and 396 nm, reflecting the incorporation of BPP probe in the resin. The monomer fluorescence intensity at the two peaks significantly increases with increasing cure temperature up to 120 °C, at which cure proceeds most profoundly, and then decreases to 150 °C exhibiting a broad structureless spectrum. The fluorescence result reflects that the increase of local viscosity and the restriction of molecular mobility of the UP resin surrounding the BPP probe with cure are responsible for the enhancement of the monomer fluorescence intensity.

Allowing the dynamically or isothermally cured UP resin with a fluorescence probe to be sufficiently rested at ambient temperature prior to each fluorescence measurement significantly enhances its fluorescence intensity. In addition, the enhanced monomer fluorescence intensity at 376 and 396 nm, which is accomplished by delayed fluorescence measurement, gradually decreases with cure temperature. The intensity also significantly increases with cure time within 30 min on quick measurement of the fluorescence while within 60 min on delayed measurement, indicating that an additional cure proceeds slowly during resting the resin at ambient temperature. The results may be explained by that the BPP probe has enough time to be rearranged and isolated prior to fluorescence so that the BPP monomer fluorescence is sufficiently emitted during measurement. Therefore, it is noted that the fluorescence behavior of the present UP resin system be importantly influenced by relaxation process of the fluorescing probe in the resin as well as cure process of the resin. Such the effect is more profound at lower temperatures in the present dynamic cure process at each temperature and at

shorter times in the present isothermal cure process at 90 °C. The isothermal cure study also reveals that a cure time of 30 min at 90 °C may be long enough for the probe in the resin to be relaxed so that the monomer fluorescence effectively emits.

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