

Cure Characterization of Unsaturated Polyester Resin by Fluorescence Spectroscopy

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Received 29 December 2003; accepted 16 July 2004

DOI 10.1002/app.21189

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A strong fluorescence emission was observed during cure of an unsaturated polyester resin containing about 30% styrene by weight. As the cure proceeded, the emission intensity at 306 nm increased. Model compound studies confirmed that the unsaturated polyester component exhibited negligible fluorescence when excited at 250 nm where styrene has strong absorption. Based on the studies of styrene/polystyrene mixtures, the fluorescence emission at 306 nm was attributed to a reduced inner-filter effect of styrene monomer. Fluorescence intensity changes

following cure at 75°C were correlated to the extent of styrene conversion determined by FT-IR spectroscopy, demonstrating that the fluorescence measurement is more sensitive to styrene conversion in the later stages of cure than conventional IR measurements. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2446–2450, 2004

Key words: curing of polymers; polyesters; resins; fluorescence

INTRODUCTION

Unsaturated polyester resin (UPE) is composed of aliphatic polyester made from propylene glycol and maleic anhydride (see Scheme I for the chemical structure of UPE) and a low-molecular-weight monomer, typically styrene. The cure reaction in UPE is a heterogeneous cross-linking copolymerization where reaction can occur between styrene–polyester vinylene, polyester vinylene–polyester vinylene, and styrene–styrene moieties. Extensive efforts have been made to understand cure reaction in UPE by many techniques including DSC, light scattering, rheometrics, IR, and electron spin resonance spectroscopy^{1–3}. Recently, we used near IR spectroscopy to characterize cure reactions in UPE⁴ in comparison to mid-IR spectroscopy.

Fluorescence spectroscopy has been used for cure monitoring in other polymers using extrinsic probes and labels^{5–8}. Several fluorescence parameters such as the emission intensity, the spectral shifts, peak ratios, and the first moment of emission intensity have been utilized to correlate with the extent of cure.

Our laboratory has been active in the development of fluorescence, phosphorescence, and UV-vis reflection techniques based on intrinsic spectral changes for

the cure monitoring of epoxy,⁹ polyimide,¹⁰ bis(maleimide),¹¹ polyurethane,¹² and polyurea urethane,¹³ polycyanurate,¹⁴ and some vinyl polymers¹⁵. Kim and Sung¹⁵ reported the use of fluorescence spectroscopy to monitor the bulk polymerization of styrene, which is much more fluorescent than polystyrene. The fluorescence emission intensity of styrene at 307 nm remained unchanged up to about 75% conversion, due to the inner-filter effect of high concentration of styrene, followed by a sharp increase up to a corresponding conversion of 85%. During the final 15% conversion, a drastic decrease in intensity was observed. They attributed this complex trend to an initial inner-filter effect and increased rigidity of the matrix, followed by a decrease in the concentration of the styrene fluorophore. Their studies indicated potential for following styrene reactions, especially at the later stages of cure when NIR or IR is not very sensitive. In this paper, we report the results of using a fluorescence technique for the cure characterization of UPE.

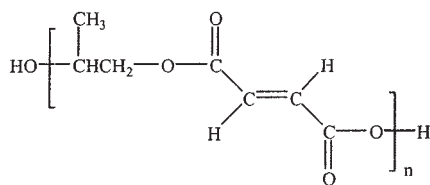
EXPERIMENTAL

Model compounds

Diethyl fumarate (98%, ACROS Chemical Company), diethyl succinate (99%, Aldrich Chemical Company), styrene (99%, Aldrich Chemical Company), and polystyrene (oligomer standard, M_n of 470 g/mol, Polymer Standards Service) were used as received without further purification.

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Contract grant sponsors: the Office of Naval Research, the Army Research Office, the National Science Foundation, Polymer Program, and the B. J. and C. H. Park Foundation.



Scheme 1

UPE resin cure

A commercially available, general-purpose, unsaturated polyester resin (Aropol Q6585) was donated by Ashland Chemical Company and used as received. This UPE resin is propylene glycol/maleic anhydride based unsaturated polyester cut to ~71% solids in styrene monomer. See Scheme I for the chemical structure of the UPE resin used, which has a number average molecular weight of 1580 g/mol resulting in approximately 10 vinylene bonds per molecule. The cure reaction was thermally induced using benzoyl peroxide (2.0% based on total resin weight), which was dissolved in the unsaturated polyester resin by mechanical stirring for 1 h. The resin/initiator mixture was subsequently degassed under vacuum for approximately 2 min prior to curing.

Fluorescence measurements

Sample preparation for all fluorescence measurements consisted of placing a drop of the model compound mixture, or resin/initiator mixture, between two $1 \times 1/8$ inch synthetic fused silica plates (Quartz Plus, Inc.) using a $12.7\text{-}\mu\text{m}$ -thick Mylar spacer to minimize evaporation. Fluorescence measurements were taken

using a Perkin-Elmer LS-50B luminescence spectrometer. Model compound mixture spectra were recorded using an excitation wavelength of 250 nm, slit conditions of 5.0/5.0 nm, and a scan speed of 120 nm/min. Styrene/polystyrene mixture spectra were obtained using a 12% (open) neutral density attenuator to keep the fluorescence intensity in scale.

RESULTS AND DISCUSSION

Styrene/polystyrene characterization

It is expected that the aliphatic unsaturated polyester in UPE is not very fluorescent. To confirm this expectation, model compound mixtures of diethyl fumarate/diethyl succinate, representing UPE before and after cure, were analyzed for fluorescence emission when excited at 250 nm where styrene strongly absorbs. All the mixtures covering from the range of 100% diethyl fumarate to 100% of diethyl succinate were found to have negligible fluorescence emission.

To analyze the fluorescence spectral changes as the styrene is polymerized, the mixtures of styrene and polystyrene in different weight compositions were used to obtain Fig. 1, also including the spectra of 100% styrene and 100% polystyrene, which are the same as the reported spectra¹⁶. FTIR spectroscopic measurements were taken for each mixture to confirm that the concentration of weighed styrene in the mixture was present in the samples used for the fluorescence measurements. From Fig. 1, as the styrene concentration in the mixtures decreased, the styrene emission peak at 306 nm due to monofluorophore increased in intensity. This trend continued for the styrene/polystyrene mixtures corresponding to poly-

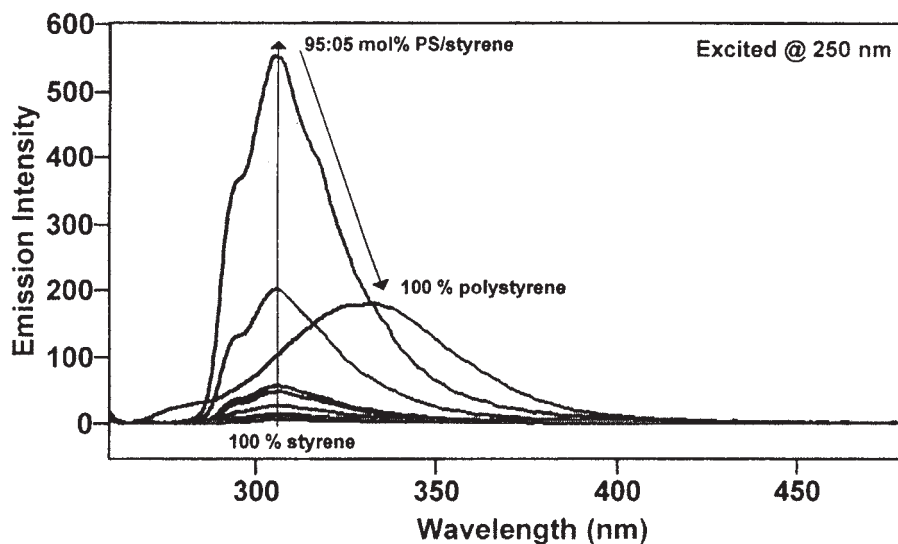


Figure 1 Fluorescence emission spectra of styrene/polystyrene model compound mixtures excited at 250 nm, polystyrene content from 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, and 100% from bottom curve.

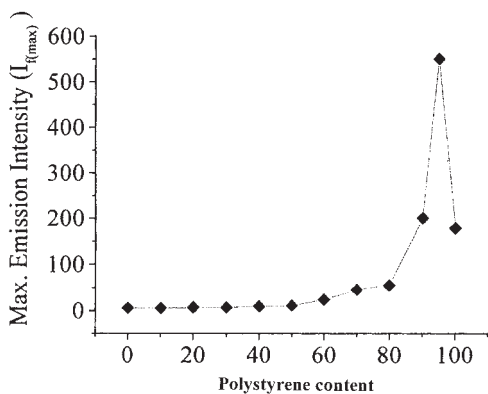


Figure 2 Maximum fluorescence emission intensity as a function of polystyrene content in styrene/polystyrene model compound mixtures.

styrene composition of less than 95%. Between 95 and 100% polystyrene composition, the maximum emission intensity decreased as well as shifted to 333 nm in 100% polystyrene due to excimer emission, in a trend similar to bulk polymerization of styrene¹⁵. Figure 2 shows a plot of the maximum fluorescence emission intensity, $I_f(max)$, as a function of polystyrene content in the mixtures. As can be seen in Fig. 2, initially $I_f(max)$ remained relatively unchanged up to approximately 60% polystyrene content. The maximum intensity then increased slightly between 60 and 80% polystyrene content, before exhibiting a drastic increase in intensity from 80 to 95% polystyrene content. After 95% polystyrene content, a decrease in intensity as well as a shift to the peak maximum at 333 nm was observed. Up to approximately 80% polystyrene (20% styrene), the inner-filter effect of styrene dominated

the fluorescence emission due to the high concentration of styrene monomer present¹⁶. Between 80 and 95% polystyrene (5–20% styrene), the styrene concentration decreased, resulting in a reduced inner-filter effect and thus an increase in emission intensity. This continued to approximately 95% polystyrene (5% styrene), partly due to the increased viscosity. The subsequent decrease in fluorescence intensity beyond 95% polystyrene (less than 5% styrene) was attributed to the decreased concentration of styrene monomer, since the intensity of styrene was about 300 times greater than the excimer emission of polystyrene¹⁵. A similar trend was observed by Kim and Sung¹⁵ during styrene polymerization.

Isothermal cure of UPE resin

The bulk copolymerization of styrenated UPE resin at 75°C was followed batch-wise using fluorescence and FTIR spectroscopic techniques. Figure 3 shows the results of the fluorescence measurements on the UPE resin during cure. As expected from the study of model styrene/polystyrene mixtures, the styrene emission peak at 306 nm increased in intensity without significant peak shifts as cure proceeded, due to the reduced inner-filter effect and an increased rigidity of the matrix. In Fig. 3, a weak broad band at about 410 nm seems to appear with increased cure time. Since the styrene excimer peak usually appears around 330 nm, this broad band may be due to impurities or charge-transfer complex, which is expected to increase its emission intensity due to increased rigidity of the resin with cure. Therefore, we did not use this band for cure characterization. A total of five sets of fluo-

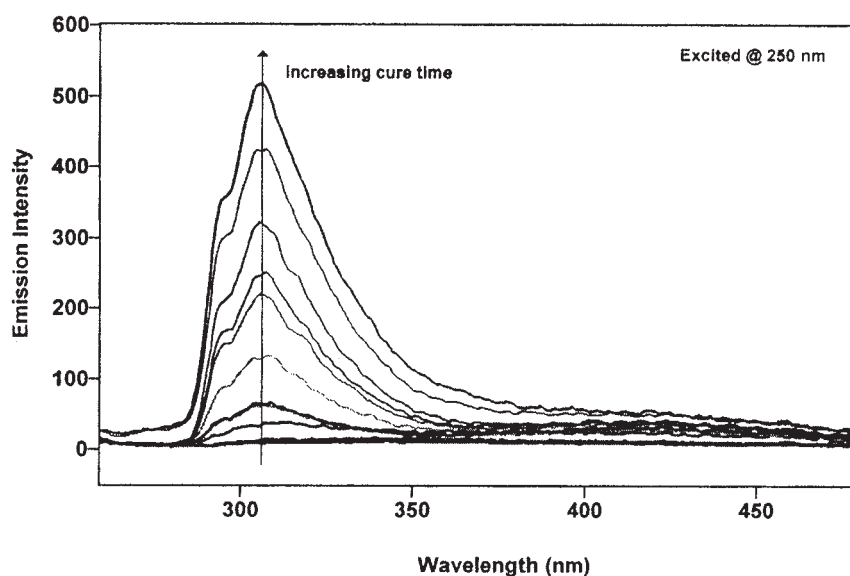


Figure 3 Fluorescence emission spectra of unsaturated polyester resin during cure. (Room temperature spectra from top to bottom corresponding to 480, 240, 180, 150, 120, 100, 80, 60, 50, 40, 30, 25, 20, 15, 10, 5, and 0 min of cure at 75°C.)

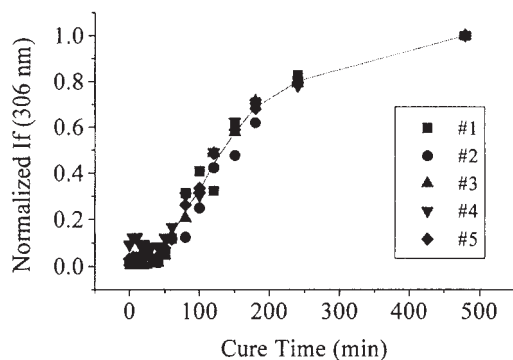


Figure 4 Reproducibility of normalized fluorescence measurements at 306 nm

rescence measurements were conducted to check the reproducibility of this experiment. Fig. 4 shows that the reproducibility of the fluorescence measurements was fair when normalized with the intensity values at 306 nm for the 480-min cure time.

Figure 5 shows the normalized fluorescence intensity and percentage styrene conversion (determined by FTIR spectroscopy) as a function of cure time at 75°C. During the first 60 min of reaction, the normalized fluorescence intensity and styrene conversion by IR remained relatively unchanged, most likely due to the consumption of free radicals by an inhibitor present in the unsaturated polyester resin. A fairly linear increase in both fluorescence intensity and styrene conversion was observed between 60 and 80 min where the styrene conversion reached a value of approximately 15%.

In the case of the styrene/polystyrene model compound mixtures, the self-quenching effect of styrene dominated the fluorescence emission spectra until the styrene conversion of 60% was reached. The fluorescence changes that occurred in the unsaturated polyester resin, corresponding to styrene conversion of

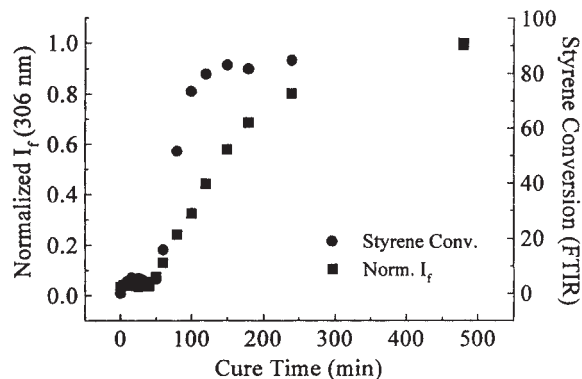


Figure 5 Normalized fluorescence intensity at 306 nm and percentage styrene conversion determined by FTIR spectroscopy as a function of cure time at 75°C.

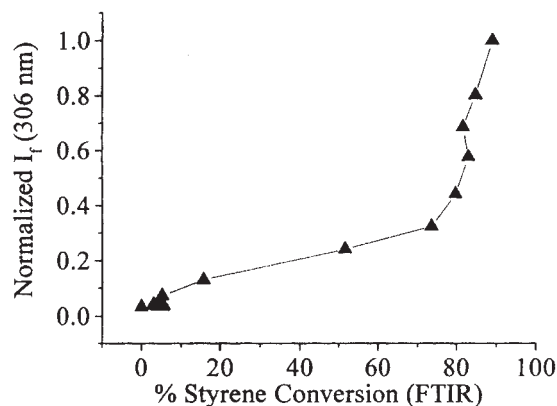


Figure 6 Correlation curve between normalized fluorescence intensity and styrene conversion determined by FTIR.

15%, are likely a result of the fact that styrene monomer is initially present at a much lower concentration (30% by weight) than in the case of styrene/polystyrene mixtures. In fact, at 15% conversion there is about 25% styrene in UPE, a concentration at which fluorescence intensity begins to increase, as illustrated in Fig. 2.

From the FTIR results, a correlation curve between normalized fluorescence intensity (I_f) at 306 nm and the percentage styrene conversion was obtained as shown in Fig. 6. The normalized fluorescence intensity was observed to increase almost linearly with styrene conversion, up to a corresponding styrene conversion of ~70%. After 70% conversion, the normalized fluorescence intensity exhibited a sharp increase with styrene conversion. The extent of styrene reaction corresponding to 480 min was found to be about 88% by FTIR. A subsequent decrease in the normalized fluorescence intensity, exhibited by the model styrene/polystyrene mixture spectra, was not observed for the case of the unsaturated polyester resin cured at 75°C. At 88% styrene conversion, the concentration of residual styrene monomer is 3.6% by weight in the unsaturated polyester resin. Basile¹⁶ found that the fluorescence emission spectra of polystyrene containing between 0.5 and 7.0% by weight of residual styrene still displayed a characteristic emission peak maximum at 310 nm due to styrene monomer. Based on Basile's results, it is reasonable to conclude that the lack of a subsequent decrease in the normalized fluorescence intensity was due to insufficient conversion of styrene. This is reasonable since the glass transition temperature of fully cured UPE resin of this type is reported to be around 120°C¹⁷ and the sample cure would have been incomplete with styrene conversion of 88%, when cured at 75°C due to vitrification.

From Fig. 6, it can be seen that the fluorescence measurement is much more sensitive to styrene conversion in the later stages of reaction than conventional FTIR measurements. This is an important fea-

ture of the fluorescence spectroscopic technique, especially in applications where the concentration of residual styrene monomer is important, such as in the lamination processes of unsaturated polyester resins. In addition, it was reported that at elevated temperatures, residual styrene monomer may cause blisters and voids on the surface of molded products¹⁸, since the cure extent at the surface or interphase may be different from the bulk as reported in epoxy resins.¹⁹

SUMMARY

Fluorescence spectroscopy was utilized to successfully follow the isothermal batch-wise cure of a commercially available unsaturated polyester resin. Fluorescence emission spectra of the unsaturated polyester resin exhibited an increase in intensity at 306 nm without significant spectral shift, with reaction time at 75°C. Results from the model compound study confirmed that the increase in intensity was due to a reduced self-quenching effect of styrene monomer. The unsaturated polyester fumarate moiety was found to exhibit negligible fluorescence under the experimental conditions employed. Therefore, only the styrene component of the unsaturated polyester resin could be monitored using fluorescence spectroscopy. A correlation between the normalized fluorescence emission intensity at 306 nm and styrene conversion, determined by FTIR, was made and showed that the sensitivity of fluorescence to the concentration of styrene was much greater than FTIR in the later stages of reaction.

Such a curve may be used to provide an accurate method to determine the residual concentration of styrene monomer in the unsaturated polyester resin, beyond conversion of 60%.

References

1. Hsu, C. P.; Lee, L. J. *Polymer* 1993, 34, 4516.
2. Hsu, C. P.; Lee, L. J. *Polymer* 1993, 34, 4496.
3. Hsu, C. P.; Lee, L. J. *Polymer* 1993, 34, 4506.
4. (a) Grunden, B. L.; Sung, C. S. P. *Macromolecules* 2003, 36, 3166; (b) Grunden, B.; Sung, C. S. P. *ACS Polym Prepr* 1998, 39-1, 248.
5. González-Benito, J.; Serrano, B.; Bravo, J.; Baselga, J., *Polymer* 2002, 43, 4331.
6. Quinn, J. C.; Torkelson, J. M., *Polymer* 2003, 44, 423.
7. Song, J. C.; Neckers, D. C., *Polym Eng Sci* 1996, 36, 394.
8. Sung, C. S. P.; Pyun, E.; Sun, H. L. *Macromolecules* 1986, 19, 2922.
9. (a) Song, J. C.; Sung, C. S. P.; *Macromolecules* 1993, 26, 4818; (b) Song, J. C.; Sung, C. S. P. *Macromolecules* 1995, 28, 5581.
10. (a) Pyun, E.; Mathisen, R.; Sung, C. S. P.; *Macromolecules* 1989, 22, 1174; (b) Dickinson, P.; Sung, C. S. P. *Macromolecules* 1992, 25, 3758; (c) Kailani, M. H.; Sung, C. S. P. *Macromolecules* 1998, 31, 5771; (d) Kailani, M. H.; Sung, C. S. P. *Macromolecules* 1998, 31, 5779.
11. (a) Phelan, J. C.; Sung, C. S. P.; *Macromolecules* 1997, 30, 6837 (b) Phelan, J. C.; Sung, C. S. P. *Macromolecules* 1997, 30, 6845.
12. Sun, X. D.; Sung, C. S. P. *Macromolecules* 1996, 29, 3198.
13. (a) Wang, S. K.; Sung, C. S. P.; *Macromolecules* 2002, 35, 877 (b) Wang, S. K.; Sung, C. S. P. *Macromolecules* 2002, 35, 883.
14. (a) Xu, Y. E.; Sung, C. S. P.; *Macromolecules* 2002, 36, 2553; (b) Xu, Y. E.; Sung, C. S. P. *Macromolecules* 2003, 35, 9044.
15. Kim, Y. S.; Sung, C. S. P. *J Appl Polym Sci* 1995, 57, 363.
16. Basile, L. J. *J Chem Phys* 1962, 36, 2204.
17. Lee, D. S.; Han, C. D. *J Appl Polym Sci* 1987, 34, 1235.
18. Shi, W.; Ranby, B. *J Appl Polym Sci* 1994, 51, 1129.
19. (a) Olmos, D.; Aznar, A. J.; Baselga, J.; González-Benito, J., *J. Colloid Interphase Sci* 2003, 267, 117; (b) Yu, J. W.; Sung, C. S. P., *J Appl Polym Sci* 1997, 63, 1769.