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Fluorescence and IR Characterization of Cure in Polyurea, Polyurethane, and Polyurethane−Urea

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ABSTRACT: Fluorescence and IR spectroscopic techniques have been used to characterize cure in polyurea (PUa), polyurethane (PU), and polyurethane−urea (PUU), based on the study of model compounds. Polyurea cured in a nonreactive diluent by reacting liquid MDI (4,4′-methylenebisphenyl diisocyanate) with 3,5-diethyltoluene diamine (DETDA) showed fluorescence intensity decrease at 339 nm due to DETDA consumption and an emerging peak near 310 nm from the formation of the urea derivative of MDI. The reaction at room temperature was complete after 50 min with supporting IR evidence of urea carbonyl at 1642 cm^{-1}. When nonfluorescent liquid MDI was reacted with ethylene oxide terminated PPO (EO−PPO) to form polyurethane, the fluorescence intensity at 310 nm increased slowly, taking approximately 1500 min to plateau with an intensity increase of at least 15 times. For PUU, which was cured by reacting MDI, EO−PPO, and DETDA, the fluorescence behavior was more complex: first, a peak at 303 nm showed up immediately following the mixing of the reactants, probably due to urea group formation, while the peak at 333 nm decreased due to DETDA consumption, and second, the peak intensity at 303 nm, after a slight decrease began to increase with a gradual shift to 310 nm. These results were correlated with the overall extent of cure as well as the extent of urea and urethane formation monitored by FTIR spectroscopy. Within certain regions, the fluorescence behavior can be correlated to the extent of urea and urethane reaction.

Introduction

Polyurethane-ureas (PUU) with outstanding thermal and mechanical properties are often made using the reaction injection molding (RIM) process. For a fast process such as RIM, real-time cure monitoring would be desirable to facilitate efficient process control. Recently, several attempts to develop such a technique have been reported. Macosko's group[1,2] monitored in-situ cure by recording the exotherm generated by the fast reacting components and obtained an overall reaction rate. Vespoli and Alberino[3] studied the pressure changes at various points of the mold when the material filled the cavity. The results reflected the viscosity changes in the material flow inside the mold. Grigsby and Rice[4] followed in-situ cure by the variation of the dielectric properties caused by trace amount of ionic impurities present in the resin, since the mobility of ions is controlled by the viscosity and cross-link buildup in the resin during cure. Priester et al.[5] studied the cure kinetics with FTIR spectroscopy by embedding an optical fiber in the RIM mold. DeThomas et al.[6] studied the in-situ cure of MDI (4,4′-methylenebisphenyl diisocyanate) based polyurethane with NIR spectroscopy by using an optical fiber bundle probe immersed in the mold.

The fluorescence technique has the potential to meet the cure monitoring needs due to its unique sensitivity, selectivity, and nondestructive nature. For polyurethanes (PU), several fluorescence-based techniques have been reported, such as using reactive probe of naphthyl diisocyanate,[7] nonreactive fluorescent probes,[8] or using intrinsic fluorescence changes in an MDI-based polymer.[9]

Polyureathane−ureas (PUU) are usually made by reacting nonfluorescent MDI with an aromatic amine and polyol. Therefore, there are at least three intrinsic fluorophores in PUU: aromatic diamine used as a chain extender, a urethane derivative of MDI from the MDI−polyol reaction, and finally, a urea derivative of MDI from the MDI−amine reaction. Previous work in our laboratory focused on characterizing the fluorescence behavior of three model compounds similar in structure to the intrinsic fluorophores found in PUU.[10] The effects of fluorophore interaction and the changes in the viscosity and the temperature on the fluorescence emission have been reported in a preceding paper.[10]

In this paper, we report on the fluorescence results obtained during cure of PUU made of MDI, 3,5-diethyltoluenediamine (DETDA) as a chain extender, and hydroxyl-terminated poly(propylene oxide) (PPO). IR results based on model compounds as summarized in the preceding paper clearly identified IR peaks characteristic of the urea and urethane group, which could be used for quantitative studies. Using these IR bands, the intrinsic fluorescence behavior during cure of PUU was interpreted with regard to the cure process.

Experimental Section

The polyol used was either PPO2000, a secondary hydroxyl terminated poly(propylene oxide) (from Aldrich Chemical Co.) with a molecular weight of approximately 2000 g/mol and functionality equal to 2, or EO-PP02800, a primary hydroxyl terminated poly(propylene oxide−ethylene oxide) copolymer (from Aldrich Chemical Co.) with a molecular weight of approximately 2800 g/mol and functionality equal to 2. All polyols were dried under 10 mmHg vacuum at 140° F for 24 h immediately before use. An isomeric mixture of 2,4- and 2,6-diamino-3,5-diethyltoluene (DETDA) (20:80) was received from Ethyl Corp. blanketed with argon gas and used without further purification. 4,4′-Methylenebisphenyl diiosocyanate (MDI) was purchased from Eastman Kodak Co. Isonate 143L, a light-yellow uretonimine-modified liquid MDI from Dow Chemical Co., was transferred from a sealed container to the sample cell by syringe with a long needle and used without further treatment.

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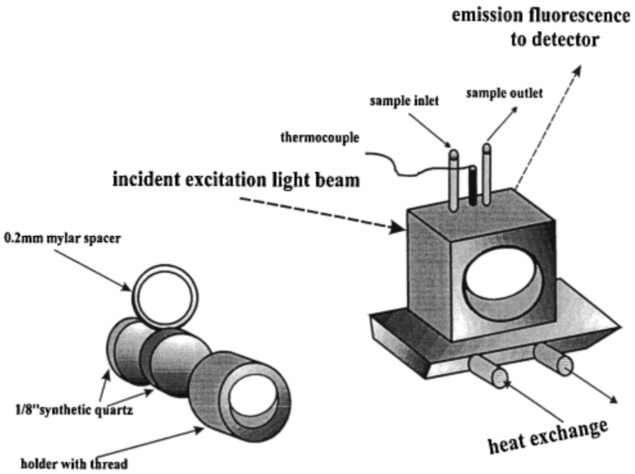
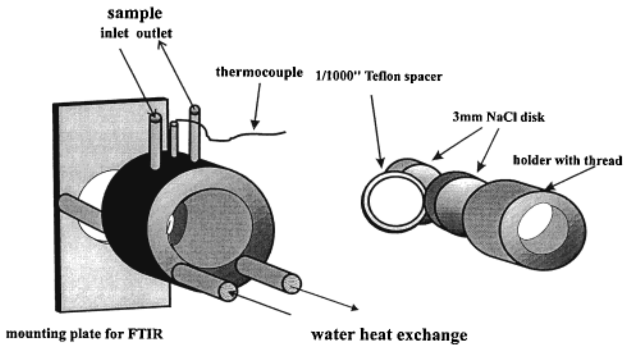
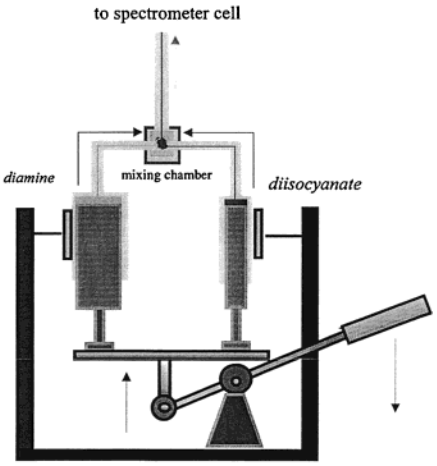
Scheme 1



Scheme 2



Scheme 3



Bulk Polymerization of MDI with EO−PPO and Chain Extender DETDA. 3.0 g of vacuum-dried EO−PPO was mixed with 0.0477 g of DETDA in a 10 mL vial by magnetic stirring. Molten MDI at 60 °C in a porcelain crucible was decanted to a clean watch glass to separate the pure MDI from its high melting dimer. After cooling, purified MDI was crushed into fine powder using a mortar and pestel. 0.3144 g of MDI was subsequently transferred into the vial that contained the well-mixed EO−PPO/DETDA. The combination of these reactants gave the mole ratio of EO−PPO:DETDA:MDI = 0.8:0.2:1. A vigorous mixing was made by magnetic stirring for 1 min. One drop of the mixture was then placed between two $^1/_8$ in. thick synthetic quartz disks spaced with a 0.02 mm thick Mylar spacer. Bubbles were carefully removed by a spatula and squeezed out from the slot between the quartz disks before placing the sandwiched sample into the preheated sample holder for in-situ fluorescence measurement, as shown in Scheme 1. A thermocouple was inserted into the edge of the sample to verify that the cure reaction was carried out under isothermal conditions.

Spectroscopic Characterization. A Perkin-Elmer LS50B luminescence spectrometer was used for measurement of the fluorescence emission, with the excitation wavelength set at 275 nm. In-situ fluorescence spectra were taken every 45 s for the first 2 h. The measuring intervals were increased as cure proceeded to higher extents of reaction. A similar procedure was used for the in-situ FTIR measurements using a Nicolet 680DSP Spectral workstation equipped with a heatable, demountable in-situ FTIR cell capable of isothermally curing the bulk resin. The in-situ FTIR cell designed and built in-house is represented schematically in Scheme 2. No spacer was used due to the high optical density in the mid-IR range of the polyurethane−urea sample.

Results of the model compound study, discussed in a previous paper, demonstrated that the absorbances at 1727 and 1647 cm^{-1} were linear with the concentration of urethane and urea, respectively.[10] During cure, urea carbonyl appeared at 1639 cm^{-1}, perhaps due to increased hydrogen bonding in urea dominated microdomains. The in-plane bending of the methylene group in PPO at 1373 cm^{-1} was chosen as an internal reference band.[11]

Therefore, the extent of urethane formation, ξ_{urethane}, was calculated using eq 1.

$$\xi_{\text{urethane}} = (A_{1727\ \text{cm}^{-1},t}/A_{1373\ \text{cm}^{-1},t})/(A_{1727\ \text{cm}^{-1},\infty}/A_{1373\ \text{cm}^{-1},\infty}) \qquad (1)$$

where $A_{1727\ \text{cm}^{-1},t}$ and $A_{1727\ \text{cm}^{-1},\infty}$ refer to the absorbance of the C=O stretching band of free urethane group at 1727 cm^{-1} at cure time $t = t$ and $t = \infty$, respectively, and $A_{1373\ \text{cm}^{-1},t}$ and $A_{1373\text{cm}^{-1},\infty}$ refer to the absorbance of the internal reference band at cure time $t = t$ and $t = \infty$, respectively. The extent of urea formation, ξ_{urea}, was calculated by eq 2.

$$\xi_{\text{urea}} = (A_{1639\ \text{cm}^{-1},t}/A_{1373\ \text{cm}^{-1},t})/(A_{1639\ \text{cm}^{-1},\infty}/A_{1373\ \text{cm}^{-1},\infty}) \qquad (2)$$

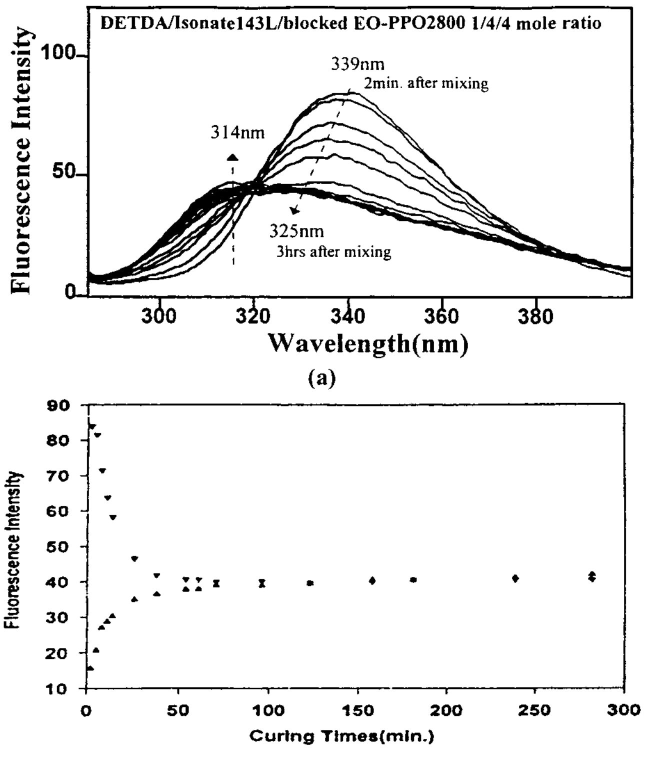
where $A_{1639\ \text{cm}^{-1},t}$ and $A_{1639\text{cm}^{-1},\infty}$ refer to the absorbance of the C=O stretching band of hydrogen-bonded urea group at 1639 cm^{-1} at cure time $t = t$ and $t = \infty$, respectively, and $A_{1373\ \text{cm}^{-1},t}$ and $A_{1373\text{cm}^{-1},\infty}$ refer to the absorbance of the internal reference band at cure time $t = t$ and $t = \infty$, respectively.

Bulk Polymerization of Liquid MDI with PPO and Chain Extender DETDA. A laboratory-scale injection mixer was used for the study of PUU using liquid MDI as shown in Scheme 3. Both syringes were driven simultaneously by the same bar. Thus, the volume of injected material was determined by the cross-sectional area of the syringes. The diameters of the syringes were carefully machined to meet the stoichiometric ratio of each component. 3.0 g of vacuum-dried PPO was mixed with 0.067 g of DETDA in a 10 mL vial by magnetic stirring, followed by degassing at 100 °F in a vacuum oven under 10 mmHg pressure until no bubbles were detected. The mixture was then carefully transferred into the barrel of the syringe which had a diameter of 11.4 mm. Approximately 0.5 g of liquid MDI (Isonate l43L) was transferred from the storage container by a syringe with a diameter of 4.48 mm. On the basis of this arrangement, the reactants were injected into the mixing chamber with the mole ratios of PPO:DETDA:liquid MDI equal to 0.8:0.2:1.0.

The diameter of the needle leading into the mixing chamber was chosen to be as small as possible in order to increase the flow rate of the materials. After impingement mixing, the mixture was directly transferred to the sample cell for fluorescence emission or FTIR measurements as shown in Schemes 1 or 2, respectively.

Results and Discussion

Polyurea Formation. Before studying the cure reactions in PUU where urea as well as urethane groups have overlapping fluorescence peaks according to the model compound study,[10] the fluorescence associated



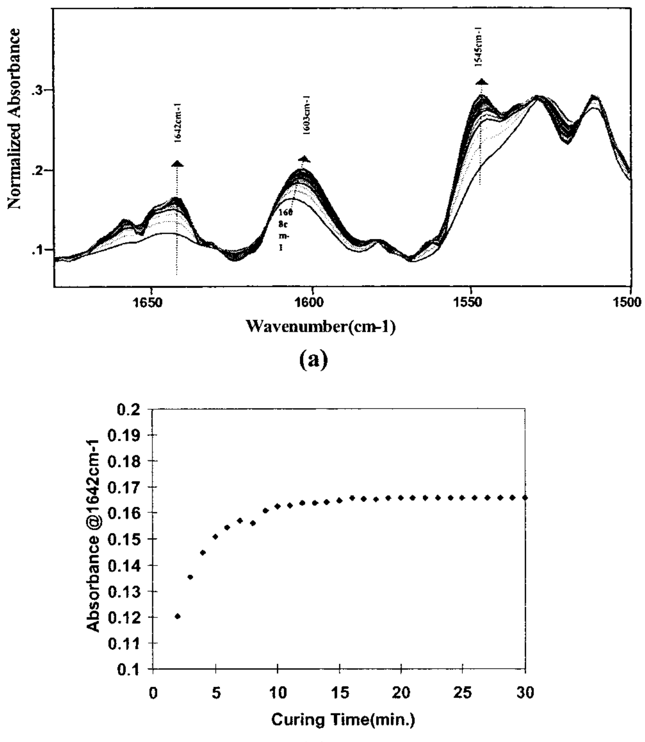
(a)

(b)

Figure 1. (a) Emission fluorescence spectra during room temperature cure for polyurea formation (DETDA/liquid MDI/nonreactive PPO: 1:4:4 mole ratio). Cure time in arrow directions: 2, 4, 5, 6, 8, 10, 20, 30 min, 1, 2, 3 h. Excitation at 275 nm. (b) Emission fluorescence intensity changes at 310 nm (▲) and 337 nm (▼) as a function of cure time for polyurea formation.

with polyurea formation was investigated. Very few studies were found in the literature on bulk polyurea formation, due to its highly exothermic and rapid cure reaction. It would be desirable to observe the fluorescence spectral changes during polyurea formation without the presence of a large exotherm to minimize the effect of temperature on the fluorescence intensity. Therefore, we used a nonreactive diluent which mimicked the nature of PPO soft segment typically found in polyurea. The active hydroxyl group of the ethylene oxide end of PPO was capped with diethyl ether using a modified Williamson reaction.[12] IR and NMR confirmed the conversion of hydroxyl groups into ether linkages. As a result, this diluent was no longer reactive with the diisocyanate group and instead acted as a heat sink.

Figure 1a shows the in-situ fluorescence observed during polyurea formation by the reaction of DETDA and nonfluorescent liquid MDI in ether-blocked nonreactive EO–PPO. To ensure complete reaction of DETDA, excess liquid MDI was used. Liquid MDI which is used extensively in RIM is a mixture of MDI and some uretonimine produced by thermal treatment of MDI.[13] Uretonimine is supposed to be converted to MDI during cure. Liquid MDI is nonfluorescent as was the case for MDI. As liquid MDI reacts with DEDTA to form polyurea, the band at 339 nm due to DETDA decreased in intensity, while a new band at 310–314 nm emerged due to the formation of urea derivative of MDI. The disappearance of the DETDA peak proceeded at about the same rate as the formation of urea peak as shown in Figure 1b. In fact, the fluorescence intensity did not change after about 50 min. This trend was supported by IR spectra as shown in Figure 2a,b, when the urea carbonyl peak at 1642 cm^{-1} was followed. When normalized with a peak at 1373 cm^{-1} from PPO, the urea peak at 1642 cm^{-1} reached a plateau after about 20 min.



(a)

(b)

Figure 2. (a) FT-IR spectra during room temperature cure for polyurea formation (DETDA/liquid MDI/nonreactive PPO: 1:4:4 mole ratio). Cure time in arrow directions: 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30 min. (b) Changes in absorbance at 1642 cm^{-1} (urea band) normalized to 1373 cm^{-1} PPO band as a function of cure time for polyurea formation.

Polyurethane Formation. As reported previously from our laboratory,[9] the fluorescence intensity at 316 nm due to urethane formation increased when MDI reacted with PPO in bulk. When EO–PPO was used with liquid MDI, similar results were obtained as shown in Figure 3a. As illustrated in Figure 3b, the fluorescence at 310 nm due to urethane formation proceeded much slower, taking 1500 min to reach a plateau in fluorescence intensity. The fluorescence intensity increased at least 15-fold, due to the fact that the urethane group is much more fluorescent than MDI.[9]

Polyurethane–Urea Formation. The intrinsic fluorescence emission spectra for the cure reaction of bulk polyurethane–urea at 25 °C containing MDI, EO–PPO, and DETDA with mole ratios of 1.0:0.8:0.2 are shown in Figure 4a,b. In Figure 4a representing the first 20 min of reaction, the fluorescence emission peak at 333 nm decreased in intensity as well as blue-shifted slightly. Meanwhile, a peak at 303 nm emerged almost immediately after mixing the components. After the first 20 min as illustrated in Figure 4b, the intensity at 303 nm increased with a gradual peak shift to 310 nm. From the model compounds study,[10] we could assign the decrease in fluorescence intensity at 333 nm to the consumption of aromatic amine chain extender, DETDA. The intensity near 303–310 nm was likely due to the emission from a combination of urea and urethane fluorophores.[10] Figure 5 describes the changes in fluorescence intensity at both 333 and 307 nm with cure

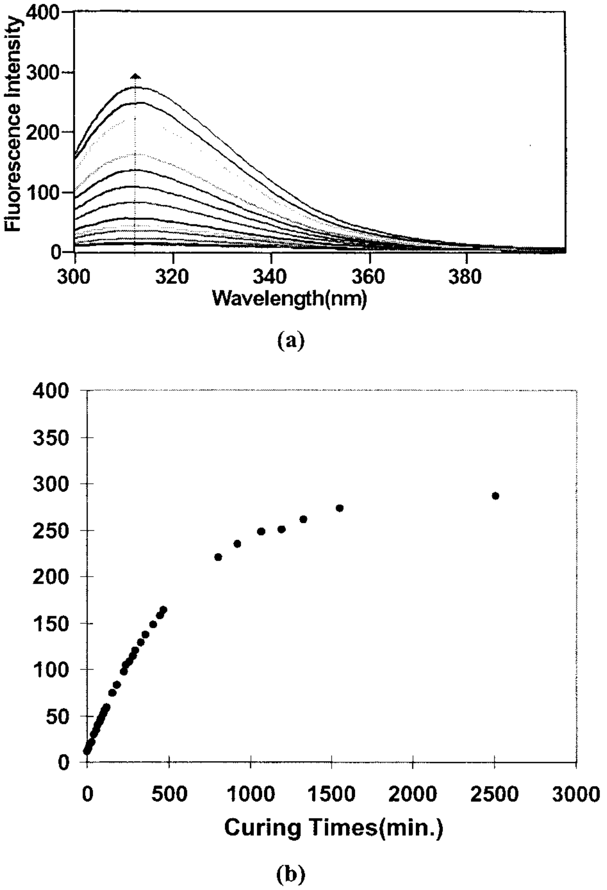


Figure 3. (a) Emission fluorescence spectra during room temperature cure for polyurethane formation (EO−PPO 2800/liquid MDI: 4:1 mole ratio). Cure time from bottom to top, 2, 3, 5, 10, 30 min, 1, 2, 3, 6, 12, 24, 36, 48 h. Excitation at 275 nm. (b) Fluorescence intensity changes at 310 nm as a function of cure time for polyurethane formation.

time. The active hydrogen in DETDA is usually more reactive than that of the hydroxyl group;[13] thus, it is highly possible that the sharp increase of the 307 nm band at the beginning of cure can be attributed to the formation of the urea linkage. A similar trend was also observed in polyurea formation, as described in the previous section. A slight decrease in fluorescence intensity at 307 nm during the first 20 min period may be caused by the phase separation of the urea domain from the resin and subsequent concentration quenching. The urethane linkage would be expected to form slower than urea as demonstrated during polyurethane formation. The urethane fluorescence band with a peak at 306−310 nm overlaps the urea linkage fluorescence band.[10] After 30 min, the fluorescent intensity increased gradually to the end, due to urethane formation. As the contribution of the urethane linkage increases, the band shifts to longer wavelengths and more closely approximates the spectrum of pure polyurethane, as described in the preceding section. The increase in fluorescence intensity is at the most 2-fold, up to cure time of 400 min, when most of the reaction is complete by IR as described in the next section. This compares with about 15-fold increase during PU formation (see Figure 3b). Therefore, a small amount of unreacted DETDA may quench the fluorescence of urethane derivative of MDI in PUU during cure.

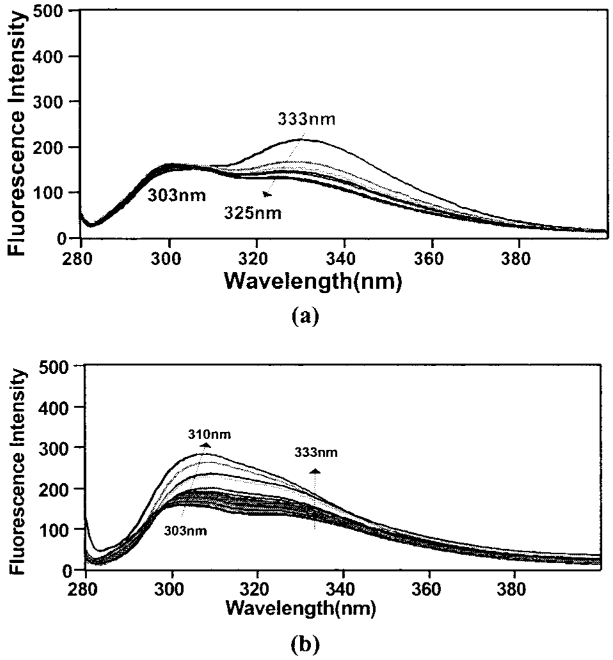


Figure 4. (a) Emission fluorescence spectra during 30 °C cure of polyurethane−urea (MDI/EO−PPO/DETDA: 1.0:0.8:0.2 mole ratio). Cure time from top to bottom at 2, 3, 4, 5, 6.5, 8, 10, 15, 20 min. Excitation at 275 nm. (b) Cure time from bottom to top: 25, 30, 50, 60, 70, 80, 90, 115, 140, 150, 270, 360, 420 min. Excitation at 275 nm.

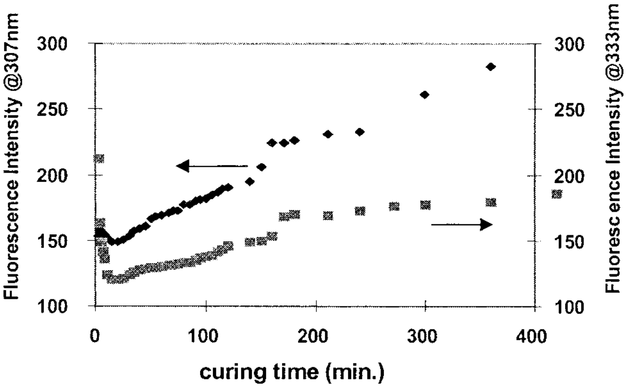


Figure 5. Fluorescence intensity changes at 307 and 333 nm as a function of cure time for polyurethane−urea formation (MDI/EO−PPO/DETDA: 1.0:0.8:0.2 mole ratio). Cure at 30 °C.

Concerning the fluorescence at 333 nm due to DETDA, it showed a sharp drop from 0 to 20 min in Figure 5, as a result of the reaction of DETDA with liquid MDI. Beyond 20 min, a gradual increase was observed, which was caused by the rising urethane fluorescence emission at 310 nm. Deconvolution of the overlapped fluorescence spectra based on the spectra of DETDA and urethane model compound[10] showed similar results as in Figure 5. When liquid MDI was used instead of pure MDI, similar fluorescence changes were observed. Also, cure at 70 °C leads to similar trends in the fluorescence spectra.

Correlation of Emission Fluorescence with FTIR Results. To gain more insight into these fluorescence changes, the fluorescence intensity at 333 and 307 nm were correlated with the extent of reaction determined from in-situ FTIR results obtained under the same cure conditions. The extent of cure was followed by the consumption of isocyanate group at 2272 cm^{-1} from in-situ FTIR spectra (Figure 6) according to eq 3, with the

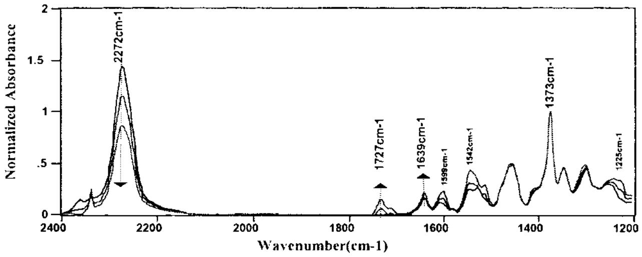
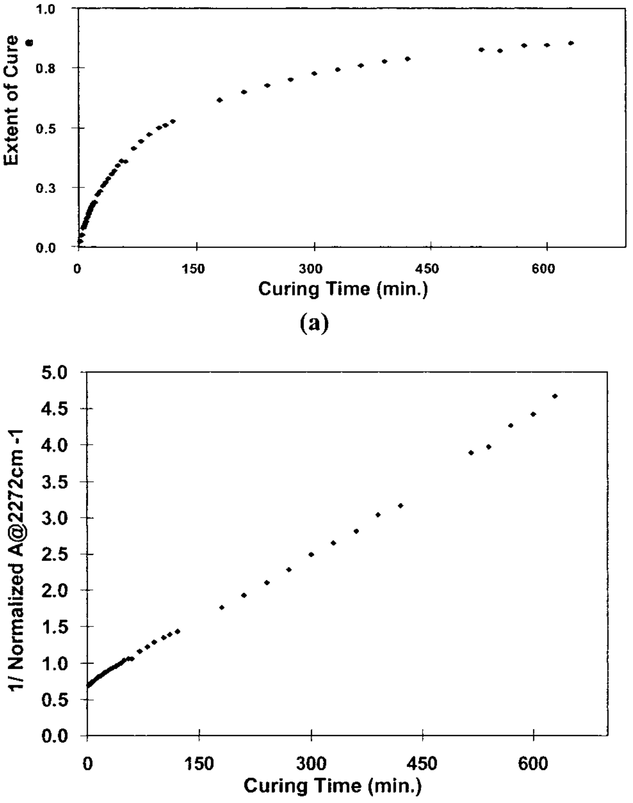


Figure 6. FT IR spectra during 30 °C cure at for polyurethane−urea formation (MDI/EO−PPO/DETDA: 1.0:0.8:0.2 mole ratio). Cure time from top to bottom: 5 min, 2 h, 8 h. All spectra normalized to the 1373 cm^{-1} PPO band.



(a)

(b)

Figure 7. (a) Extent of cure as a function of 30 °C cure time by IR monitoring of NCO consumption at 2272 cm^{-1} for polyurethane−urea formation (MDI/EO−PPO/DETDA: 1.0: 0.8:0.2 mole ratio). (b) Second-order kinetic plot from IR data for polyurethane−urea formation.

result shown in Figure 7a. From Figure 7a, it can be seen that the extent of cure gradually reached about 90% after 600 min of reaction.

$$\xi_{\mathrm{cure}} = 1 - (A_{2272\ \mathrm{cm}^{-1},t}/A_{1373\ \mathrm{cm}^{-1},t})/(A_{2272\ \mathrm{cm}^{-1},0}/A_{1373\ \mathrm{cm}^{-1},0}) \quad (3)$$

where $A_{2272\ \mathrm{cm}^{-1},t}$ and $A_{2272\ \mathrm{cm}^{-1},0}$ refer to the absorbances of the isocyanate group at 2272 cm^{-1} at cure time $t = t$ and $t = 0$, respectively, and $A_{1373\ \mathrm{cm}^{-1},t}$ and $A_{1373\ \mathrm{cm}^{-1},0}$ refer to absorbances of the internal standard at cure time $t = t$ and $t = 0$, respectively. The second-order kinetic plot based on the absorbance at 2272 cm^{-1} is shown in Figure 7b. It was found that the second-order kinetics could be applied up to about 75% extent of cure. A slight deviation from the second-order kinetics was observed at high conversion possibly due to the autoacceleration effect.

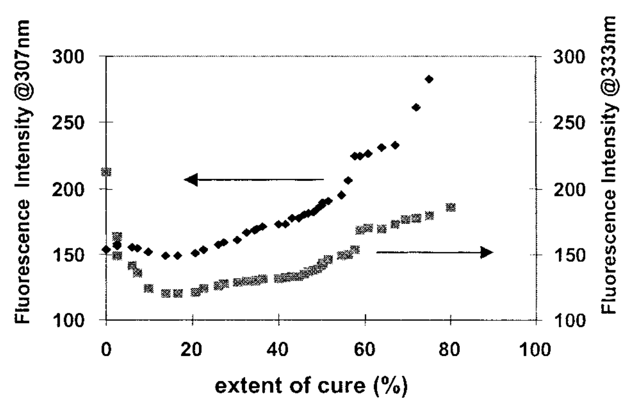
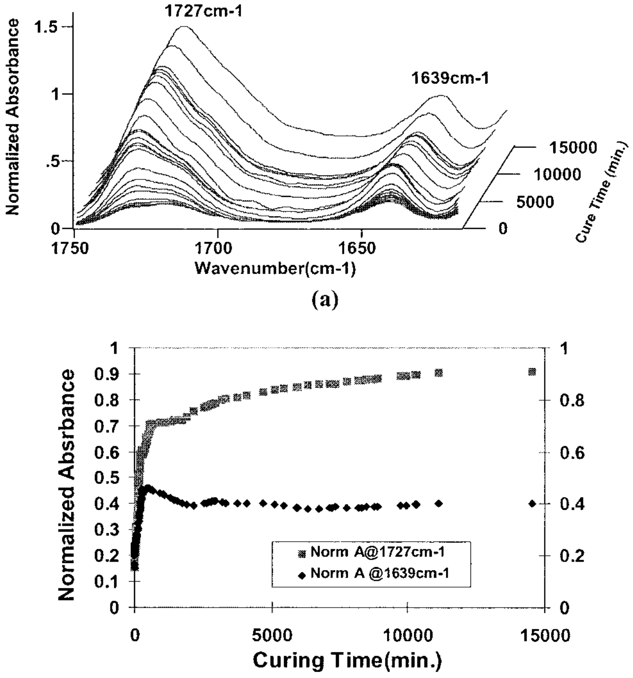


Figure 8. Correlation of fluorescence intensity at 307 and 333 nm with the extent of cure for MDI/EO−PPO/DETDA: 1.0: 0.8:0.2. Cured at 30 °C.



(a)

(b)

Figure 9. (a) FT IR spectra during cure of polyurethane-urea formation (MDI/PPO/DETDA: 1.0:0.8:0.2 mole ratio). Cure time from front to back: 1, 2, 5, 10, 20, 40, 60, 120, 240, 360, 480, 1440, 2880, 5760, 6000, 7200, 8400, 9600, 12 000, 14 400, 19 880 min. Cured at 30 °C. (b) Changes in absorbances at 1727 cm^{-1} (urethane band) and 1639 cm^{-1} (urea band) as a function of cure time for polyurethane−urea formation.

The fluorescence intensity at 333 and 307 nm was then correlated with the overall extent of cure obtained by IR, as in Figure 8. The sharp drop at 333 nm during the first 20% of cure is due to the consumption of DEDTA with MDI to form urea groups. The slow increase in intensity at 333 nm after 20% cure is due to the contribution of the growing 307 nm peak. Throughout the first 20% of the reaction, the intensity at 307 nm is likely due to urea formation. Beyond 20%, the intensity at 307 nm increases from the formation of urethane, which is about 11 times more florescent than urea. From the model compound studies, we know the relative quantum yields of DETDA, the urea, and the urethane derivatives of MDI.[10] However, their intensity can also be affected by quenching, temperature, and viscosity. Therefore, the fluorescence intensity alone is not sufficient to provide quantitative information such

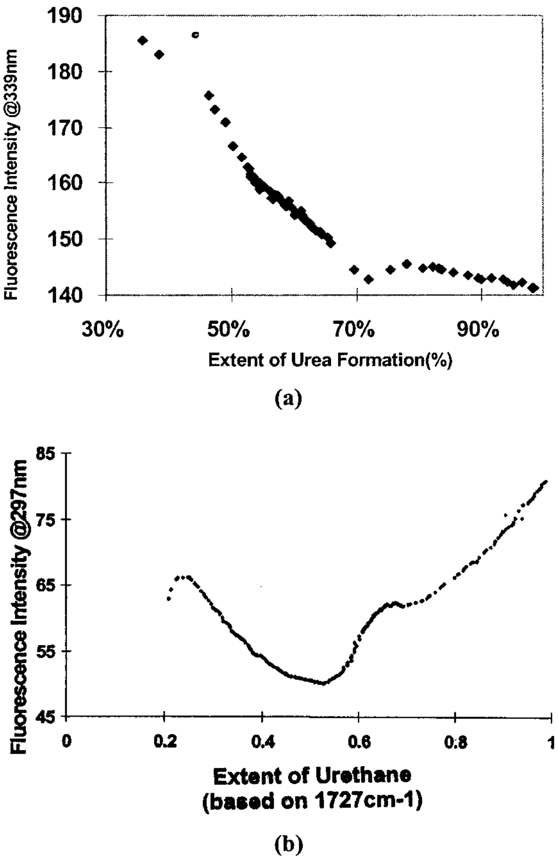


Figure 10. (a) Correlation of fluorescence intensity at 339 nm (due to DETDA) with the extent of urea formation by IR peak at 1639 cm^{-1} during polyurethane–urea cure at 30 °C (MDI/PPO/DETDA: 1.0:0.8:0.2 mole ratio). (b) Correlation of fluorescence intensity at 297 nm with the extent of urethane formation by IR peak at 1727 cm^{-1} for 70 °C cured polyurethane–urea (liquid MDI/PPO/DETDA: 1.0:0.8:0.2 mole ratio).

as the extent of urea or urethane formation. Figure 8 is an attempt to correlate fluorescence intensity to the overall extent of cure obtained by IR.

IR spectra also provide well-separated, characteristic bands of urea and urethane which have been demonstrated to be proportional to their concentration in PPO.[10] Therefore, it may be possible to correlate the fluorescence intensity with the extent of urea or urethane formation independently. Figure 9a shows the changes observed for these two IR peaks during the cure reaction of PPO/DETDA/MDI (molar ratios: 0.8:0.2:1.0). Instead of EO–PPO, which reacts rapidly, PPO was used to slow the reaction and to observe the reaction carefully. From Figure 9a it can be seen that urethane carbonyl exhibit two peaks, one at 1715 cm^{-1} and one at 1727 cm^{-1} at early cure times, due to H-bonded and free carbonyl, respectively. At later cure times, the peak at 1727 cm^{-1} due to free C=O becomes stronger, indicating greater microphase separation in PUU. This trend is in agreement with the fluorescence of the urea at 307 nm which showed concentration quenching after phase separation. The urea carbonyl peak appears at 1639 cm^{-1} throughout the cure reaction. This peak position is slightly different from the model urea compound in PPO, which appeared at 1647 cm^{-1}. This discrepancy may be due to improved hydrogen bonding in PUU's urea domains. Figure 9b shows the changes in urethane and urea carbonyl peaks. The formation of urea group as detected at 1639 cm^{-1} is faster than the urethane formation detected at 1727 cm^{-1}.

When the fluorescence intensity at 339 nm due to DETDA was correlated with the extent of urea formation according to eq 2, we obtained Figure 10a. A fairly linear region of fluorescence intensity vs the extent of urea formation was observed from about 30% to approximately 70% conversion. Urea formation for the first 30% occurred prior to performing any fluorescence measurements, in other words, during the mixture process. Beyond 70%, DETDA fluorescence does not decrease because of the contribution from the overlapping peak at 307 nm due to the fluorescence of urethane derivative of MDI.

An example of the correlation between fluorescence and the extent of urethane can now be described. When the fluorescence intensity at 297 nm due to urethane and urea formation, was plotted as a function of urethane formation determined by IR according to eq 1, we obtained Figure 10b. The fluorescence intensity at 297 nm was chosen to minimize the contribution of DETDA fluorescence. The intensity at 297 nm increased rapidly, probably due to urea formation. This was followed by a slight decrease in intensity, due to self-quenching of urea, as discussed in this section. Within the region from 55% to 100% of the extent of urethane formation, the fluorescence intensity increased with the extent of urethane formation. Since urethane's fluorescence quantum yield is 11 times stronger than urea, the fluorescence in this region is most likely from urethane formation. Therefore, we concluded that this region could be employed to correlate the fluorescence intensity with urethane formation.

References and Notes

(1) Boyer, E. C.; Macosko, C. W. *Polym. Eng. Sci.* **1978**, *18*, 382.
(2) Richter, E. B.; Macosko, C. W. *Polym. Eng. Sci.* **1978**, *18*, 1012.
(3) Vespoli, N. P.; Alberino, L. M. *J. Elast. Plast.* **1985**, *17*, 173.
(4) Grigsby, R. A.; Rice, D. M. *Proceedings of the SPI-33rd Annual Technical/Marketing Conference, Orlando, FL, Oct 1990.*
(5) Priester, J. R.; McClusky, J. V.; Cortelek, D. I.; Carleton, P. S.; Porter, J. R.; DeHaseth, J. A. *Proceedings of the SPI-34th Annual Technical/Marketing Conference, Orlando, FL, Oct 1992*; p 206.
(6) DeThomas, F. A.; Hall, J. W.; Monfre, S. L. *Talanta* **1994**, *41*, 425.
(7) Huang, X. Y.; Yu, W. C.; Sung, C. S. P. *Macromolecules* **1990**, *23*, 390.
(8) Vatanparast, R.; Li, S.; Hakala, K.; Lemmetyinen, H. *Macromolecules* **2000**, *33*, 438.
(9) Sun, X. D.; Sung, C. S. P. *Macromolecules* **1996**, *29*, 3198.
(10) Wang, S. K.; Sung, C. S. P. *Macromolecules* **2002**, *35*, 877.
(11) Yokoyama, T. *Adv. Urethane Sci. Technol.* **1978**, *6*, 1.
(12) (a) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry;* Benjamin, New York, 1964; p 386. (b) Wang, S. K. Ph.D. Dissertation, Study of Polyurethane–Urea Cure Reaction by In-Situ Emission Fluorescence Spectroscopy, University of Connecticut, 1997; Appendix 2, p 162.
(13) Macosko, C. W. *RIM Fundamentals of Reaction Injection Molding;* Hanser: New York, 1989; p 13.

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