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UV, Luminescence, and FTIR Characterization of Cure Reaction in Bisphenol A Dicyanate Ester Resin

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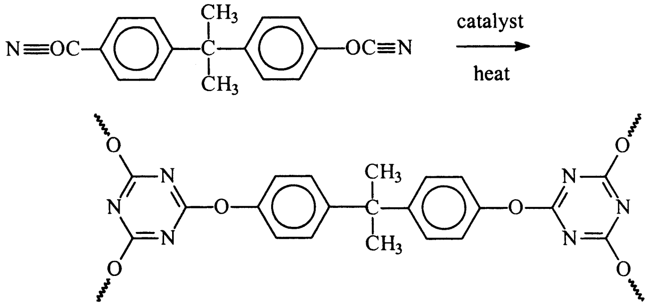
ABSTRACT: To develop cure monitoring techniques for bisphenol A dicyanate ester (BPADCY) resin, UV, fluorescence, phosphorescence, and IR spectra were investigated. UV−vis spectra during the cure reaction indicates that the cyclotrimerization of cyanate esters to form triazine rings is the principal reaction, as supported by IR spectroscopic results. During the cure reaction, very strong luminescence emission has been found. Fluorescence emission intensity around 420 nm first increases, followed by decrease with a small red shift as the cure reaction proceeds. The aromatically substituted cyanurates formed during the cure reaction and their inner filter effect are responsible for the observed emission and its trend in intensity. In-situ fluorescence characterization showed similar results for the catalyzed cure reaction with cobalt acetylacetonate/nonylphenol as well as bisphenol A catalyzed resin in comparison to purified BPADCY, except for the faster rate in fluorescence spectral change. Phosphorescence emission of polycyanate resins appears at a 440 nm, which is about 20 nm longer than that of fluorescence. The phosphorescence lifetime has been found to be about 20 ms at room temperature and remains relatively unchanged throughout the cure reaction. FTIR in situ cure studies of BPADCY monomer indicates a linear relationship between the consumption rate of cyanate ester groups and the formation rate of the substituted triazine rings. Fluorescence changes are correlated to the extent of cure by IR technique.

Introduction

Dicyanate ester resins are relatively new, high-performance materials used in electronic and composite applications. Because of their thermal stability, low dielectric loss, and good adhesion, polycyanate resins have received intensive commercial and scientific attention recently.[1] The polymerization of cyanate ester groups results in three-dimensional network structure, as depicted in Scheme 1, where polycyclotrimerization to form cyanurates is believed to be the main curing reaction.[1] The unique and highly symmetric structure of amorphous polycyanate resins provides superior property compared to other thermosets.

Many characterization techniques such as FTIR, DSC, TBA (torsional braid analysis), NMR, and HPLC have been applied to understand the cure kinetics and mechanisms of polycyanate resins.[2] From the spectroscopic characterization point of view, both the reactant and product have strong and well-defined IR absorption bands.[2c] A strong and a medium intensity ^{13}C NMR signal appears for the reactant and product, respectively, and the ^{15}N NMR spectrum of monomer and polymer is very simple and clean.[2e] In addition, the cure reaction has been monitored by dielectrometry,[3] dilatometry,[4] refractometry,[5] and tubidimetry.[6] An almost full conversion of cyanate ester groups can be achieved for various monomers at high cure temperatures. The polymerization is highly selective to cyanuration of cyanate ester groups to generate cyanurates. An autocatalytic characteristic exists, and the cure reaction can be described by simple kinetic models.[2c,d,7] The polycyclotrimerization is known to be very sensitive to small amount of impurities and catalysts. For example, an impurity of residual phenolic OH group from the synthesis of monomers is speculated to react with a cyanate group to form an iminocarbonate.[2c,7] The iminocarbonate intermediate can react with two more OCN groups to generate a stable cyanurate and release the phenolic compound.

Scheme 1. Polycyclotrimerization of BPADCY Monomer



Intrinsic UV and luminescence spectroscopic techniques have been successfully used to characterize the cure reactions of various polymers in our laboratory.[8] The aromatically substituted cyanurates formed during cure reaction of polycyanate resins were found to be responsible for UV spectral change and strong fluorescence emission observed around 420 nm according to the model compound studies.[9] It is desirable to utilize these changes in UV and emission to develop cure monitoring techniques. One advantage of UV and fluorescence technique is that it can be applied as in-situ method by fiber-optic attachment. This work will report on UV−vis, fluorescence, and phosphorescence characterization of the cure reaction in polycyanate resins, complemented by the IR method.

Experimental Section

A bisphenol A dicyanate ester (BPADCY) monomer with a purity greater than 99.5% was supplied by Ciba-Geigy Corp. The monomer was recrystallized in acetone three times and is referred as recrystallized monomer, while the commercial monomer is designated as unpurified monomer. The amount

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of impurities in recrystallized monomer was not determined. UV−vis, fluorescence, and phosphorescence characterization of these monomers and its mixture with 2.4 mol % bisphenol A (BPA) during cure were investigated. The BPA-catalyzed resin was prepared by mixing recrystallized BPADCY monomer and BPA in a saturated acetone solution. Another catalyzed resin was studied with cobalt acetylacetonate/nonylphenol. Cobalt acetylacetonate (293 ppm) and nonylphenol (1.25%) were mixed in methyl ethyl ketone (MEK) solution, before blending with a saturated BPADCY monomer in MEK solution. After the solvent was evaporated at room temperature, the sample mixture was dried in a vacuum oven for 24 h at room temperature.

For FTIR cure characterization, BPADCY monomer or the sample mixture was molten between two NaCl disks at 100 °C for 3 min, followed by cure at different temperatures in argon. FTIR spectra were obtained in situ at certain time intervals with the sample in a homemade heating cell or recorded at room temperature by using a Mattson Polaris 100 FTIR spectrometer with a continuous argon purge. For UV−vis and luminescence measurement, thin films of BPADCY monomer or the catalyst/monomer mixture was molten between two quartz plates at 100 °C for 3 min, followed by cure in argon at 200 °C. Samples were removed from the oven at certain time intervals and cooled to room temperature before UV−vis transmission spectra were recorded at room temperature using a Perkin-Elmer Lambda 6 UV−vis spectrometer, with a scan speed of 300 nm/min. Luminescence measurement was performed on a Perkin-Elmer LS50B luminescence spectrophotometer, with a scan speed of 120 nm/min and 2.5/2.5 nm slit conditions with a 12% (open) neutral density attenuator. In-situ measurement was accomplished with thin films between two quartz plates in a sample holder with a temperature controller by a bifrucated fiber-optic cable attached to a Perkin-Elmer LS50B luminescence spectrophotometer with 15/15 nm slit conditions. The phosphorescence spectrum and lifetime measurement were performed on a Perkin-Elmer LS50B luminescence spectrometer in the phosphorescence mode with both excitation and emission slits at 15/15 nm. The gate time and the delay time were optimized by maximizing phosphorescence intensity and eliminating fluorescence interference.

Results and Discussion

FTIR Characterization. Cure investigations of different cyanate ester resins in argon by FTIR spectroscopy were carried out at 160, 200, and 240 °C. With the CH stretching at 2970 cm^{-1} due to methyl group in monomer as the internal reference, cyanate ester conversion is obtained by monitoring the disappearance of OCN stretching band at 2270 cm^{-1}. The extent of cyanate ester reaction (X_{IR}) is calculated from the following equation:

$$X_{\mathrm{IR}} = 1 - (I_{2270}/I_{2970})_t/(I_{2270}/I_{2970})_0 \qquad (1)$$

where the initial intensity ratio for BPADCY monomer is represented by $(I_{2270}/I_{2970})_0$. Figure 1 shows cyanate ester conversion measured in situ as a function of cure time for unpurified, recrystallized, and BPA added BPADCY resins at 160 °C under an argon atmosphere. The results indicate that the cure reaction is slower for recrystallized BPADCY monomer (curve 1) than unpurified one (curve 2) at 160 °C. A similar trend was observed at 200 °C. However, the difference between these two resins is almost negligible during cure at 240 °C. This trend can be explained in view of the presence of impurity in monomer which is known to catalyze the cure reaction with its catalytic capacity depending upon cure temperature.[7] In the resins without added catalyst, the impurity has been considered to include the residual phenol and adventious water.[7] It was claimed that 0.5−1.5 mol % arylphenol is present in dicyanate ester monomers by the conventional synthesis and purification procedure.[7] The UV spectra show that the commercial BPADCY monomer in this study has a phenol content of 0.25−0.62 mol %.[10] Curve 3 in Figure 1 shows the fastest rate of cure in 2.4% BPA added BPADCY in comparison to unpurified or recrystallized resin.

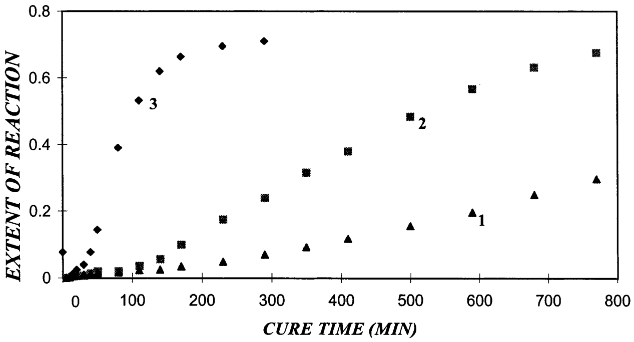

Figure 1. Extent of reaction by disappearance of OCN stretching at 2270 cm^{-1} as a function of cure time for recrystallized (curve 1), unpurified (curve 2), and 2.4% BPA added (curve 3) BPADCY monomer at 160 °C in argon.

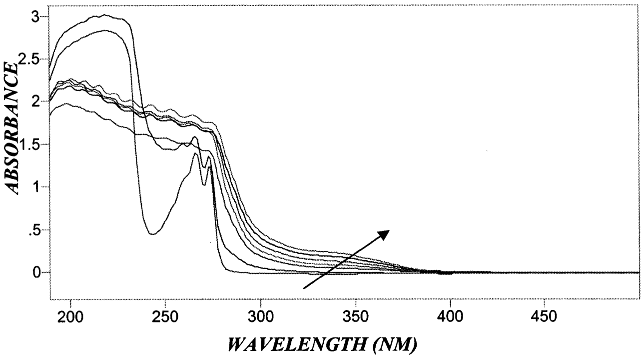

Figure 2. UV−vis transmission spectra of unpurified BPADCY monomer during cure in air at 200 °C (along arrow direction, cure time = 0, 20, 80,140, 230, 350, and 500 min).

A paper on model cure compounds supports that the UV spectral change and fluorescence emission are associated with the formation of the substituted cyanurates during the cure reaction of polycyanates.[9] The formation of cyanurate can be represented by the planar ring stretching at 1565 and 1365 cm^{-1}, normalized with the 2970 cm^{-1} peak. The progress of triazine formation of purified BPADCY resin as calculated by the area of 1365 cm^{-1} shows the same trend as cyanate ester consumption.

UV−vis Characterization. UV−vis transmission spectra during cure of unpurified BPADCY monomer at 200 °C in air are illustrated in Figure 2. The spectrum of solid BPADCY monomer (the lowest in Figure 2) is very similar to that of BPADCY in THF solution.[10] The peak maximum around 270 nm is shifted less than 1 nm, implying that the polarity of BPADCY monomer matrix is similar to that of THF solution.

The strong absorption below 250 nm is likely due to benzene chromophore in BPADCY structure, since triazine's extinction coefficient is much smaller.[10] As demonstrated in model compound studies,[10] the peak at 280 nm has contributions from both the B band of the π−π* transition of benzene and the R band of the n−π* transition of triazine. The B band of benzene and the R band of triazine appear at 255 nm (ϵ = 215) and 270

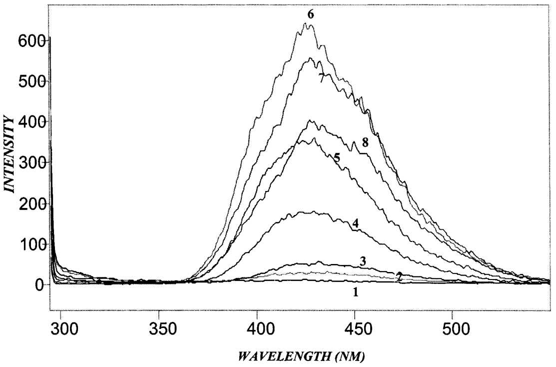

Figure 3. Ambient fluorescence emission spectra of recrystallized BPADCY monomer during cure at 200 °C (excited at 280 nm; spectra 1−8 correspond to cure time = 0, 10, 20, 80, 140, 230, 350, and 500 min, respectively).

nm ($\epsilon = 881$), respectively.[11] The molar extinction coefficient of the former is smaller. Therefore, it is expected that the UV absorption from cyanurate makes a greater contribution as the cure reaction proceeds, thus leading to an increased absorbance in the 280 nm region. This trend is consistent with the model cure product, tricumylphenoxytriazine, which shows a greater extinction coefficient (1.93×10^3 L/(cm mol)) in comparison to BPADCY monomer (1.18×10^3 L/(cm mol)) in THF.[10] The response of the n−π^* transition of triazine to the decrease in matrix polarity as demonstrated by lower dielectric constant[12] during cure is a red shift, which is observed as the cure reaction proceeds. Since the UV spectrum of the cure reaction in argon also yields the same results near 280 nm, the red shift may not be due to oxidation caused by oxygen in the air. The emerging absorbance near 340 nm may be due to some side reaction, since it is not present in model triazine compounds.[10]

Fluorescence Characterization. (a) Uncatalyzed BPADCY Monomer Reaction. The model compound studies show that the model cure product, tricumylphenoxytriazine, has three distinct emissions at 300, 350, and 420 nm.[9] The first one comes from the benzene structure, and the other two are associated with the cyanurate structure. Model compound studies also indicate that when the hydroxyl group in BPA is replaced by a cyanate ester group, the molecule becomes much less fluorescent.

Thin films of unpurified and recrystallized bulk BPADCY monomer between quartz plates also show a weak emission around 300 nm when excited at 265 nm. However, benzene fluorescence emission at 300 nm is extremely weak compared to the emission at 430 nm as in Figure 3, which shows the changes of ambient fluorescence emission following the cure reaction of recrystallized BPADCY monomer at 200 °C in argon. This emission is so strong that the signal has to be filtered off by 88% when the smallest excitation/emission slits are used with a Perkin-Elmer LS50B spectrometer. The BPADCY monomer does not show any fluorescence emission around 400 nm. The intensity around 420 nm at longer cure times is extremely intense so that the emission at 350 nm is essentially negligible in comparison. The model compound studies indicate that large aromatic substituents and solid-state enhance the emission around 420 nm.[9] The unpurified BPADCY monomer following the cure reaction at 200 °C shows very similar fluorescence results. The cure experiments in argon, further purification of BPADCY monomer, and model compound study suggest that the fluorescence comes from cure species rather than from impurities, air oxidation, or moisture-induced hydrolysis.

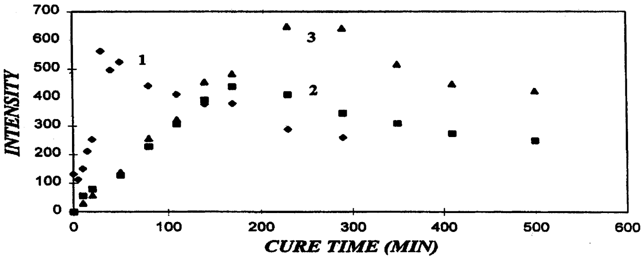

Figure 4. Fluorescence emission intensity at 430 nm as a function of cure time for BPADCY resins following cure at 200 °C (excited at 280 nm; curve 1, BPA catalyzed; curve 2, unpurified; curve 3, recrystallized BPADCY monomer).

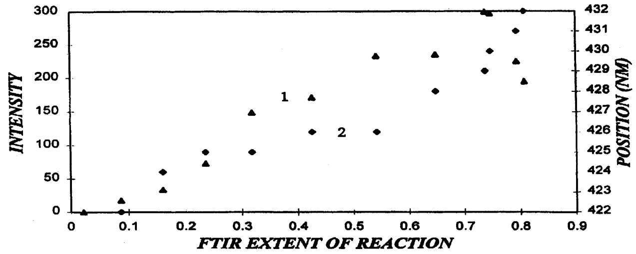

Figure 5. Correlation between fluorescence emission intensity/emission maximum position as a function of the extent of cyanate reaction for recrystallized BPADCY resin following cure at 200 °C (curve 1, intensity; curve 2, peak position).

The emission intensity of the resin around 420 nm initially increases and then decreases; at the same time the peak maximum in the spectra undergoes a small red shift with the cure time. Excitation spectra shows a similar trend as in emission spectra with a peak around 280 nm as a function of cure time. The initial increase of intensity is likely due to the formation of the substituted cyanurate and the viscosity effect as the cure reaction proceeds. When the cyanurate concentration becomes high enough, the fluorophores start to have the inner-filter effect, which results in a decrease in emission intensity. This inner-filter effect was confirmed by studying the concentration effect of the model cure product, soluble BPADCY oligomer in THF. However, it is possible that the side reaction products observed in UV spectra around 340 nm may be partially responsible for the decrease in fluorescence.

Fluorescence intensity changes as a function of cure time are plotted in Figure 4 for all three cured resins. BPA added monomer (curve 1) reaches the intensity maximum fastest, followed by unpurified BPADCY monomer (curve 2). The recrystallized BPADCY monomer (curve 3) is the slowest, a trend agreeing with FTIR results. Both the fluorescence intensity and the shift in peak maximum for the three cured resins can be correlated with the FTIR extent of reaction (by eq 1) as shown in Figure 5. A good relationship exists before the intensity (curve 1) reaches the maximum at about 72% cure extent, while the peak's maximum position (curve 2) shows gradual progressive red shifts up to about 82%.

(b) Catalyzed BPADCY Monomer Reaction. There are generally two kinds of catalysts used in polycyanate cure. One is a phenol-type compound such as nonylphenol. The other is transition-metal compounds, including cobalt acetylacetonate, zinc octoate, and other organometallics.[12] These two kinds of compounds are often formulated together. In the current study, BPA

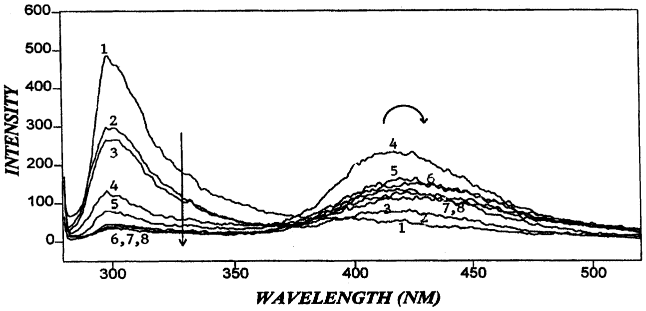

Figure 6. Ambient fluorescence emission spectra of 2.4% BPA added BPADCY monomer during cure at 200 °C (excited at 265 nm; spectra 1−8 correspond to cure time of 0, 20, 50, 80, 110, 170, 230, and 290 min, respectively).

is used as a sole catalyst in addition to the commercial cobalt acetylacetonate and nonylphenol mixture. The model compounds study shows that BPADCY in THF solution has fluorescence emission at 295 nm, while BPA emits at 305 nm.[9] At the same concentration, BPA is about 500 times more fluorescent than BPADCY monomer.[9] Fluorescence emission spectra of recrystallized BPADCY monomer containing 2.4% BPA during cure at 200 °C as shown in Figure 6 also have an emission around 300 nm, which is much stronger than the emission in uncatalyzed resins. This emission initially dominating the spectrum is mainly due to the addition of 2.4 mol % BPA. The intensity decrease near 300 nm due to BPA can be explained by the consumption of BPA in the formation of iminocarbonate. The fluorescence emission at 420 nm due to cyanurate is very similar to that of uncatalyzed resin, with its intensity first increasing, followed by decrease. However, the BPA-catalyzed system reaches the maximum much earlier than uncatalyzed systems, due to the faster rate of cyanurate formation.

The fluorescence characterization was also attempted for cobalt acetylacetone/nonylphenol. Step cure following the supplier's recommendation was conducted for 293 ppm cobalt acetylacetonate/1.25% nonylphenol-catalyzed resin. As in uncatalyzed resin and BPA-catalyzed resin, fluorescence intensity shows a similar pattern as a function of cure time. Since this commercial catalyst system does not interfere with the fluorescence characterization of the cure reaction, it holds promise for industrial applications.

(c) In-Situ Cure Monitoring of Catalyzed Systems. On-line quality control of manufacturing materials is crucial to improve productivity. Although more demanding technologically, fluorescence has superior advantages for this application. On the basis of the previous study of catalyzed formulations, two BPADCY resins are chosen to conduct fluorescence characterization at a low cure temperature (150 °C) for in-situ measurement. Fluorescence spectra from 293 ppm cobalt acetylacetonate/1.25% nonylphenol-catalyzed BPADCY system show similar trends as those obtained at room temperature, except for lower intensity.

Phosphorescence Characterization. Phosphorescence spectroscopy has been used as a complementary technique to fluorescence spectroscopy for cure monitoring of polymer thermosets.[8b] Because of the energy difference between singlet and triplet states, the compounds with the lowest transition of n−π^* such as *s*-triazine should have substantial intersystem crossing. The phosphorescence of *s*-triazine in EPA rigid glass or in the pure solid at 77 K has a peak maximum around 450 nm with a mean lifetime of 0.44 s.[11c] Laser-induced phosphorescence of triazine vapor has a peak maximum at 400 nm, and the lifetime is 7.1 × 10^{-6} s.[13] Therefore, moderate phosphorescence is expected for dicyanate ester polymers. Phosphorescence emission is detected for recrystallized BPADCY after cure as shown in Figure 7. The phosphorescence emission maximum (spectra 3) occurs only 20 nm longer than that of fluorescence (spectra 4), and these two emissions overlap. The phosphorescence spectrum of BPADCY polymer is very similar to the low-temperature results of triazine.

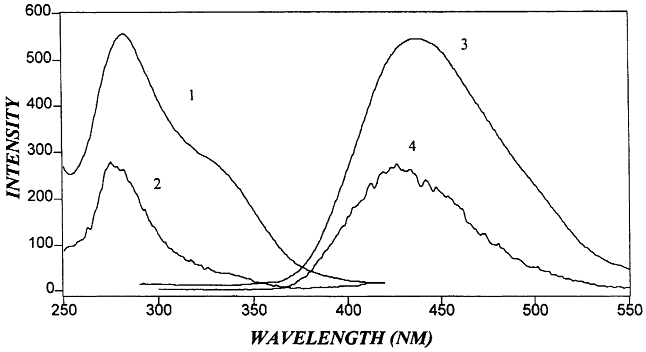

Figure 7. Luminescence spectra of recrystallized BPADCY resin cured at 200 °C for 410 min (excited at 280 nm and emitted at 430 nm; 1-phosphorescence excitation spectrum, 2-fluorescence excitation spectrum, 3-phosphorescence emission spectrum, 4-fluorescence emission spectrum).

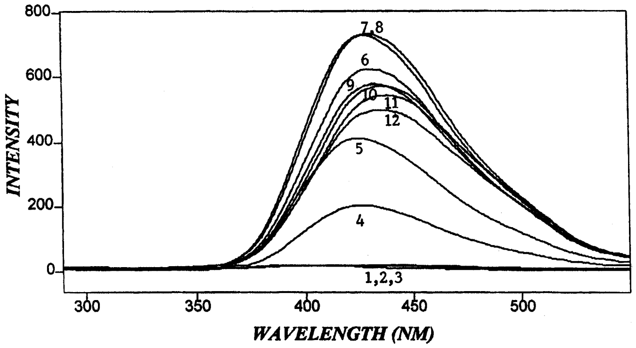

Figure 8. Ambient phosphorescence emission spectra of unpurified BPADCY during cure at 200 °C (excited at 280 nm; spectra 1−12 corresponds to cure time of 0, 20, 50, 80, 110, 140, 170, 230, 290, 350, 410, and 500 min, respectively).

Figure 8 illustrates the ambient phosphorescence emission of unpurified BPADCY following cure at 200 °C, when excited at 280 nm. As in fluorescence emission, phosphorescence emission intensity reaches a maximum, followed by the decrease. The increase of cyanurate concentration and the inner-filter effect may also be responsible for this trend, as in the case of fluorescence. The ambient phosphorescence emission intensity of BPADCY monomer with cobalt acetylacetonate and nonylphenol during the cure reaction at 150 °C is similar. The phosphorescence lifetime was measured to be about 20 ms, which does not change much during cure.

Summary

UV spectra of cure reaction support that the cyanuration is the dominant reaction during the cure reaction. A strong fluorescence emission around 420 nm was detected for all the cured resins. Fluorescence intensity first increases, reaches a maximum, and then decreases, while the peak maximum undergoes a small red shift.

The inner-filter effect of triazine formed during the cure reaction may be responsible, at least in part, for the observed trend in intensity. Introduction of catalyst does not interfere with fluorescence emission of polycyanate resins. The phosphorescence intensity shows a similar trend as in fluorescence intensity. FT IR studies show a linear relationship between the extent of reaction by the consumption of cyanate ester group and the formation of the triazine rings. Fluorescence spectral changes are correlated to the extent of cure by IR in order to develop cure characterization techniques.

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