Cure Characterization in Diamine-Cured Epoxy and Polyimide by UV Reflection Spectroscopy

Jae-Woong Yu and Chong Sook Paik Sung*

Institute of Materials Science, Department of Chemistry, University of Connecticut, 97 North Eagleville Road, Storrs, Connecticut 06269-3136

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ABSTRACT: UV specular reflection spectroscopy has been investigated for the characterization of cure reactions in an aromatic diamine cured epoxies and their composites, as well as in the imidization characterization of an aromatic polyamic acid. The UV reflection peak due to the reaction of the curing agent bis(*p*-aminophenyl) sulfone (DDS) with epoxide shows a red shift of about 24 nm in the spectral range of 300 nm to 350 nm. After the Kramers−Kronig conversion of the reflection spectra which is shifted to longer wavelength than the transmission spectra, the DDS peak occurs at a similar position as the transmission peak. The spectral shifts obtained by three different techniques, UV reflection, UV transmission, and fluorescence excitation were similar as a function of cure time at 160 °C. Therefore, the peak position in the reflection spectra may be used without the Kramers−Kronig conversion in order to correlate to the extent of cure, as established for the excitation spectral shift. The UV reflection spectral analysis is also obtained in DDS containing epoxy reinforced with glass or carbon fiber. Since the reflection probes only the first 0.5 μm layer of the resin, the presence of the fiber does not influence the spectral quality. In following the imidization of a polyamic acid made from 1,4-phenylenediamine (PDA) and an aromatic dianhydride, the spectral deconvolution of the UV reflection spectra provides a way to determine the relative composition of polyamic acid and polyimide. The resulting extent of imidization was compared with the result by IR analysis. Thus, UV reflection technique can be a useful cure characterization method with the samples which have smooth surfaces, strong UV absorption, but weak fluorescence.

Introduction

High-performance composites reinforced with fibers containing either epoxy or polyimides are increasingly used in many structural applications. In situ characterization of the cure extent during actual manufacturing process is important for reproducible properties.

While microdielectrometry[1] and fiber-optic FT-IR[2] techniques have been reported as in situ cure characterization methods, the research from our laboratory has focused on the development of fluorescence and UV−visible spectroscopic techniques based on either extrinsic or intrinsic probe molecules. These molecules undergo chemical reactions during cure with the subsequent changes in their substituent groups attached to the aromatic ring, leading to the changes in UV−visible and fluorescence spectra. These techniques were applied to diamine-cured epoxy,[3] polyimide,[4] polyurethane,[5] and vinyl polymers.[6]

The intrinsic fluorescence technique based on the curing agent in the resin can be applied to the solid samples by the front surface illumination method, even though the sample may contain fibers or exhibit strong absorption in UV range. Therefore, fiber-optic fluorescence[7] was a convenient in situ cure monitoring method applied even in epoxy composites, when an aromatic diamine, bis(*p*-aminophenyl) sulfone (DDS) was used as a curing agent. However, not all polymers show significant changes in fluorescence during cure. For example, during imidization of some polyamic acids to polyimides, the fluorescence changes are rather small.[4,8]

As for the UV−visible spectra, many of these high-performance polymers exhibit sensitive spectral changes as a function of cure. The UV transmission technique, however, is only possible in a very thin film[3a,d] or after dilution for cure reactions taking place in solution,[4] because of the high extinction coefficients in the UV range. For samples which are thick, reinforced with fibers or fillers, or cast on substrates such as metals, UV transmission is not applicable. For these cases, UV external reflection technique may provide a way of obtaining a sensitive UV spectra.

External reflectance spectra in UV range for inorganic single crystals[9] have been used to provide information on their optical properties. By using the Kramers−Kronig dispersion relation, the refractive index and the absorption coefficient had been determined from the reflection spectra. UV reflection studies on polymers have not been explored extensively until recently, due to the small reflectivity from the organic polymers. Kaito et al.[10] applied UV reflectance spectra with polarized light to study the surface orientation of poly(ethylene terephthalate) (PET) and a liquid-crystalline polymer. UV reflection spectra of polyaniline[11] and polysilanes[12] have also been recently reported to probe their molecular and electronic structure.

In this study, we explore the capabilities of UV reflection spectra in following cure reactions in a diamine-cured epoxy and imidization of a polyamic acid to a polyimide. In earlier studies, we reported a bathochromic spectral shift in UV spectra as DDS is cured with epoxide,[3c,d] and a hypsochromic spectral shift as polyamic acid is imidized to polyimide.[4] These spectral changes were found to be correlatable with the extent of cure.[3,4]

In order to understand the relationship between the reflection spectral peak positions and the absorption peak positions, it is useful to briefly review the relevant theory and the Kramers−Kronig conversion. In the reflection spectra which is obtained by the geometry shown in Figure 1, the percent reflectance, R, is obtained as a function of wavelength. The reflection spectra is shifted from that of transmission spectra by a phase shift Φ. The refractive index, n and absorption

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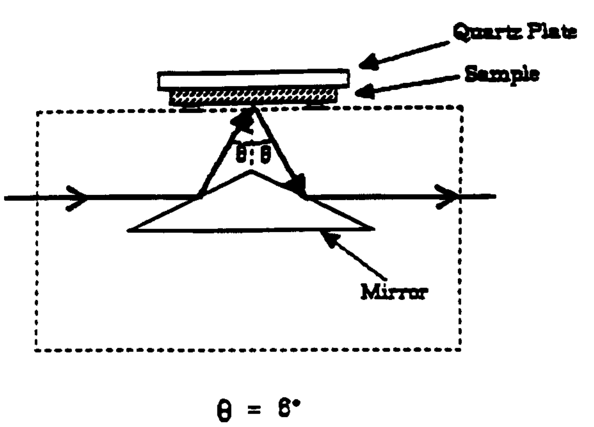


Figure 1. Schematic diagram showing optical pathway of specular reflection on polymer sample.

index, k, are related to R and Φ obtained at normal incidence, according to the following equations:[10]

$$n = \frac{1 - R}{(1 + R - 2\sqrt{R}\cos\Phi)} \qquad (1)$$

$$k = \frac{-2\sqrt{R}\sin\Phi}{(1 + R - 2\sqrt{R}\cos\Phi)} \qquad (2)$$

Therefore, n and k can be obtained by measuring the percent reflectance, R, and by calculating Φ through the following Kramers–Kronig dispersion equation:[9]

$$\Phi(\nu') = \frac{1}{\pi}\int_0^\infty \ln\left|\frac{\nu + \nu'}{\nu - \nu'}\right| \frac{\mathrm{d}\ln\sqrt{R(\nu)}}{\mathrm{d}\nu}\,\mathrm{d}\nu \qquad (3)$$

where ν' is a particular wavenumber. Equation 3 shows that the phase shift, Φ at ν' can be calculated from the dispersion of reflectance by integrating from zero to infinite frequencies. However, only a limited region of the whole spectral range makes a significant contribution to $\Phi(\nu')$. The major contributions came from the neighborhood of ν', since the function, $\ln|\nu + \nu'/\nu - \nu'|$ is strongly peaked when ν approaches ν'. Also at this region, the reflectivity is changing rapidly, so that the function $(\mathrm{d}/\mathrm{d}\nu)\{\ln\sqrt{R}\}$ is large. Thus, only the part of the spectrum representing the absorption band is required to calculate $\Phi(\nu')$. Equation 3 can be calculated by a fast Fourier transform algorithm on a personal computer as described by Bortz and French,[13a] or by commercially available software.[13b]

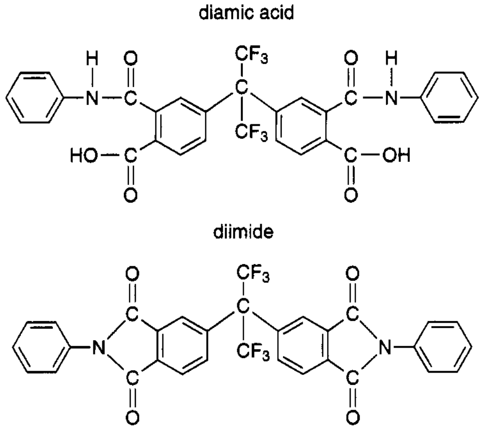
In general, the reflection spectrum shows peak maxima at longer wavelengths than the transmission spectrum. For example, PET reflection spectra reported by Kaito et al.[10] showed a peak at 258 nm while the transmission spectrum showed a peak at 244 nm. The absorption coefficient spectra after the Kramers–Kronig conversion of the reflection spectra showed a peak very close to the transmission peak at 244 nm.

Experimental Section

Sample Preparation for Epoxy Cure Studies. For neat epoxy cured with DDS (Aldrich), a difunctional epoxide, diglycidyl ether of butanediol (DGEB) was used as purchased from Aldrich. A stoichiometric mixture of DGEB/DDS was prepared by mixing 2.98 g of DGEB with 1.825 g of DDS under constant stirring at 120 °C for 2 min. The samples were cured between two quartz plates separated by two 25 μm thick Mylar spacers which were placed on the edges.

For epoxy prepregs, two types of Hexcel F263 prepregs containing either glass mat or carbon fiber were used. These prepregs contain about 50% by weight of a tetrafunctional epoxide, bis[p-(diglycidylamino)phenyl]methane (TGDDM) and DDS curing agent with a small amount of catalyst ($BF_3-NH_2C_2H_5$).

Scheme 1. Chemical Structures of Model Diamic Acid and Diimide used for IR Studies



Sample Preparation for Imidization Studies. For polyamic acid made from 1,4-phenylenediamine (PDA) and 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzofurane dione (6FDA) a stock solution of 10% by weight was prepared by slowly adding 0.411 g (0.925 mmol) of 6FDA into a NMP solution (4.7 mL) containing 0.1 g (0.925 mmol) of sublimed and zone-refined PDA. The solution was stirred at room temperature for 6 h and stored in a refrigerator. For imidization studies, this polyamic acid solution was coated onto a quartz plate (1 in. × 1 in. in size) using a blade (Gardner knife by Gardner Labs), followed by drying at 85 °C for 30 min to remove excess solvent without inducing imidization.[14]

Synthesis of Model Compounds. Scheme 1 shows the chemical structures of the model compounds used to calibrate the IR measurement of imidization, since it is often difficult to obtain completely imidized polyimide. A model diamic acid was synthesized by reacting 2 mmol of aniline and 1 mmol of 6FDA in acetone at room temperature for 10 h. Also, a diimide was obtained by chemically imidizing 1 mmol of this diamic acid with 8 mmol of acetic anhydride and 7 mmol of pyridine in NMP in 100 °C oil bath for 2 h. The diimide was recovered by precipitation in water and dried in a vacuum oven at 110 °C for 18 h. The diimide was further purified by precipitation from NMP solution in water and drying in vacuum. FT-IR spectra were carefully examined for all the characteristic imide bands and for any impurities such as anhydride and carboxylic acid peaks.

Spectroscopic Analysis. For both neat epoxy cured with DDS and polyamic acid samples, UV reflection spectra following cure at elevated temperature were obtained after cooling the samples to room temperature by using a specular reflectance accessory (Perkin-Elmer accessory No. 5500228) in a Perkin-Elmer Lamda-6 UV–vis spectrophotometer. Figure 1 shows the optical alignment in the accessory where the incident and the reflection angles are set at 6°. For in situ cure monitoring at the actual cure temperatures, a fiber-optic UV–vis spectrometer from Guided Wave (Model 200) was used with a sample holder designed for heating capacity, as shown in Figure 2. The fiber-optic cable contains seven silica single fibers (320 μm diameter) in a PVC jacket, which is terminated with a connector. The connector is fitted to a radiance probe which holds two fused silica lenses, which are 0.4 in. apart with the focal length of 1 and 3 in., respectively in order to collimate the diverging light emanating from the fiber bundle. In thin (<1 μm) or thick (>10 μm) epoxy films, 2 or 1 quartz plate(s) was placed respectively under the front surface mirror for the background correction. For thick (>10 μm) polyamic acid films, the front surface mirror without a single quartz plate was used for the background correction. Kramers–Kronig transformation to convert the reflectance spectra to the absorptivity spectra was carried out by a commercial software (Lab Calc) purchased from Galactic Industries Corporation.

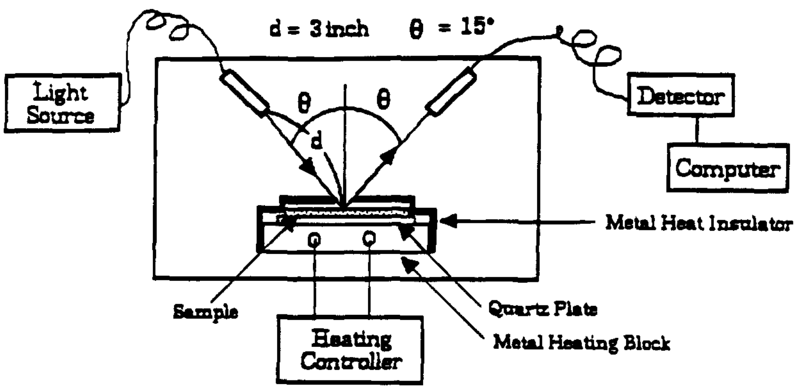


Figure 2. Schematic diagram showing in situ reflection UV–vis setup using a fiber-optic instrument.

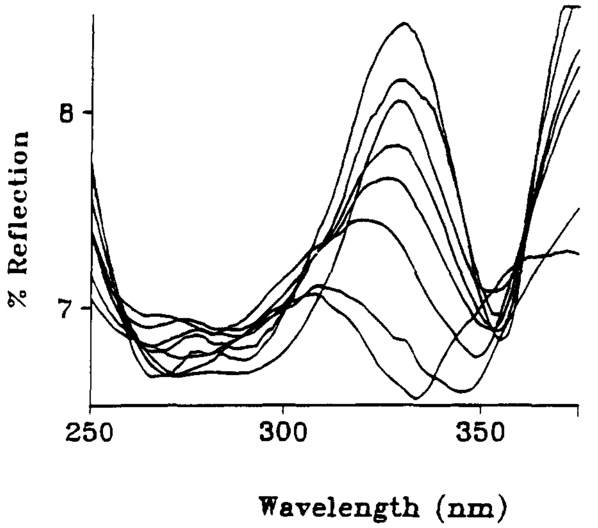


Figure 3. Room temperature UV reflection spectra as a function of cure time (from bottom to top: 0, 10, 25, 50, 80, 120, 150, and 180 min at 160 °C).

Thin films (about 100 nm for epoxy-DDS and 700 nm for polyamic acid) were used to obtain transmission UV spectra on a quartz plate and FT-IR spectra on a salt plate (Nicolet 60SX FT-IR).

As for cure conditions, isothermal cure temperatures were used for epoxy-DDS, while a stepwise cure cycle was used for imidization of polyamic acid.

Results and Discussion

A. Epoxy Cured with an Aromatic Diamine. In high-performance epoxy composites, an aromatic diamine, bis(*p*-aminophenyl) sulfone (DDS) is the most often used curing agent. During cure reaction with epoxide, the primary amine groups in DDS are converted to the secondary amine and eventually to the tertiary amine groups. As a consequence, both UV spectra and fluorescence excitation spectra show about a 24 nm red shift, which has been correlated to the extent of amine reaction.[3d] Before we explore UV reflection spectra for imidization of a polyamic acid which shows little fluorescence, we tested UV reflection method in DDS-cured epoxy since its fluorescence and UV spectra were extensively investigated.[3d] Figure 3 shows the UV reflection spectra obtained after cooling a diepoxide (diglycidyl ether of butanediol, DGEB) cured at 160 °C with a stoichiometric amount of DDS to room temperature. The spectral region between 300 and 350 nm is of interest due to DDS absorption. Beyond 350 nm, the spectra show high reflectance from multiple reflection at both surfaces of the sample since it is a transparent region. The reflection peak around 307 nm is progressively shifted to around 330 nm after 120 min. This trend is plotted in Figure 4 as a function of cure time at 160 °C, showing an overall shift of 23 nm. Transmission UV spectra with very thin films of the same epoxy–DDS composition showed the absorption maximum to change progressively from 298 to 322 nm. While the overall shift in both reflection and absorption spectra is very close, the reflection spectra are shifted to the longer wavelength, by about 8 nm. In order to see if we can produce the comparable absorptivity spectra from the reflection spectra by the Kramers–Kronig conversion, all the reflection spectra were converted to absorptivity spectra. Figure 5 shows the comparison of the UV transmission spectra of DGEB/DDS before cure with that of the converted absorptivity spectra from the reflection spectra. The main peak due to DDS in reflection spectra (curve 2) occurs at a longer wavelength than that of the transmission spectra (curve 1). After the Kramers–Kronig conversion, the DDS main peak (curve 3) occurs at a similar position as the

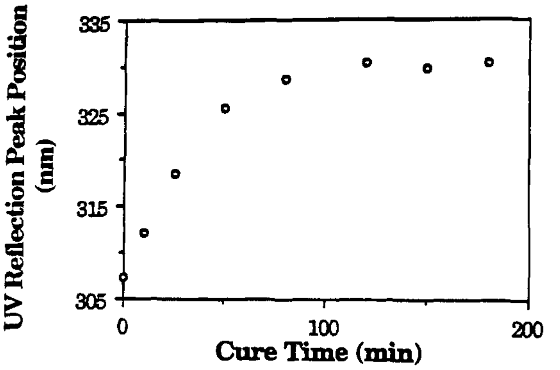


Figure 4. UV reflection peak position of DDS in DGEB/DDS at room temperature as a function of cure time at 160 °C.

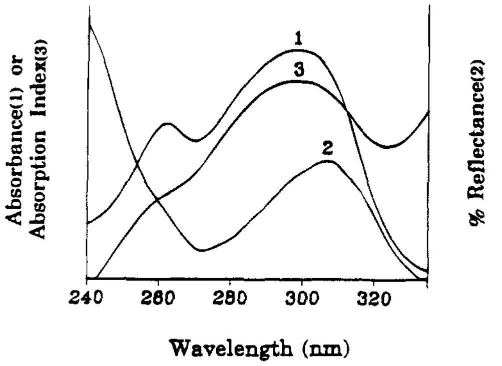


Figure 5. Comparison of transmission (1), reflection (2), and Kramers–Kronig transformed reflection (3) spectra for DGEB/DDS before cure.

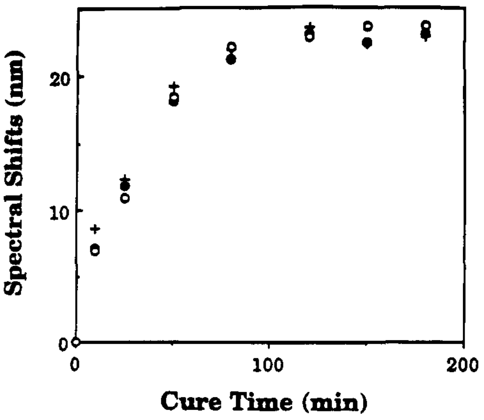


Figure 6. Comparison of spectral shifts in DGEB/DDS as a function of cure time at 160 °C: (○) transmission; (●) reflection; (+) fluorescence excitation.

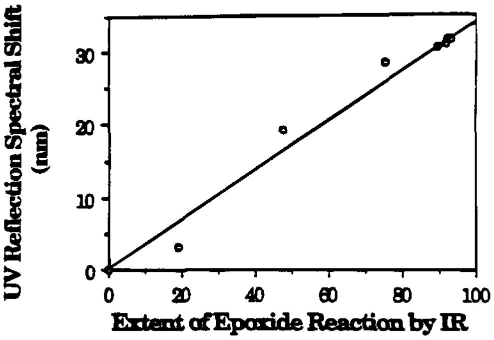


Figure 7. Correlation between UV spectral shift and extent of epoxide reaction for in situ cure monitoring of DGEB/DDS at 160 °C.

transmission peak (curve 1). Figure 6 shows the comparison of the spectral shifts obtained by three different techniques, UV reflection, UV transmission, and fluorescence excitation, as a function of cure time at 160 °C. The three curves are almost indistinguishable. Therefore, the peak position in the reflection spectra may be used without the Kramers–Kronig conversion in order to correlate to the extent of cure as described for the excitation spectral shift.[3d]

In order to see how the reflection spectra is affected by cure temperature, in situ cure monitoring was carried out at the cure temperature of 160 °C by using a fiber-optic UV instrument with the setup as shown in Figure 2. While the reflection spectra are very similar to those obtained at room temperature by the external reflection accessory, the total spectral shift of 27 nm was obtained, which is about 3 nm greater than the shift measured at room temperature. This difference is found to be due to the high measurement temperature (160 °C), since the peak position is blue shifted by 3 nm after cooling the cured sample. In order to correlate the spectral shift observed during in situ measurement with the extent of epoxide reaction, we measured the epoxide disappearance at 915 cm^{-1} in IR spectra calibrated with the phenyl ring stretching in DDS at 1590 cm^{-1} at 160 °C. The extent of reaction (ξ) is defined as

$$\xi = 1 - (A_{\text{epoxide}}/A_{\text{reference}})_t/(A_{\text{epoxide}}/A_{\text{reference}})_{t=0} \quad (4)$$

where t is the cure time and A is the absorbance. Figure 7 shows a plot between the spectral shift observed in UV reflection spectra at 160 °C and the extent of epoxide reaction determined by IR. In our previous work,[3d] we showed a similar relation between UV transmission shift or fluorescence excitation shift and the extent of amine reaction. Since there is a one to one relationship between amine consumption and epoxy consumption in a stoichiometric mixture of DGEB/DDS, such a plot as Figure 7 is reasonable.

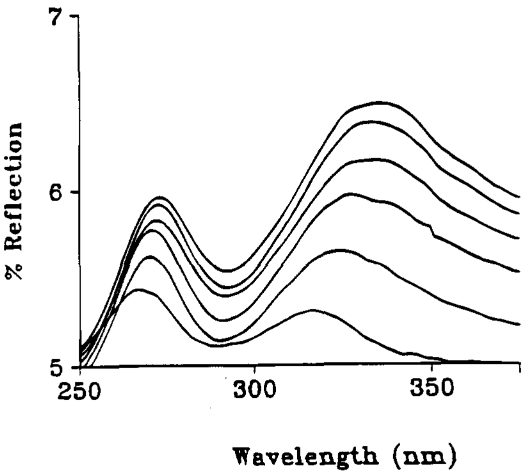


Figure 8. Room temperature UV reflection spectra of epoxy/glass prepreg, as a function of cure time at 160 °C (from bottom to top: 0, 10, 25, 50, 80, and 120 min).

Next, the UV reflection technique was tested in prepreg composites, i.e., epoxy–DDS reinforced with either glass or carbon fibers. These samples come as slightly precured for the convenience of handling. The composition of resin is known to contain 2 mol of tetrafunctional epoxide (TGDDM) to 1 mol of DDS with a small amount of $BF_3NH_2C_2H_5$ as catalyst. Figure 8 shows UV reflection spectra obtained on glass fiber-reinforced epoxy composites as a function of cure time at 160 °C. Carbon fiber-reinforced epoxy prepregs also showed spectra of similar quality. The peak occurring near 270–280 nm is due to the aromatic groups in TGDDM and DDS. In the case of DGEB and DDS, the corresponding peak is very small as shown in Figure 3 because of the absence of the aromatic ring in DGEB. It is noted that the spectral quality is quite good, with clearly changing DDS peaks between 300 nm and 350 nm in spite of the presence of the reinforcing fibers. Due to the precure, DDS peak starts from 317 nm in glass prepreg and 319 nm in carbon prepreg. The extent of precure was determined by comparing with the starting point of the uncured reinforced resin containing the same composition as in prepreg. The initial peak position for these uncured composites was 313 nm and 315 nm for glass and carbon composites, respectively, which was 4 and 5 nm lower than the corresponding prepreg. On the basis of the correlation reported between the spectral shift and amine reaction,[3d] we estimate that the extent of precure in the glass or carbon prepreg is 12% or 15% in amine cure, respectively, before additional cure in our laboratory. Figure 9 shows the reflection peak positions as a function of cure time for prepregs. Carbon prepreg shows a faster cure rate than the glass prepreg, probably due to a different amount of the catalyst included in the pregreg. The overall shift in the prepegs is only observed to be about 19 nm, because of the precure. When the initial shift of 4 or 5 nm in the prepreg is added to 19 nm, the total of 23–24 nm is obtained, corresponding to the complete reaction of DDS, as expected from the excess epoxide in the composition of the prepregs.

B. Imidization of Polyamic Acid. Polyamic acids and polyimides made of the aromatic diamines and

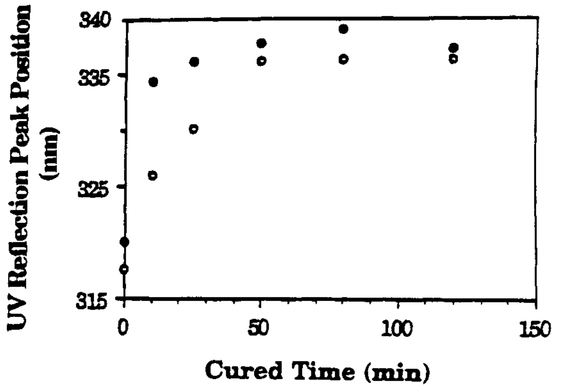


Figure 9. Glass (○) and carbon (●) prepreg peak position change in room temperature UV reflection spectra as a function of cure time at 160 °C.

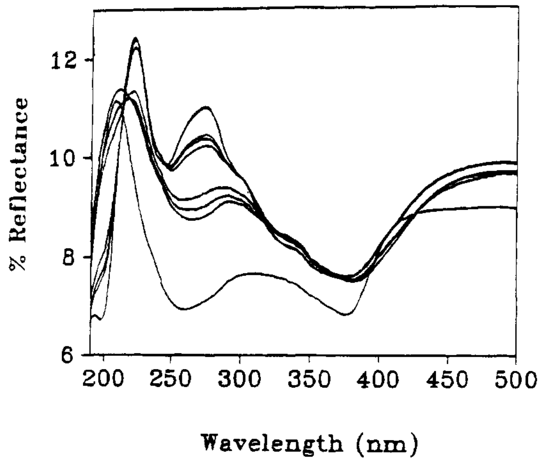


Figure 10. UV reflection spectra of thick (100 μm) polyamic acid (6FDA/PDA) film as a function of stepwise imidization (from bottom to top: 0 min, 10, 20, 30 min at 160 °C, 10, 20, 30 min at 200 °C, followed by 20 min at 250 °C).

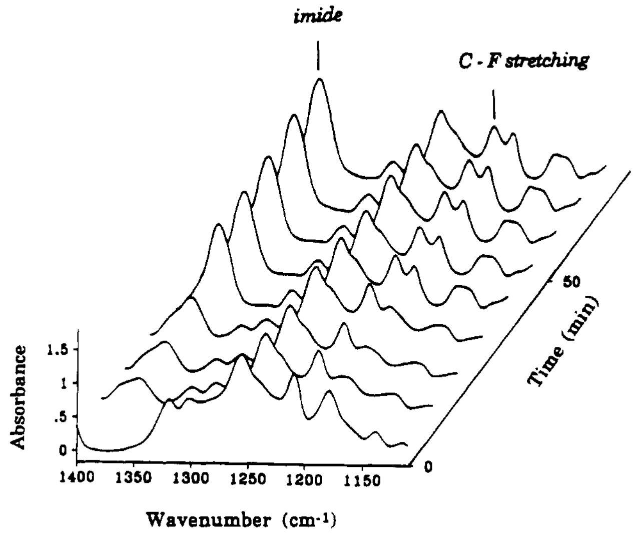


Figure 11. FT-IR spectra of thin (0.5 μm) polyamic acid (6FDA/PDA) film as a function of stepwide imidization (from left to right, 0 min, 10, 20, 30 min at 160 °C, 10, 20, 30 min at 200 °C, followed by 10 and 20 min at 250 °C).

Table 1. Composition Analysis Based on Spectral Deconvolution of UV Reflection Spectra as a Function of Stepwise Imidization

imidization time (min)/ temperature (°C)	composition of PAA (%)	composition of PI (%)
0	100	0
10/160	51	49
20/160	48	52
30/160	42	58
10/200	21	79
20/200	19	81
30/200	17	83
20/250	7	93

dianhydrides generally exhibit strong absorption in UV−visible range. However, their fluorescence is generally weak.[8] In monitoring the extent of imidization from polyamic acid to polyimide, the UV reflection technique may be quite promising, since UV absorption by transmission would be too strong. In this study, we tested an important polyimide resin often used in composites. It is composed of 1,4-phenylenediamine (PDA) and fluorinated aromatic dianhydride (6FDA).

In a thin film (about 700 nm thickness) of polyamic acid made from 6FDA/PDA, the transmission absorption maxima appears at 290 nm, which is gradually blue shifted to about 262 nm, after stepwise cure of 20 min at 250 °C following 30 min of cure each at 160 and 200 °C. UV reflection spectra of thin polyamic acid film (~1 μm) made from 6FDA/PDA gave poor spectra at early stages of imidization. However, UV reflection spectra of thick polyamic acid film (>10 μm) were very good throughout the imidization step, as shown in Figure 10. It is noted that the broad PAA peak is not only blue shifted but also its reflectance is increased probably due to increasing density. As expected, the reflection spectral position occurs at longer wavelength than the transmission spectra. The peak position, however, stops changing after about 60% imidazation. In solid state thermal imidization, we could assume that PAA and PI (polyimide) are major species.[4] In order to obtain their composition at each cure step, the spectral deconvolution was attempted by using a computer program called PLSPLUS from Galactic Industries Corp. before or after Kramers and Kronig conversion, based on the spectra of PAA and PI. The composition analysis was found to be easier to do on the reflection spectra, due to the peak shape change after Kramers and Kronig conversion. Table 1 summarizes the composition analysis on the basis of UV reflection spectra. The regenerated spectra based on the composition analysis results in Table 1 match the peak heights of the experimental spectra, but the peak shapes show some deviation in some cases. Therefore, we would estimate the error in the composition analysis to be around 5%.

It is useful to compare the extent of imidization by this UV method with that obtained by IR. Since UV method probes the first 0.5 μm layer, IR spectra were obtained on a thin film of 0.5 μm in thickness. Figure 11 illustrates the changes in FT-IR spectra as a function of the same stepwise imidization step. It is noted in Figure 11 that the imide band at 1365 cm^{-1} increases with imidization. The extent of imidization was measured using this imide band in reference to 1209 cm^{-1} C−F stretching band, after calibrating IR method using model diimide and diamic acid described in Scheme 1. The experimental errors in IR method are less than 5%.

Figure 12 compares the percent imidization obtained by UV method on 100 μm thick film and by IR method on 0.5 μm thick film. It shows that the percent imidization is faster at early stages by the UV method than by the IR method, while the values eventually approach at late stages of imidization. This type of behavior has been reported by IR studies in different thickness samples by Ginsburg and Susko[15] due to the plasticizing effect of NMP solvent in thicker samples.

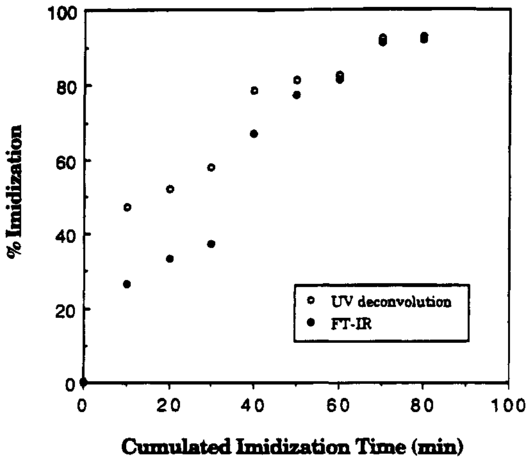


Figure 12. Comparison of the percent extent imidization by IR and UV as a function of stepwise imidization (from left to right, 0 min, 10, 20, 30 min at 160 °C, 10, 20, 30 min at 200 °C, followed by 10 and 20 min at 250 °C).

Therefore, the trend observed in Figure 12 seems reasonable.

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