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Excitation Spectroscopy of a Reactive Label for Characterization of the Cure Process in an Epoxy Network

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ABSTRACT: Fluorescence excitation spectra of a reactive label, *p,p'*-diaminoazobenzene (DAA), were investigated to characterize the cure process in an epoxy network composed of a stoichiometric mixture of diglycidyl ether of Bisphenol A and diaminodiphenyl sulfone. Under ideal conditions, the corrected excitation spectra should resemble UV–visible absorption spectra with an intensity proportional to the fluorescence quantum yield. Therefore, corrected excitation spectra of the model cure products as well as a function of various composition of cure products were simulated. Due to the sharp increase in the fluorescence quantum yields of the later cure products, such simulated excitation spectra are well separated from each other. Experimentally obtained excitation spectra of the model cure products and of the curing epoxy showed some distortions in the spectra that are probably due to instrumental factors. Nevertheless, the excitation maximum was observed near 470 nm, corresponding to the absorption maximum of the tertiary–tertiary amine product of DAA. The intensity of the experimental excitation spectra after calibration with UV–visible absorption spectra was found to show sharp increase as a function of cure time, followed by leveling off after vitrification of the epoxy network. This profile was very similar to that of the intensity of fluorescence emission, reported in our previous study. Under the assumptions that the reactions between the diamines and the epoxide are the main cure reactions and the primary amine and the secondary amine react at similar rates, the cure product composition has been estimated, on the basis of the excitation intensity. The results show a reasonable trend of the formation and the disappearance of the cure species. Therefore, this study demonstrates that excitation spectra can be used for cure characterization of epoxy network.

Introduction

Recently, we introduced the approach of reactive labeling techniques for the study of polymerization and crosslinking in polymers. In this approach, the reactive label is designed to have similar reactivities as one of the polymerizing components and to exhibit spectral changes in the region of UV–visible absorption and fluorescence spectra where the polymerizing matrix has little absorption or emission. Basically, we take advantage of the magnified effects of the substituent changes in the para and para primed positions of aromatic reactive labels on the UV–visible and fluorescence spectra. This approach has been applied to several polymers such as cross-linked epoxies,[1] polyimides,[2] polyurethanes,[3] and polyamides.[4] One particular advantage of this approach is that we can often distinguish between several cure species in some polymers while with other spectroscopic techniques such as IR or NMR we cannot. This is because the electronic spectra such as UV–visible absorption are influenced by both of the substituents at the para and para primed positions of conjugated aromatic compounds, while IR or NMR is determined only by the functional groups in each substituent. For example, we have shown that each of the several cure species in polyimide synthesis such as polydiamic acids, polyamic acid–imide, and polydiimide has its characteristic UV–vis absorption spectra and is thus clearly distinguishable.[2a,5] This advantage makes it possible to follow cure composition throughout the cure process and to analyze the kinetics and the mechanisms of several consecutive polymerization steps in some polymers.

In the characterization of epoxy cure, we found that a reactive label, *p,p'*-diaminoazobenzene (DAA), showed significant red shifts in UV–vis spectra and drastic enhancement of fluorescence emission intensity when reacted with epoxide. Thus, the deconvolution of UV–vis absorption spectra provided the estimates of the fraction of each cure species. The fluorescence intensity at the emission maxima was also used to quantify the fraction of each cure species, assuming a certain kinetic scheme. In UV–vis absorption spectra, significant spectral overlap between different cure species made the deconvolution difficult, especially at the intermediate cure extent. This overlap

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was due to the fact that the extinction coefficients of several cure species are quite similar.

The fluorescence excitation spectrum is a plot of emission intensity (I_e) at a fixed emission wavelength as a function of the exciting wavelength. Under certain favorable experimental conditions, the excitation spectral intensity (I_e) is proportional to the extinction coefficient and the fluorescence quantum yield for a weakly absorbing molecule.[6] In such cases, the excitation spectrum has the same spectral features as the UV–vis absorption spectrum, but its intensity is proportional to the fluorescence quantum yield. Since the fluorescence quantum yields of the initial cure products of DAA in epoxy are much lower than those of the later products, the excitation spectra under ideal circumstances could be similar to UV–vis spectra but they are expected to be well separated. However, the instrumental factors such as wavelength-dependent intensity of the exciting light and of the monochromators and the presence of multiple fluorophores are known to distort the excitation spectra.[7] It is important to assess the extent of such distortion due to instrumental factors. Other research groups have explored fluorescence excitation spectroscopy as a way to characterize cure in polyimides.[8]

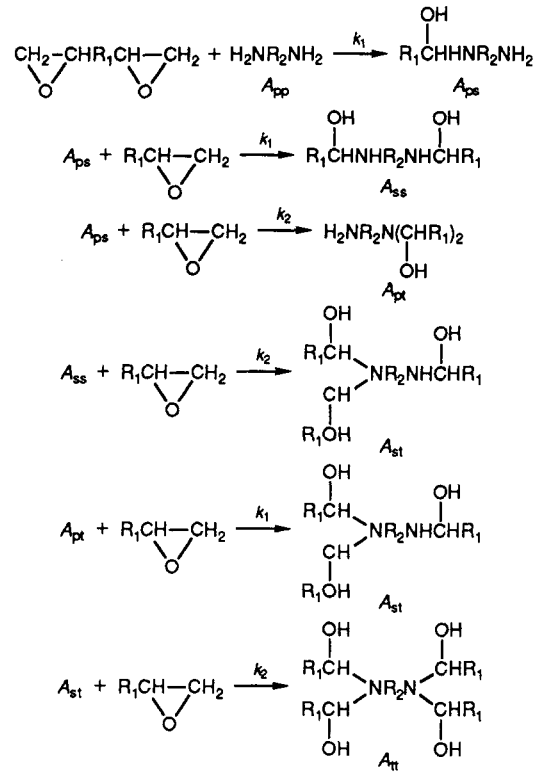
In order to assess if the observed excitation spectra can be useful in the quantitative characterization of epoxy cure, we carried out cure studies in an epoxy network composed of the stoichiometric mixture of a diepoxide (diglycidyl ether of Bisphenol A, DGEBA) and an aromatic diamine (diaminodiphenyl sulfone, DDS) including a small amount of DAA reactive label. Corrected excitation spectra of the model cure products as well as a function of various cure products composition were simulated based on UV–vis absorption spectra and fluorescence quantum yields, in order to assess the instrumental factors on excitation spectra. Next, they were compared with the experimentally obtained excitation spectra of the model cure species and of the curing epoxy. Last, the experimental excitation spectra were analyzed to correlate with cure time and to estimate the composition of cure products as a function of cure time. The latter was compared with the results obtained by the deconvolution of UV–visible absorption spectra.[1]

Experimental Section

Synthesis of Model Cure Products. Model cure products were made by reacting *p,p'*-diaminoazobenzene (DAA) with a large excess of monoepoxide, phenyl glycidyl ether (PGE) at 150 °C under nitrogen either for 50 or 120 min. The mixtures of the reaction products were separated by using an analytical, reversed-phase HPLC system (Varian 5000 LC). A reversed-phase column (micro Bondapak C_{18}) was employed using a programmable solvent gradient by varying amounts of tetrahydrofuran in water. An ultraviolet detector was set at 500 nm. The flow rate and the gradient of tetrahydrofuran were set at 1 mL/min and +1%/min, respectively. The elution profiles from HPLC showed five well-separated fractions. The reaction mixture after 50-min reaction gave greater amounts of the second and the third fractions while the fourth and the fifth fractions increased after 120 min of reaction. We assigned these five peaks as pp, ps, ss, st, and tt species of DAA with PGE, as illustrated in Scheme I. In this designation, p, s, and t refer to primary, secondary, and tertiary amino species of DAA, respectively. Model cure species were dried before spectroscopic characterization, following precipitation from water after evaporating THF in a nitrogen-purged hood.

Spectroscopic Analysis. Dried model compounds were characterized by UV–visible and fluorescence spectrophotometers. A small amount of model compounds (0.01% by weight) was mixed to an unreacted stoichiometric mixture of DGEBA–DDS epoxy. For cure studies, the same procedure described in a previous paper was used with a stoichiometric mixture of DGEBA–DDS containing a small amount (0.01% by weight) of DAA.[1] For the excitation spectra, the emission wavelength was set at 565 nm, which corresponds to the wavelength for maximum emission. The slit width was set at 2 and 5 nm for excitation and emission, respectively, using either Perkin-Elmer MPF-66 spectrofluorimeter with a Model 7500 data station or SLM 4800 fluorimeter. For UV–vis spectra, a diode array detection system (Perkin-Elmer Model 3840) was used with a Model 7500 data station.

Scheme I
Kinetic Scheme of Epoxy Cure Reactions



Results and Discussion

1. Simulated Excitation Spectra. The UV–vis absorption spectra of five model epoxy cure species (pp, ps, ss, st, tt) show their absorption maxima at 410, 420, 445, 460, and 470 nm, respectively. These are in agreement with a previous study where model compounds were separated by a different procedure.[4] From these absorption spectra, we can predict excitation spectra, since the excitation spectral intensity, I_e, can be expressed by eq 1 for a weakly absorbing solution of a fluorescent molecule[6] where $I_0(\lambda)$ is the intensity of the incident light, ϵ_A is the extinction coefficient of the absorbing molecule, l is the optical path length, ϕ_e is the fluorescence quantum yield, [c] is the concentration of a fluorescent molecule, and A is the absorbance obtained in UV–visible absorption spectra.

$$I_e = 2.3I_0(\lambda)\epsilon_A l\phi_e[c] = 2.3I_0(\lambda)A\phi_e \quad (1)$$

If $I_0(\lambda)$ is constant, I_e is proportional to the absorbance (A) and the fluorescence quantum yield (ϕ_e), according to eq 1. We can simulate excitation spectra that would represent corrected excitation spectra. Figure 1 illustrates the simulated spectra of model cure species by multiplying absorbance with the relative quantum yield of the model cure species. As can be seen in Figure 1, the simulated excitation spectra are very well separated

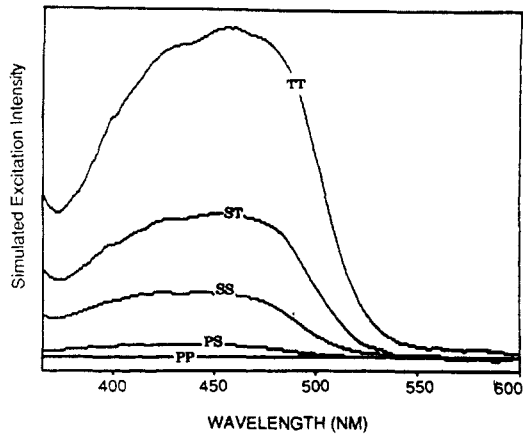


Figure 1. Simulated excitation spectra for various cure species of monoepoxide and *p,p'*-diaminoazobenzene (DAA) based on eq 1.

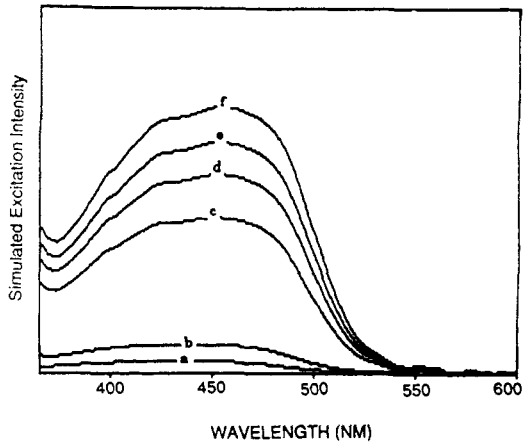


Figure 2. Simulated excitation spectra for various composition of cure species corresponding to Table I.

depending on the cure species, while their general shapes are similar to absorption spectra.

We also simulated excitation spectra as a function of different composition of cure products by using eq 2 where

$$I_e = A_{pp}I_{pp} + A_{ps}I_{ps} + A_{ss}I_{ss} + A_{st}I_{st} + A_{tt}I_{tt} \qquad (2)$$

A_{pp}, A_{ps}, A_{ss}, A_{st}, and A_{tt} are the respective fractions of each cure product and I_{pp}, I_{ps}, I_{ss}, I_{st}, and I_{tt} are the simulated excitation intensity ratios ($A\phi_e$) from model cure species. Figure 2 illustrates the case where each curve corresponds to a certain composition summarized in Table I. The compositions in Table I are the expected values as a function of increasing cure extent under the assumptions that two major reactions are between diepoxide and diamine and the reactivity ratio ($r = k_1/k_2$) is unity when k_1 and k_2 are the rate constants for the primary amine and the secondary amine to react with epoxide, respectively. These composition values were calculated on the basis of the solutions of several consecutive kinetic equations (eq 9) and reported in our previous study.[1] Such solutions are also used in the last section of this paper to estimate cure product composition from the excitation spectra. As can be seen in Figure 2, the excitation spectral intensity increases with the overall extent of cure and the concentration of tertiary amine species.

2. Experimental Excitation Spectra. Figure 3 shows experimentally obtained uncorrected excitation spectra corresponding to the model cure species. As expected, the spectral intensity increases as the cure species change from primary amines to tertiary amines. For the tertiary–tertiary (tt) species, which will be equivalent to the cross-linker in epoxy network, the excitation maximum occurs around 470 nm, which corresponds to the absorption maximum. The same excitation maximum is simulated in Figure 1, which corresponds to the corrected excitation spectra. However, the oserved spectra are distorted in comparison to the simulated excitation spectra, due to the instrumental factors such as wavelength dependency of the light source, monochromator efficiency, and detector sensitivity.

Table I
Predicted Composition of Cure Products in an Epoxy–Diamine Network as a Function of Overall Reaction Extent[a]

	ξ_A[b]	A_{pp}	A_{ps}	A_{ss+pt}	A_{st}	A_{tt}
a	0.16	0.50	0.38	0.106	0.0135	0.0005
b	0.29	0.25	0.41	0.261	0.071	0.0073
c	0.62	0.02	0.153	0.33	0.365	0.152
d	0.65	0.015	0.111	0.311	0.384	0.179
e	0.68	0.01	0.086	0.281	0.404	0.219
f	0.70	0.008	0.075	0.264	0.412	0.241

[a] Under the assumption that the secondary amine reacts at the same rate as the primary amine. [b] ξ_A is defined as the extent of amine reaction as follows: $\xi_A \equiv [A_{pp} + 2(A_{ss} + A_{pt}) + 3A_{st} + 4A_{tt}]$.

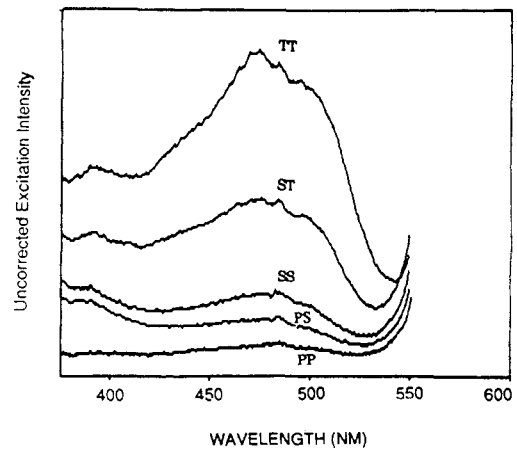


Figure 3. Uncorrected excitation spectra for various cure species of monoepoxide and *p,p'*-diaminoazobenzene (DAA) in uncured stoichiometric mixture of DGEBA–DDS.

Figure 4 shows experimentally obtained excitation spectra as a function of cure time at 160 °C in DGEBA–DDS epoxy containing a small amount of DAA label. The intensity at the excitation maximum around 470 nm increases with cure time up to 100 min. Beyond 100 min, the intensity decreases with concomitant decrease in UV–vis absorption. This trend, which has also been observed in fluorescence emission spectra, is believed to be due to the partial degradation of DAA label by the hydroxyl groups after reaction of DAA with epoxide. This degradation seems to occur when the diepoxide is either in excess or in equal stoichiometry but does not seem to occur when the diamine curing agent is in excess of the stoichiometry. In order to account for any degradation for the quantitative analysis of cure, the excitation or emission intensity has to be calibrated by the UV–visible absorption peak height at the absorption maximum or the absorption area.

As shown in Figure 5, the excitation intensity after calibration with UV–visible absorption spectra shows an S-shaped curve as a function of cure time. This curve is in fact very similar to the calibrated emission intensity profile reported earlier.[1] Basically, no excitation fluorescence is observed at the beginning of the cure. However, near gelation (about 35 min at 160 °C), a sharp

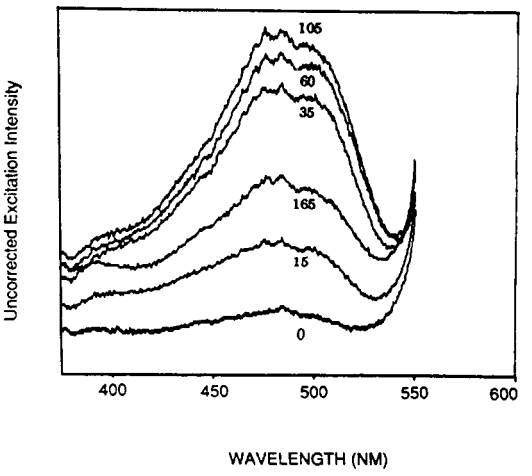


Figure 4. Uncorrected excitation spectra of *p,p'*-diaminoazobenzene (DAA) in a stoichiometric mixture of DGEBA–DDS as a function of cure time (in minutes) at 160 °C.

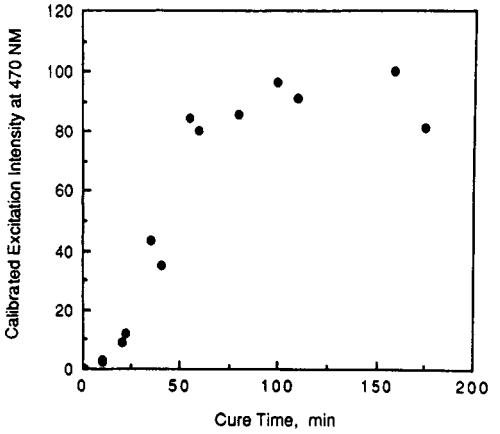


Figure 5. Calibrated excitation intensity at 470 nm as a function of cure time at 160 °C.

increase in excitation fluorescence is observed. Beyond 60 min, the excitation intensity levels off due to the vitrification of the epoxy matrix.

3. Analysis of Cure Composition by Excitation Spectra and Comparison with UV–Vis Results. We made attempts to correct excitation spectra obtained experimentally by using Rhodamine A as a photon counter, according to the procedure provided by both of the instrument manufacturers. While these procedures work well for an ultraviolet standard such as anthracene, the corrected spectra were not entirely satisfactory for our label, which absorbs in the visible range. The correction procedure apparently shifted the main excitation maximum to 515 nm. However, the ratios of the spectral intensity seem to be similar, as in uncorrected excitation spectra, both for the model cure species and in curing epoxy resins.

Therefore, we chose to use the calibrated excitation intensity of the uncorrected spectra to analyze the cure composition. Since we use the ratios of uncorrected excitation intensity of model cure species for quantitative analysis of the curing epoxy, the influences due to the instrumental factors are assumed to be canceled out.

In this analysis, we make the following additional assumptions, as explained in a previous paper:[1] (a) Epoxy homopolymerization is neglected. Only the two reactions between the primary amine and an epoxide with the rate constant k_1 and the secondary amine and an epoxide with the rate constant k_2 are considered. (b) The ratio of the rate constant ($r = k_2/k_1$) is assumed to

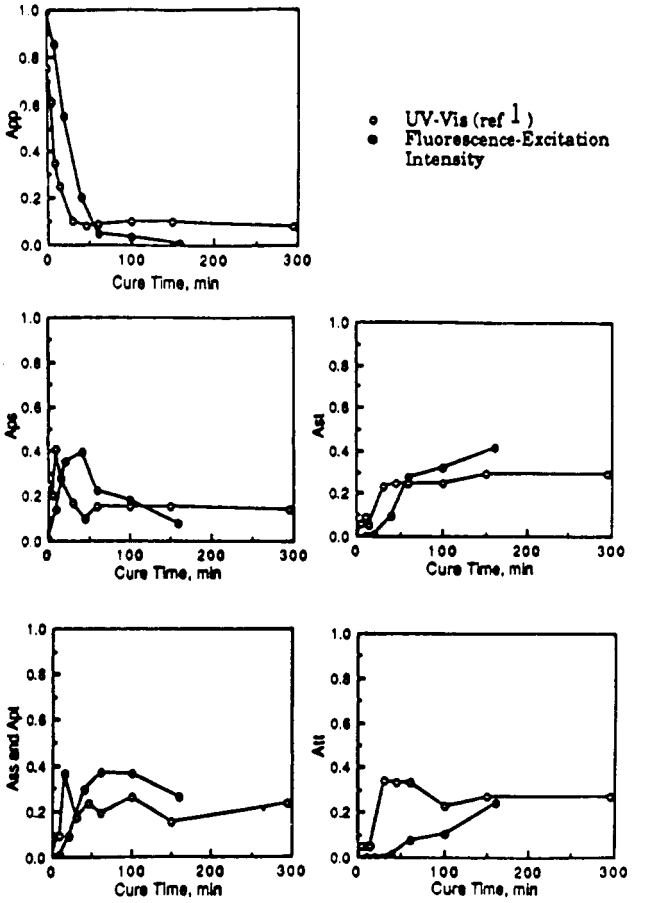


Figure 6. Comparison of cure species composition by UV–vis deconvolution[1] and by excitation intensity, in DGEBA–DDA epoxy matrix.

be unity. The solutions of the kinetic differential equations yield the following expressions for the composition of cure species[9] as a function of unreacted diamine (A_{pp}) and the rate constant ratio (r)

$$A_{ps} = 2p(A_{pp}^{q} - A_{pp}) \quad (3)$$

$$A_{ss} = p^2(-2A_{pp}^{q} + A_{pp} + A_{pp}^{r/2}) \quad (4)$$

$$A_{pt} = -2pA_{pp}^{q} + rpA_{pp} + 2A_{pp}^{1/2} \quad (5)$$

$$A_{st} = p^2[(r+2)A_{pp}^{q} - rA_{pp} - (2-r)A_{pp}^{1/2} - 2A_{pp}^{r/2} + (2-r)A_{pp}^{r/4}] \quad (6)$$

$$A_{tt} = p^2[-rA_{pp}^{q} + (r^2/4)A_{pp} + (r/p)A_{pp}^{1/2} + A_{pp}^{r/2} - (2-r)A_{pp}^{r/4} + (r/2-1)^2] \quad (7)$$

where $p = 1/(1 - r/2)$ and $q = (1 + r/2)/2$.

Since the excitation intensity is proportional to the fluorescence quantum yield and the concentration of each species, we can express the overall calibrated excitation intensity as the sum from all five cure species as shown in eq 8 where c is the experimental constant. The exci-

$$I_e = c(F_{pp}A_{pp} + F_{ps}A_{ps} + F_{ss}A_{ss} + F_{st}A_{st} + F_{tt}A_{tt}) \quad (8)$$

tation intensity ratios of $F_{pp}:F_{ps}:F_{ss}:F_{st}:F_{tt}$ were 1:9:45:100:230, as determined from the uncorrected excitation spectra of the model cure species. We ignored the contribution from the primary–tertiary species since its concentration is small when the rate constant ratio is unity.[1] By substituting the expressions of each cure species fraction (eq 3–7) into eq 8, we obtain eq 9, which

$$I_e = c[A_{pp} + 9p(A_{pp}^{q} - A_{pp}) + 45p^2(-2A_{pp}^{q} + A_{pp} + A_{pp}^{r/2}) + 100p^2[(r+2)A_{pp}^{q} - rA_{pp} - (2-r)A_{pp}^{1/2} - 2A_{pp}^{r/2} + (2-r)A_{pp}^{r/4}] + 230p^2[-rA_{pp}^{q} + (r^2/4)A_{pp} + (r/p)A_{pp}^{1/2} + A_{pp}^{r/2} - (2-r)A_{pp}^{r/4} + (r/2-1)^2]] \quad (9)$$

relates I_e in terms of A_{pp}. The constant c in eq 9 has been adjusted based on the excitation spectra of the model cure species. From eq 9, we can estimate the fraction of unreacted diamine label (A_{pp}) as a function of cure time from the corresponding excitation intensity after calibration. Once A_{pp} is estimated, the rest of the cure compositions can be calculated on the basis of the solutions of the kinetic equations (eq 3–7). Figure 6 illustrates the results by the analysis of the excitation spectra in comparison to the deconvolution results of UV–vis absorption spectra.[1] The results by excitation spectra show the trends of the formation and the disappearance of the cure species. In comparison to the results by the deconvolution of the UV–visible absorption spectra, the results by the excitation spectra show somewhat slower appearance/disappearance of the cure species. This may be due to the error in the deconvolution of overlapping peaks in absorption spectra. Therefore, the compositional analysis may be more reliable by fluorescence excitation spectra, especially for tertiary amine species.

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Registry No. DAA, 538-41-0; PGE, 122-60-1; (DAA)(DGEBA)(DDS) (copolymer), 123933-43-7.

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Studies of Model Urethane Reactions and Cure in Polyurethanes by UV Absorption and Fluorescence Spectroscopy

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ABSTRACT: UV absorption and fluorescence spectroscopy are used as main tools to characterize the kinetics of the reaction between 1,5-naphthyl diisocyanate (NDI) and 1-butanol and the cure in polyurethanes using NDI as a chemical sensor. When advantage is taken of the red shifts in UV absorption and of a large enhancement in fluorescence intensity as the reaction progresses, the kinetics of the reaction are analyzed. The reactivity of the first isocyanate group in NDI is found to be similar to that of the second isocyanate group, both in model reactions in dilute solution and in polyurethane matrix. The kinetic plots for the reaction of NDI with dihydroxy-terminated poly(tetramethylene oxide) (PTMO) were linear up to 70–80% conversion but displayed an upward curvature beyond such conversion, probably due to the weak catalytic effect of the urethane groups. Similar trends were observed from IR monitoring of methylenediphenylene diisocyanate (MDI) used for the polyurethane matrix with PTMO. The rate constants for MDI are found to be slightly greater than those for NDI, with similar activation energies for both diisocyanates. From these results, a calibration curve was established to correlate the extent of the reaction for MDI with that for NDI.

Introduction

During the last few years, we have developed a method to track cure products throughout the cure process, based on labeling with reactive compounds as molecular sensors to mimic one of the polymerizing reactants. These reactive labels were chosen to exhibit spectral changes in the region of UV–visible and fluorescence spectra where the polymerizing matrix has little absorption or emission. In this method, we take advantage of the magnified effects of the substituent changes in the para and para′ positions of conjugated aromatic reactive labels on the UV–visible and fluorescence spectra. We have applied this method to characterize the kinetics and mechanisms of the cure in epoxy networks,[1] the imidization process in polyimides,[2] and the acylation in polyamides.[3]

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