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Fluorescence and IR characterization of epoxy cured with aliphatic amines

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Abstract

Cure reactions of the stoichiometric mixtures of diglycidyl ether of bisphenol A (DGEBA) and two very low molecular weight aliphatic polyether diamines (PED) were studied by using fluorescence and mid- and near-IR spectroscopic techniques. As the cure proceeded, the primary amine groups in PED are converted to the secondary and the tertiary amines. Near-IR spectral analysis was used to calculate the concentration of the three amine groups as a function of cure time. The decrease in the fluorescence intensity of DGEBA at about 307 nm was observed due to more effective quenching of the tertiary amine groups in PED, in comparison to the primary and the secondary amine groups. A large decrease in fluorescence intensity at 75 and 95 °C cure was observed. The amount of all the amine species was estimated from NIR spectra to shed light on the cure kinetics of PPO (polypropylene oxide) in comparison with PEO (polyethylene oxide) epoxy, as well as to explain their fluorescence behavior.

The fluorescence intensity changes were correlated to the extent of epoxy reaction obtained by mid- and near-IR spectroscopy.

Keywords: Epoxy resin; Fluorescence spectroscopy; Diglycidyl ether

1. Introduction

Epoxy resins cured with the aliphatic amines are extensively used in the protective coating applications [1]. Since the degree of cure or the chemical conversion is related to the performance and properties of epoxy coatings, several methods have been used to monitor the cure reactions of epoxy/amine resins [1–4].

Among them, fluorescence techniques using molecular probes as extrinsic fluorophores have been applied to monitor the crosslinking process of epoxy/aromatic amines as well as epoxy/aliphatic amines. Non-reactive probes, such as excimer-forming probes [5], viscosity-sensitive probes [5,6], fluorescence quenching probes [7], polarity probes [8], free volume probes [9], and dual probe-label [10], as well as other probes [11,12] have been used to monitor the cure reactions.

A unique approach was reported by monitoring the intrinsic fluorescence spectral shifts in epoxy/aromatic diamine resins [13]. The fluorescence excitation and the emission spectra of diamino diphenyl sulfone (DDS) as a curing agent was used to study the cure reaction with bi-functional or tetra-functional epoxy [14]. As curing proceeds, a red shift of about 25 nm to longer wavelength due to the conversion from the primary amine to the tertiary amine in DDS was correlated to the extent of cure obtained by mid-IR spectroscopy.

The main objective of this research is to monitor the cure reactions by intrinsic emission fluorescence from diglycidyl ether of bisphenol A, DGEBA, cured with non-fluorescent, low molecular weight polyether diamines, PEDs. The chemical structures of DGEBA and PEDs are shown in Scheme 1. Aliphatic amines are well known quenchers of the aromatic hydrocarbons [15–21]. It has been reported that the quenching of the fluorescence of the aromatic hydrocarbons by aliphatic amines increase with electron-donating ability of the amine groups in the order of $R_3N > R_2NH > RNH_2$ [15,16]. Thus, we may expect a decrease in the fluorescence intensity as cure proceeds, since the primary amines become the secondary and the tertiary amine with cure as shown in Scheme 2 in the reactions (1) and (2), if the quenching effect is stronger than the intensity enhancing effect of increasing viscosity during cure. The third reaction, etherification is neglected in epoxy/aliphatic amine reactions [22,26]. Fluorescence results will be compared with IR

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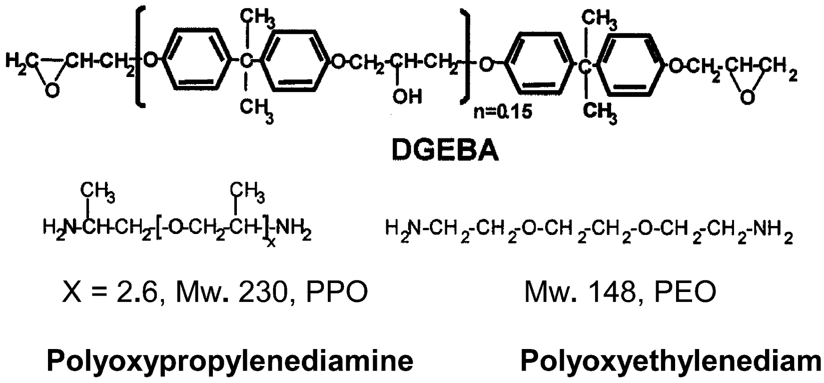


Scheme 1. Chemical structures of diglycidyl ether of bisphenol A (DGEBA) and polyetherdiamines (PED).

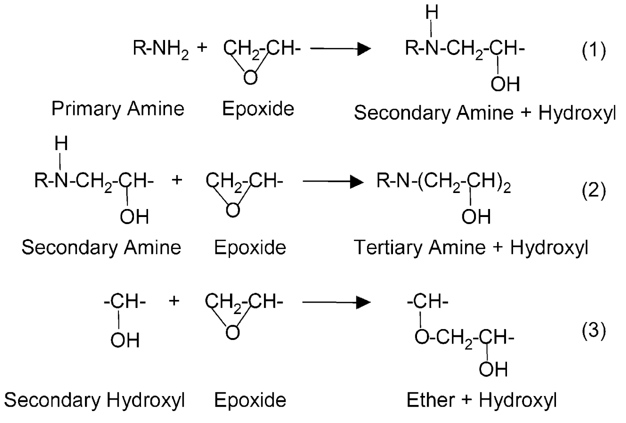
spectroscopy in the mid and near range. Mid-IR has been extensively used to monitor cure reactions of epoxy/amine resins. However, the mid-IR spectra in epoxy/amine systems is very complex, with the epoxy peak at 915 cm^{-1} difficult to follow as described by several authors [23–25]. Since near-IR spectra contains overtones and combinations [26] of N–H, C–H, and O–H groups, it has become useful in following epoxy/cure reactions. As the epoxy peak at 4530 cm^{-1} and the primary amine peak at 4940 cm^{-1} show up in the region between 4000 and 5100 cm^{-1}, satisfactory quantitative results have been obtained in this region in epoxy/aliphatic amine resins [10,26,27].

We used two different PEDs, a very low molecular weight (230) polyoxypropylene diamine (PPO) and a very low molecular weight (148) polyoxyethylene diamine (PEO). The effect of the pendant methyl groups in PPO which are absent in PEO was investigated by near-IR and fluorescence techniques for its effect on cure kinetics.

2. Experimental section

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA), Shell's Epon 828, was donated by Loctite Corporation. Huntsman Corporation supplied all polyether diamines (PEDs), including Jeffamine D-230, a polyoxypropylene diamine, PPO with a low molecular weight of 230 and Jeffamine EDR-148, a polyoxyethylene diamine (PEO) with a low molecular weight of 148.



Scheme 2. Epoxy/amine reactions.

2.2. Cure analysis

Stoichiometric mixtures of DGEBA/PEDs were mixed using a glass rod and magnetic stirring, followed by cure in a convection oven at 75 or 95 °C. At certain time intervals, samples were removed from the oven and spectra were taken at room temperature of 25 °C. Samples cured at room temperature were stored in a desiccator. A drop of mixture was placed between two NaCl disks for the mid-IR characterization, using a Nicolet Magna-IR 560 instrument with a 32 scan averaging at a resolution of 4 cm^{-1}. For the near-IR characterization using a Mattson 2050 Galaxy instrument, sample mixture was molten between two plain glass plates separated by 1/32-inch thick rubber spacer. To assure a fixed path length during curing process, the edge of the samples were covered with high strength epoxy paste. Fluorescence spectra of epoxy amine films were performed between two quartz plates ($1'' \times 1'' \times 0.125''$) using a 25 μm thick Mylar spacer on the edges, with a Perkin–Elmer LS 50B luminescence spectrometer with a scan speed of 120 nm/min and 5/5 nm slit with a 9% (open) neutral density filter. Fluorescence emission at about 390 nm of poly (ethylene terephthalate) film was used as a standard, in order to calibrate for lamp intensity fluctuations.

3. Results and discussion

3.1. Cure characterization

3.1.1. Mid-IR studies

The extent of epoxy reaction of DGEBA/PPO and DGEBA/PEO were determined by the peak areas of epoxy peak at 916 cm^{-1} in reference to the peak at 1183 cm^{-1}, which is due to C–H stretching of aromatic ring of DGEBA

[28]. Epoxy conversion is thus given by:

$$\alpha_{\mathrm{MIR}} = 1 - \frac{[(A_{916,t})(A_{1183,0})]}{[(A_{916,0})(A_{1183,t})]} \qquad (1)$$

where $A_{1183,0}$ and $A_{1183,t}$ refer to the areas of the reference peak at time zero and after certain time, t, respectively. $A_{916,0}$ and $A_{916,t}$ are the areas of epoxy peak for uncured resin and partially cured resin after a certain time, respectively.

The filled symbols in Fig. 1 show the extent of epoxide reaction of DGEBA/PPO as a function of cure time at RT, 75 and 95 °C. At 95 °C, which is 10 °C above its maximum T_g of 85 °C, the cure is fastest, reaching about 94% cure after 160 min, while the cure at 75 °C produces about 91% cure after 240 min. Room temperature cure only pushes the reaction to about 75% cure after 6 days.

The filled symbols in Fig. 2 show similar plots for epoxy cured with PEO, with the cure proceeding faster than those with PPO. At 95 °C which is close to its maximum T_g of 96 °C, the cure reaches about 96% after 60 min, while it reaches about 92% after 129 min when cured at 75 °C. At RT, the reaction only produces about 77% after 4 days. The cure at room temperature and at 75 °C for both resins are diffusion controlled since the resins are vitrified at these temperatures.

3.1.2. Near-IR studies

Fig. 3 shows near-IR spectra of DGEBA/PPO during cure at 95 °C. The peaks of the primary amine at 4935 cm^{-1} and the epoxy at 4528 cm^{-1} decrease during the curing process as shown in the cured spectra. There was no interference in the near-IR spectra due to ether groups as in the mid-IR spectra. Subtraction [29] was carried out to remove the small peak at 4564 cm^{-1} in the epoxy peak area. This unknown peak absorbance was also found by Peck et al. [30]. Similar treatment was carried out in DGEBA/PEO resins.

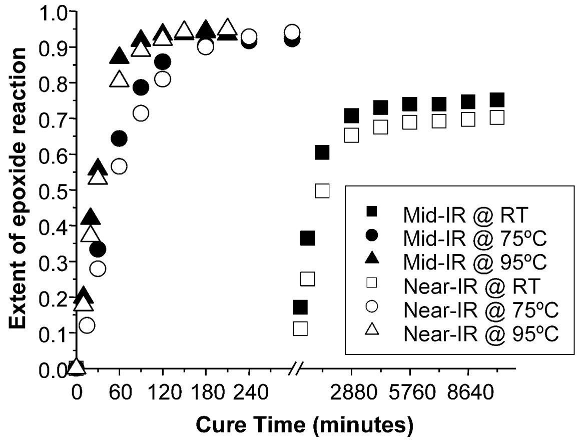


Fig. 1. Extent of epoxide reaction in DGEBA/PPO (LMW) followed by mid- and near-IR spectroscopy at 23 °C (RT), 75 and 95 °C.

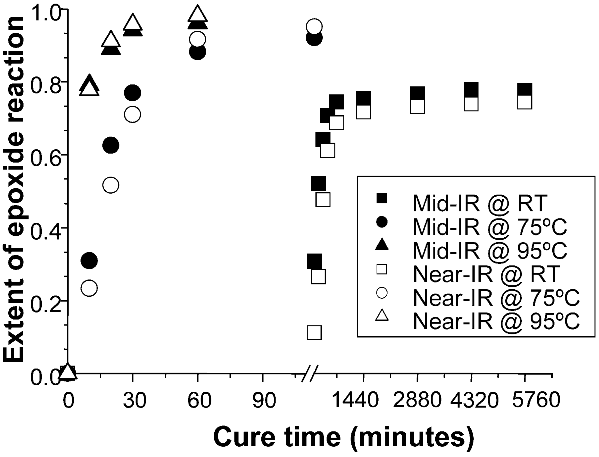


Fig. 2. Extent of epoxide reaction in DGEBA/PEO followed by mid- and near-IR spectroscopy at 23, 75 and 95 °C.

The extent of reaction by NIR, α_{NIR} is defined as follows:

$$\alpha_{\mathrm{NIR}} = 1 - \frac{A_t}{A_0} \qquad (2)$$

where A is the peak area of the absorbance at 4528 or 4935 cm^{-1}.

The open symbols in Fig. 1 show the extent of epoxy reaction by near-IR as a function of cure time for DGEBA/PPO resin at RT, 75 or 95 °C. The trends at each cure temperature are similar to the results obtained by mid-IR, while the extent of cure measured by near-IR is slightly smaller than that observed by mid-IR at low epoxide reaction. Similar trend was observed for DGEBA/PEO resin in Fig. 2. The faster reaction kinetics for DGEBA/PEO resin is better explained if we analyze the amount of all the amine species as described in Section 3.1.3.

3.1.3. Estimation of the secondary and the tertiary amines

The methods described by Paz-Abuin et al. [26] and Xu et al. [27] allowed the calculations of the concentration of the secondary and the tertiary amine. The concentration of

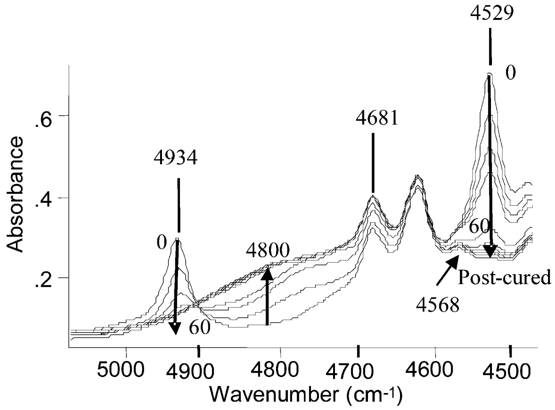


Fig. 3. Near-IR spectra of DGEBA/PPO (LMW) cured at 95 °C. Cure time: 0, 10, 20, 30, 60, 90, 120, 150, 180, 210 min and post-cured for 30 min at 180 °C from top to bottom.

the primary amine, A_p is determined by near-IR using the area of the peak at 4934 cm^{-1} in all of DGEBA/PED resins. The concentration of the secondary amine, A_s is determined by using the following Eq. (3) [26,27],

$$A_s = 2([A_p]_0 - [A_p]) - ([E]_0 - [E]) \tag{3}$$

where $[E]_0$ and $[E]$ corresponds to the epoxy concentration before cure and after a certain cure time, respectively. The concentration of the tertiary amine, A_t was calculated from Eq. (4).

$$A_t = [A_p]_0 - [A_p] - [\mathrm{A_s}] \tag{4}$$

Fig. 4(a) shows the concentration of the amine groups as a function of curing time for the DGEBA/PPO cured at 95 °C. Most of the primary amine disappears after 90 min. There is a maximum concentration of the secondary amine before 30 min, and the maximum concentration of the tertiary amine is obtained at 210 min.

Fig. 4(b) shows the concentration of amine groups in DGEBA/PEO cured at 95 °C. In this resin, the maximum concentration of the secondary amine was observed after only 10 min. The concentration of the tertiary amine is 1.99 mol/kg from the resin cured at 75 °C after 120 min, which is very close to the concentration of 2.12 mol/kg from the resin cured at 95 °C after 60 min. Thus, DGEBA/PEO shows faster conversion of amine group than those in DGEBA/PPO. There is more tertiary amine concentration in DGEBA/PEO than DGEBA/PPO throughout the overall reaction as a function of cure time.

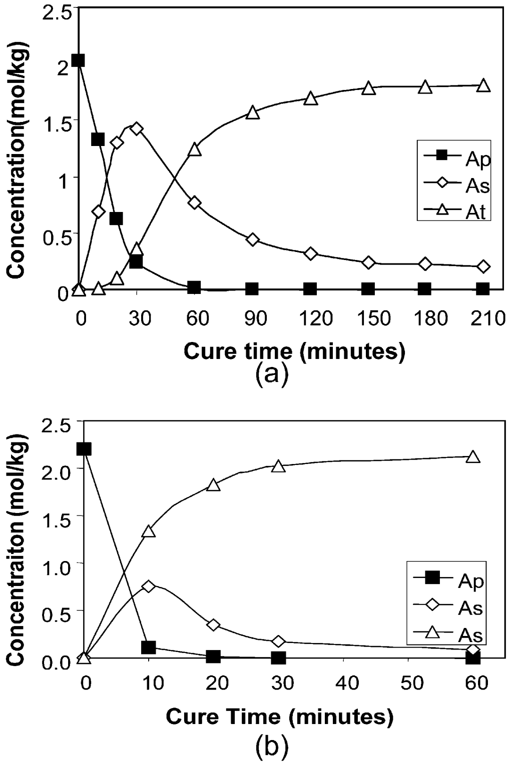


Fig. 4. Concentration of the three amine groups in (a) DGEBA/PPO (LMW) and (b) DGEBA/PEO, cured at 95 °C as a function of cure time. A_p, A_s, A_t represents the concentration of the primary amine, the secondary amine, and the tertiary amine, respectively.

3.1.4. Fluorescence studies

Fig. 5 shows the fluorescence emission spectra of DGEBA/PPO as a function of cure time at 95 °C. Upon curing, there are no changes in the wavelength position in the emission peak at 307 nm although the intensity decreases about 40% during this process as seen in the insert in Fig. 5. A similar trend was observed in DGEBA/PEO resin.

The aliphatic amine quenching of aromatic hydrocarbons is a well-known dynamic process [31,32] which follows the Stern–Volmer equation: Eq. (5).

$$\frac{I_0}{I_f} \approx \frac{\Phi_0}{\Phi_f} = 1 + k_d \tau_0 [Q] \tag{5}$$

where $[Q]$ is the concentration of the quencher, τ_0 the lifetime of the excited molecule, I_0 and Φ_0 are the intensity and the quantum yield of the fluorophore in the absence of quencher, respectively. I_f and Φ_f are the intensity and the quantum yield in the presence of the quencher. The efficiency of aliphatic amines to quench aromatic compounds has been measured in solutions. Vasilescu et al. [16] showed k_d of the secondary amine, diethylamine (DEA) and the tertiary amine, triethylamine (TEA) in fluoranthene–cyclohexane solutions to be 3.90–4.45 and 35.80, respectively, in comparison to the primary amines. Thus, the ability of amine groups to quench a fluorophore could be estimated as: 1:4:36 for the primary, the secondary and the tertiary amine, indicating that the tertiary amine is a dominant quencher. During cure, the viscosity increases, to infinity after gelation, generally enhancing fluorescence intensity of an unreacted probe molecule about three times from the uncured state [14]. Thus, the effect of the conversion to

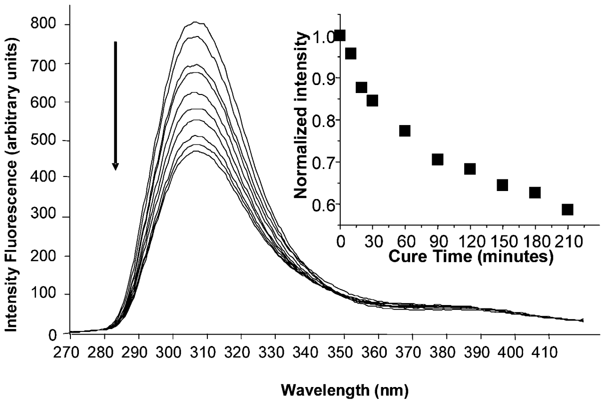


Fig. 5. Fluorescence emission spectra of DGEBA/PPO (LMW) cured at 95 °C. Cure time: 0, 10, 20, 30, 60, 120, 150, 180, 210 min from the top. The insert shows the intensity changes at 307 nm as a function of cure time.

the tertiary amine would be expected to outweigh the opposite effect of viscosity on the fluorescence intensity, except in the early stages of cure.

The Stern–Volmer equation relates the amount of amine to the fluorescence emission intensity. The order of the concentration of the amine is $[A_{\mathrm{p}}]_{\mathrm{PEO(LMW)}} > [A_{\mathrm{p}}]_{\mathrm{PPO(LMW)}}$, as indicated in Fig. 4. This trend was directly observed in the absorbance peak of the primary amine at about 4940 cm^{-1} in near-IR spectra [31].

The structure of the amine also influences the quencher efficiency. PPO has pendant methyl groups located on the carbon at the end of the chain and in the backbone of the repeating oxypropylene units. The pendant methyl groups located at the end of the PPO chain increase and reduce the concentration of the secondary and the tertiary amine, respectively [22], in comparison to PEO which does not have this pendant methyl group. The conversion of the tertiary amine in PEO is observed at the beginning of the reaction like classical aliphatic amine.

Wolfbeis and Urbano [32] extended the Stern–Volmer equation for two or three dynamic quenchers present in solution and showed that one fluorophore can interact with several dynamic quenchers simultaneously, thus contributing to the whole quenching process. In the uncured resins, the primary amines have an insignificant quenching effect. Upon cure, the secondary and the tertiary amines contribute to the overall quenching process.

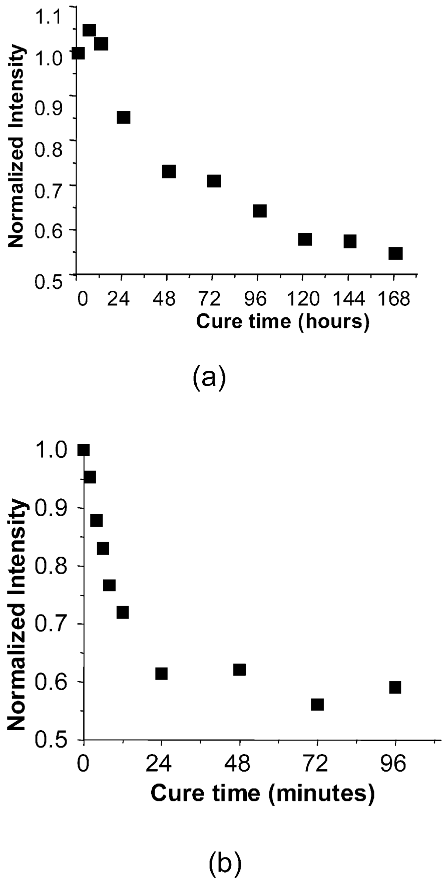


Fig. 6. The fluorescence intensity changes at 307 nm as a function of cure time in (a) DGEBA/PPO (LMW) and (b) DGEBA/PEO, when cured at 23 °C (RT).

Fig. 6(a) shows a behavior of the fluorescence intensity of DGEBA/PPO cured at RT. There is an initial increase in the intensity after 6 and 12 h, probably due to the intensity enhancement of the rising viscosity during slow cure at RT, but a decrease after 24 h. Fig. 6(b) shows the fluorescence spectra of DGEBA/PEO cured at RT, showing a constant decrease in the intensity during the first 2 h of cure. This can be explained by much greater concentration of the tertiary amine in PEO cured resin as supported by Fig. 4(b) obtained by near-IR results.

3.1.5. Correlation of cure reaction obtained by mid-IR, near-IR and fluorescence spectroscopy

While the fluorescence intensity of DGEBA at 307 nm decreased as cure proceeded extensively due to the formation of the secondary and the tertiary amines reacted with aliphatic diamines, it increased in the early stages of cure due to the viscosity effect on it. Due to these two opposing effects, quantitative analysis on cure characterization based on intrinsic fluorescence alone is not possible. Therefore, we only tried to correlate overall—observed fluorescence intensity reduction with the extent of cure analyzed by mid- and near-IR techniques.

Using extrinsic fluorescence of unreacted probe molecule may be possible in the neat epoxy resin, as long as its fluorescence spectra is far from that of DGEBA. But in pigmented resin coatings, such extrinsic fluorescence from probe molecule may be difficult to detect. Fig. 7(a) shows the correlation between the extent of epoxy reaction of DGEBA/PPO at 75 °C followed by mid- and near-IR and fluorescence spectroscopy. The correlation of the extent of conversion of DGEBA/PPO followed by mid-IR has a slightly steeper slope than that followed by near-IR when cured at 75 °C. The same tendency was found in the correlation plots of the DGEBA/PEO at cure temperatures of 95 °C, as shown in Fig. 7(b).

In the case of DGEBA/PPO (LMW) cured at RT as shown in Fig. 7(c), the correlation is less sensitive after 60% conversion when cured at RT which is between T_{g0} and $_{gel}T_{\mathrm{g}}$ around 42 °C [33]. When cured below $_{gel}T_{\mathrm{g}}$, the system vitrifies and resin changes from liquid to glass [32]. For this reason, when the resins are cured at RT, there is not enough secondary and tertiary amine because the reaction is practically stopped due to vitrification and the small amount of secondary and amine groups cannot diffuse and quench DGEBA effectively. Similar correlations were obtained for DGEBA/PEO samples [31].

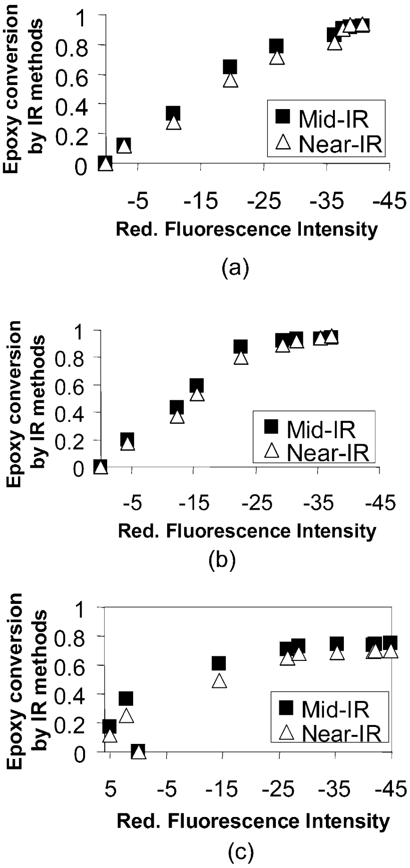


Fig. 7. Correlation plot of the reduced fluorescence intensity with epoxide conversion in DGEBA/PPO (LMW) at (a) 75 °C and (b) 95 °C.

4. Summary

Intrinsic fluorescence of DGEBA at about 307 nm decreased as cure reactions with aliphatic amine proceeded. Quenching of fluorescence emission of DGEBA is due to aliphatic amine, which is converted from the primary to the tertiary amine as a result of the curing process. Tertiary amine is a much more efficient quencher than the primary or the secondary amine, which results in a decrease in fluorescence intensity in spite of the rising viscosity with cure which tends to increase fluorescence intensity. DGEBA/PEO showed faster reduction of fluorescence intensity (about 40%) than DGEBA/PPO (LMW). The lack of pendant methyl groups next to the terminal amine groups contributed to early conversion of the tertiary amines in DGEBA/PEO as supported by near- and mid-IR results, thus leading to the faster reduction in fluorescence intensity. The correlation between the fluorescence intensity changes and the extent of epoxy obtained by mid- and near-IR spectroscopy is found to be useful.

Quenching of fluorescence of DGEBA is a promising technique for analyzing epoxy/aliphatic amine coatings in several environments. Cure reactions in moist environments, diffusion of ion chloride, and permeability of oxygen might be studied via quenching fluorescence of DGEBA. Near-IR shows advantages over mid-IR in cure of epoxy/amine resins and can be applied in several applications used in conjunction with fluorescence spectroscopy to study epoxy/aliphatic amines coatings.

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