Thermal Cure Monitoring of Phenolic Resole Resins Based on *In Situ* Fluorescence Technique

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ABSTRACT: The thermal curing reaction of two phenolic resole resins is monitored using the fluorescence technique. The intrinsic fluorescence can be used as an indicator for cure monitoring for the first resole. As the thermal curing proceeds, the intrinsic fluorescence intensity of the resole resin decreases and exhibits a few nanometers of redshift. The fluorescence intensity of the emission maxima is correlated with the conversion measured by differential scanning spectroscopy. A linear correlation is found at three different temperatures. The intrinsic fluorescence cannot always be used for monitoring the curing process of phenolic resole resins. Thus, three intramolecular charge transfer compounds and two organic donor–π-acceptor salts are selected and applied for the cure monitoring of the second phenolic resole resin. As the curing reaction proceeds, the fluorescence emission spectra of the probes exhibit a blue spectral shift and the intensity changes because of environmental changes. An intensity ratio method is applied in which the ratios of the low- to high-intensity changes in the emission bands are used to determine the degree of the curing process. There is a smooth correlation between the intensity ratio method and the degree of cure. The method enables one to follow the changes in the polymer structure at low and intermediate degrees of the curing process (below 70%) and obtain comparable results from different types of probes during the same curing process. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1773–1780, 2002

Key words: thermal cure; phenolic resole resins; *in situ* fluorescence

INTRODUCTION

Phenol-formaldehyde polymers are among the first known thermosetting materials used in electronic and composite applications.[1] Resoles are obtained by the alkaline reaction of phenols and aldehydes, the latter being used in excess. Resoles, which are low molecular weight polymers, are transformed into 3-dimensional, crosslinked, insoluble, and infusible high molecular weight network polymers by the application of heat and a slightly acidic solution.[2] Heat curing is the most important crosslinking process for resoles. Curing of phenolic resins involves methylene bridge formation, and quinone methides are intermediates in the heat curing of resoles.[3] Ether formation is a significant crosslinking reaction in acidic or neutral media, particularly at lower temperatures. This is due to the protonation of the alcohol groups by phenolic protons or by protons from added acids.[2] The products resulting from acid curing are well established.[4] The formation of dihydroxydibenzyl ether is considered the product

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under neutral or weak acidic conditions and temperatures up to 130°C.[5] Methylol groups react at the ortho and para phenolic hydrogen to give diphenylmethane units in rapid curing in acidic media.[6] Phenolic resins were modified by a reaction with drying oils to incorporate some flexibility into the otherwise very rigid structure. It is apparent that high molecular weight phenolic resins have extremely complex structures. The degree of the phenolic resin cure is one of the most important variables affecting the performance of a resin in composites. The curing of phenolic resins was monitored using several methods such as differential scanning calorimetry[7–10] (DSC), thermogravimetric analysis[7] (TGA), dynamic mechanical analysis[11] (DMA), and FTIR spectroscopy.[7,12]

Fluorescence spectroscopy has gained considerable interest as a tool for monitoring the curing of polymers because of its high sensitivity, selectivity, and nondestructive characteristics.[13–16] Fluorescence probes are widely used in chemistry for monitoring the specific properties of a medium in which they are incorporated. Generally probes have relatively low dipole moments in the ground state and large dipole moments in the excited state that re due to considerable intramolecular charge separation. The emission maxima of these molecules shift to longer wavelengths as the polarity of the solvent increases because the stabilization of the dipolar excited state is larger in polar solvents. In a solvent of low viscosity the mobility of the solvent molecules compared to the lifetime of the emitting species is such that emission occurs from a fully relaxed state. In a highly viscous medium in which the mobility of the molecules or molecular fragments is strongly decreased the situation is fundamentally changed and the reorientation of the medium cannot be completed within the lifetime of the excited state. The emission takes place from a partially relaxed medium at wavelengths shorter than those observed when the medium is fully relaxed.[17]

An important application of fluorescence probes in polymer chemistry is the monitoring of a polymerization process. Changes in the fluorescence of many probes accompanying polymerization are related to changes in the microviscosity and local polarity of the media.[18–23] Interactions between the probe molecules and their surroundings are known to affect the energy difference between the ground and excited states.[24] As the polymerization progresses, monomer units are immobilized by linking them together in a polymeric network. The response of the probes upon immobilization of molecular fragments in the network and polarity changes of the media will be a blueshift in the fluorescence emission.[18,23,25] If the stabilization that a certain polymeric network achieves during the probe's excited state lifetime is constant for series of probes, the wavelength shift is proportional to the probe's sensitivity for solvent polarity. When such a probe is incorporated in a polymerizing medium, its fluorescence changes with the conversion of monomers into a polymer. Probes, whose fluorescence intensities increase upon the polymerization[26–28] or during other rigidification processes such as physical aging,[29] and probes whose emission wavelengths shift during polymerization process[30] are well known.

As a phenolic resin cures, its refractive index increases and its dipolar mobility decreases; as a result, the dye molecules fluoresce from progressively less relaxed states.[31] Therefore, one of the significant features of some fluorescent dyes is that they display a fluorescence wavelength shift as the resin cures. The shift itself cannot be used as an indicator of the progress of polymerization because the fluorescence spectrum of most of the probes is broad. Thus, it is difficult to measure the spectral shift precisely by measurement of just the difference of the emission wavelength. In the phenolic resole resins a redshift was observed in some probes after 70% of the curing, which makes it impossible to use the emission wavelength as an indicator of the curing. This behavior is not typical for flexible molecules, which show intramolecular charge transfer.[25] For most probes and polymers the intensity of the fluorescence cannot be directly used as an indicator of the polymerization progress.[15]

Recently Neckers et al.[21,25] reported the use of fluorescent probes for monitoring the curing process using an intensity ratio method. In previous reports[15,16] we applied a low- to high-intensity change (LHIC) method, which can be used to obtain comparable results from different types of probes and polymers. This article presents the results of a recent study in which the intrinsic fluorescence intensity of a resole was used for monitoring curing processes and the intensity ratio method was applied for five fluorescent probes in order to test its suitability for an evaluation of the curing of a resole resin. Remote sensing was achieved by using fiber-optic cables to transmit optical signals to and from a polymerization system in real time.

EXPERIMENTAL

Two phenolic resole resins were obtained from Bakelite AG. The two-component phenolic resin system (Phenolharz M1-0100-WD) consists of a water-based phenolic resole (85.47 wt %) and a solid neutral catalyst (14.53 wt %). The three-component phenolic resin system (Rütaphen PL-2501) consists of a water-based phenolic resole (92.17 wt %), a modifier (0.92 wt %), and a liquid acid catalyst (6.91 wt %). The two phenolic resins were developed for filament winding and can be used for oilfield pipe and equipment, ventilation ducts, electrical conduit, and paper machine rolls. Excitation of the Phenolharz M1-0100-WD near 320 nm produced a strong fluorescence emission peak near 420 nm from the phenolic species. The intensity of this peak was used for monitoring the curing processes. The samples of the Phenolharz M1-0100-WD were prepared by dissolving the solid acid catalyst in the phenolic resin for 15–20 min at room temperature. The mixtures were sandwiched (0.05 mg) between two glass plates, and the thickness of the mixtures was controlled by double-coated tape (92 μm). The *in situ* cure monitoring profile of the studied resin was obtained by isothermal curing of the Phenolharz M1-0100-WD at the recommended temperatures of 80, 90, and 100°C.

After a selection process, three intramolecular charge transfer and two organic donor–π-acceptor salts[25] were chosen for the cure monitoring of the Rütaphen PL-2501. The structures of the chosen probes and the abbreviations used in this article are shown in Figure 1. 7-(Dimethylamino)-4-(trifluoromethyl)coumarin (CO152), 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (4HP), 2-[4-(dimethylamino)styryl]-1-methylquinolinium iodide (DASQEI), and 2-[4-(dimethylamino)-styryl]-1-ethylpyridinium iodide were purchased from Aldrich. 1-Anilinonaphthalene-8-sulfonic acid was purchased from Sigma. All the probes were spectroscopic grade and used as received without further purification. The samples for Rütaphen PL-2501 were prepared by doping the fluorescence probes into the phenolic resin (0.25×10^{-3} mol dm^{-3}) and then mixing with the modifier for 2 min. Finally liquid acid catalyst was added to the premixture and mixed for 5 min. The *in situ* cure monitoring profile of the resin under study was obtained by curing an approximate 2-mm layer of the mixture at 80 and 90°C.

The steady-state fluorescence emission spectra of the samples during the curing processes were obtained via a Spex Fluorolog 3 spectrofluorometer. Remote measurements were carried out using a fiber-optic cable attached to the excitation and emission monochromators. The excitation light was focused into an optical fiber, which carried the light to the measurement site. The measurement site included a sample fixed in a sample holder inside an oven. The fluorescence emitted by the sample upon irradiation with the excitation beam was picked up by the optical fibers. A model 821 DSC calorimeter (Mettler) was used to observe the overall curing process and to determine the curing degree of the phenolic resins at different temperatures. The measurements were

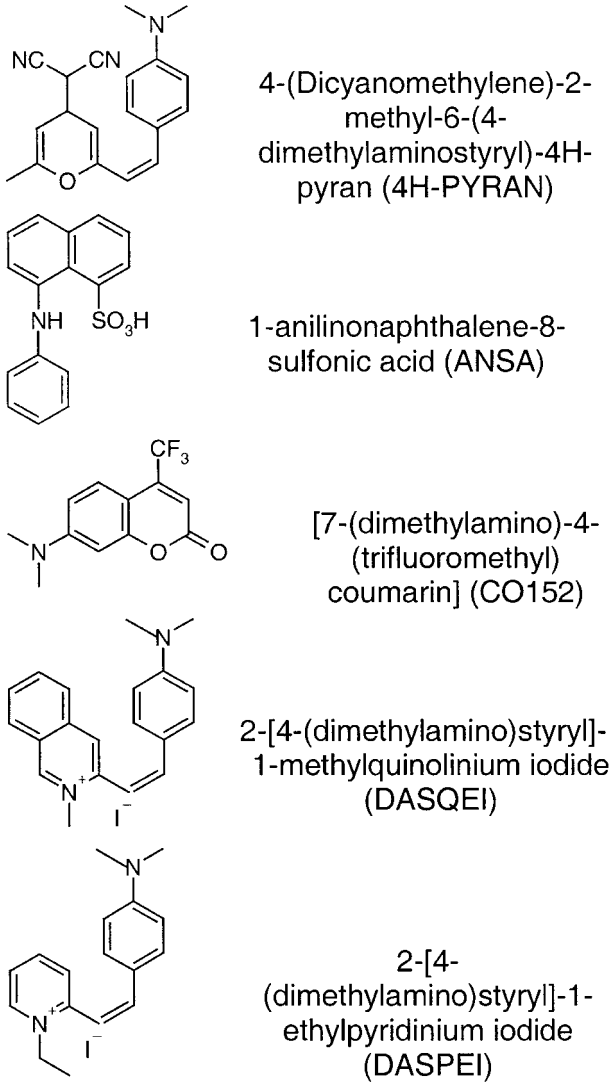

Figure 1 The chemical structures and abbreviations of the five probes that were used for monitoring the curing process of the phenolic resole resin Rütaphen PL-2501.

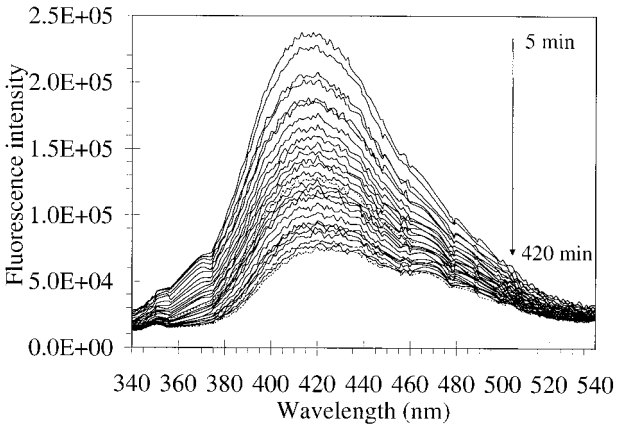

Figure 2 The fluorescence emission spectra of the phenolic resole resin Phenolharz M1-0100-WD during the curing process at 80°C. The arrow shows the order of the spectra during the curing process.

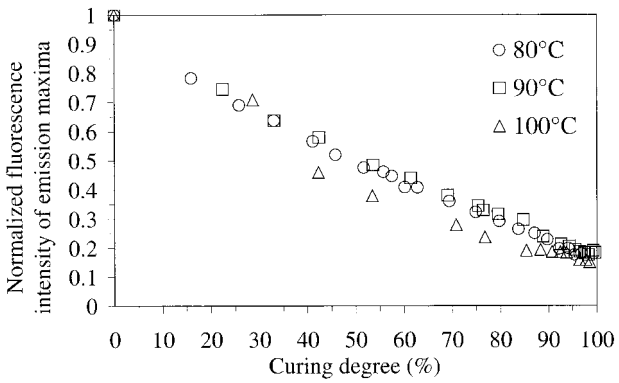

Figure 3 The normalized fluorescence intensity of the emission maxima and the degree of curing percentage at 80, 90, and 100°C as a function of the curing time for Phenolharz M1-0100-WD.

done in isothermal mode in sealed high-pressure pans.

RESULTS AND DISCUSSION

Phenolharz M1-0100-WD

Excitation at 320 nm produced a strong fluorescence emission peak near 420 nm from the phenolic species. Figure 2 shows the fluorescence emission spectra during curing at 80°C. The arrow indicates the evolution of the spectra during the curing process. The curing was monitored by measuring the quenching of the broad intrinsic fluorescence emission band. The fluorescence emission exhibits a few nanometers of redshift upon the curing process. The redshifting might be due to a decrease in polarity, which accompanies curing. The normalized (R/R_0) intensities of the emission maxima and the curing degree measured by DSC at 80, 90, and 100°C are presented as a function of the curing time in Figure 3. A comparison of these curves demonstrates that the intensity changes of the intrinsic fluorescence of the emission maxima can be directly correlated to the degree of curing percentage. A linear correlation between the normalized intrinsic fluorescence intensity of the emission maxima and the degree of curing percentages measured by DSC at 80, 90, and 100°C are shown in Figure 4.

Rütaphen PL-2501

The curing of Rütaphen PL-2501 was monitored by measuring the broad fluorescence emission bands of the selected probes as a function of the curing time at constant temperatures of 80 and 90°C. The probes produced fluorescence emission at different wavelengths and behaved differently depending on the temperature. The emission spectra of CO152 at 80°C and DASQEI at 90°C are shown in Figure 5. There were no pronounced changes in the shapes of the fluorescence spectra, indicating that there were no significant specific interactions among the five fluorescence probes with the Rütaphen PL-2501. The largest spectral shifts were observed for CO152. However, as mentioned above, the maximum emission shifts of the probes could not be used as the sole reliable indicators of the degree of cure.

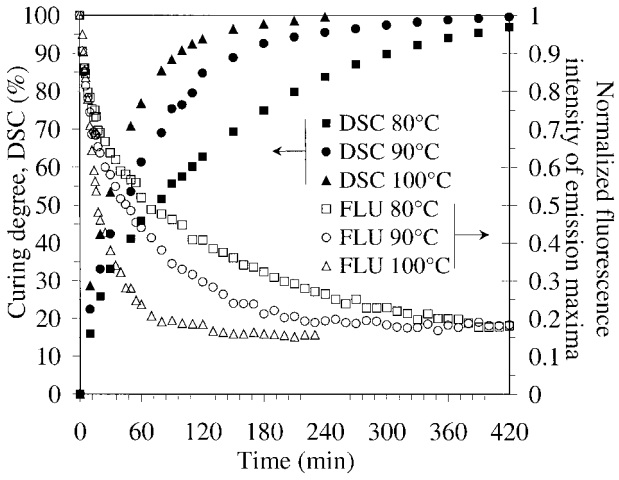

Figure 4 The linear correlation between the normalized fluorescence intensity of the emission maxima and the degree of curing percentage for the Phenolharz M1-0100-WD at 80, 90, and 100°C.

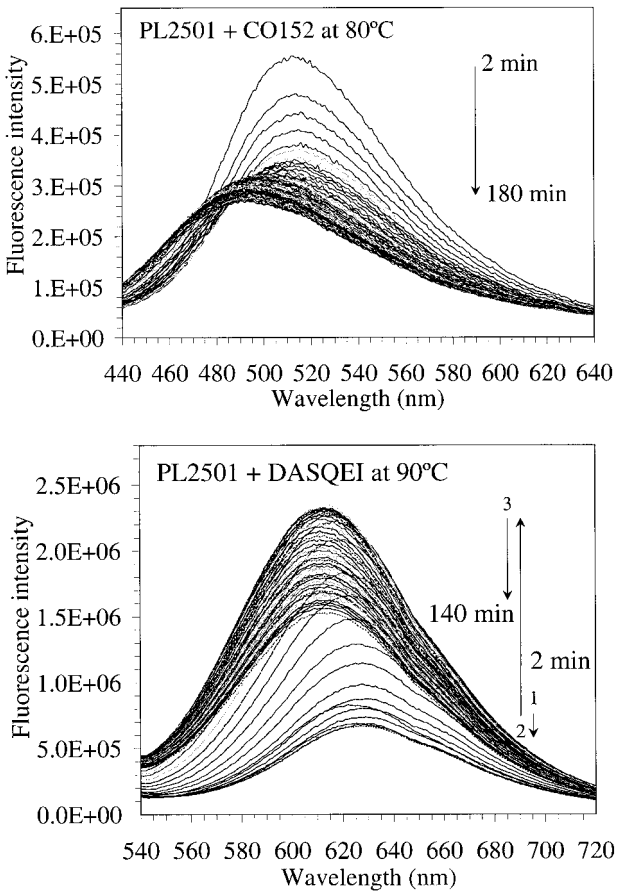

Figure 5 The fluorescence emission spectra of CO152 and DASQEI during the curing process of the Rütaphen PL-2501 at 80 and 90°C, respectively. The arrows show the order of the spectra during the curing process.

When the crosslinking of a polymer matrix increases, the intramolecular charge transfer of organic salt probes is expected to yield an increase in the fluorescence intensity.[21] The relative fluorescence intensities of the emission maxima of the tested probes and the degree of curing percentages determined by DSC as a function of the curing for Rütaphen PL-2501 are presented in Figure 6. A comparison of the probes demonstrates that the fluorescence intensity changes vary, depending on the probe–polymer system. Different probes in the same curing environments exhibit different behaviors, and thus the fluorescence intensity for a given probe cannot necessarily be directly correlated with the degree of curing percentage. All the probes showed a decrease in the emission intensities during a part of the curing process, which cannot be attributed to the changes in the viscosity or mobility as polymerization proceeds.[27] A decrease in the emission intensities as the crosslinking of a polymer matrix increases is not a generally observed phenomenon. However, this behavior is inconsistent with the work of Loutfy and Arnold[32] who showed that environmental factors resisting the internal molecular rotation of donor–acceptor dyes led to a decrease in the nonradiative decay and a consequent increase in the fluorescence yield.

External factors such as the temperature, optical alignment of the system, optical fiber position, excitation area, thickness of the sample, and input light intensity can contribute to the differences in the observed fluorescence intensities.[24] It is therefore necessary to have an internal reference with which the intensity can be normalized, irrespective of the external variables affecting the intensity fluctuations. Thus, an LHIC ratio[16] was used to determine the degree of the curing. This

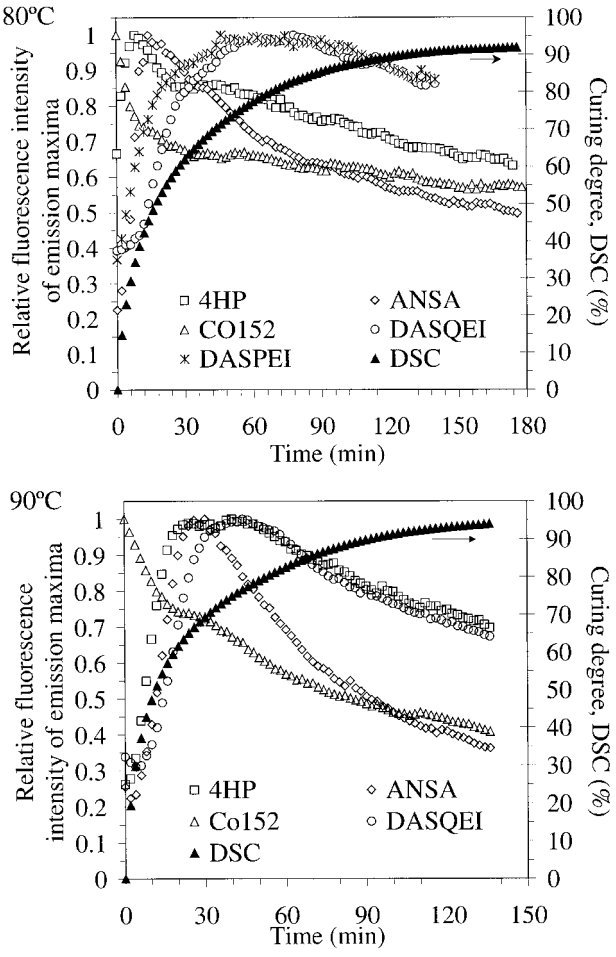

Figure 6 The relative fluorescence intensity of the emission maxima of the probes and the degree of curing percentage as a function of the curing time for the Rütaphen PL-2501 at 80 and 90°C.

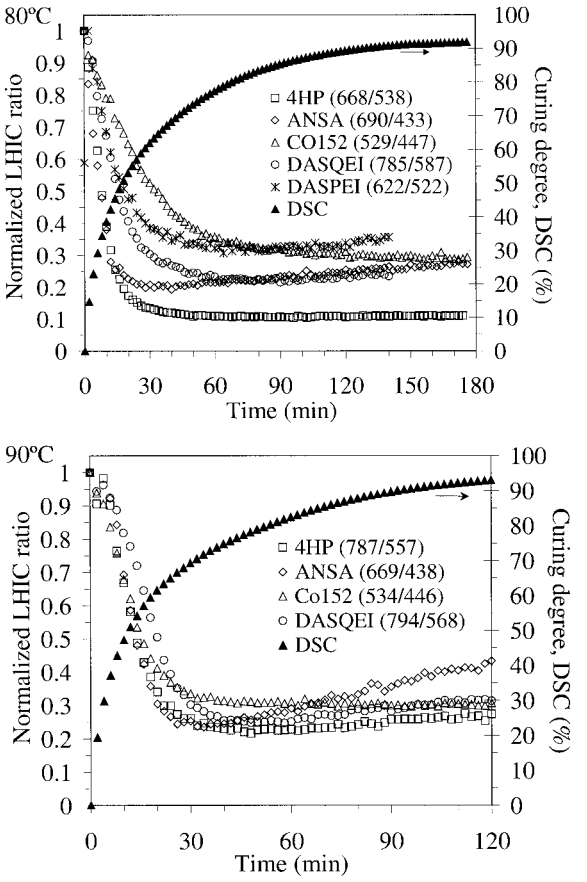

Figure 7 The normalized LHIC ratio of the probes and the degree of curing percentage as a function of the curing time for the Rütaphen PL-2501 at 80 and 90°C.

method is independent of the type of probe and the experimental conditions. LHIC curves are obtained by dividing the intensities at a certain wavelength in the longer wavelength region by the intensities of a certain wavelength at the shorter wavelength region at all moments of the curing time. Normalized LHIC ratios of the selected probes as a function of the curing time for the Rütaphen PL-2501 are shown in Figure 7. The wavelengths that were chosen for applying the LHIC ratio method for each probe at 80 and 90°C are given in Figure 7. It can be seen that the chosen wavelengths, which have the lowest and highest intensity changes, cover certain areas of the wavelengths for each probe. Thus, when the method is applied, two wavelength regions can be chosen for each of the probes. A comparison of these curves demonstrates that, by applying the LHIC ratio method, similar behavior can be observed for all the probes in the same environment. Normalized LHIC ratios of the selected probes indicated increases in some cases when around 70% of the curing was reached. This is due to the redshift of the emission maxima, which is not a general phenomenon in the curing process of polymers. Generally the probes exhibit a blueshift[21,25] upon polymerization, because the increase in the microviscosity of the matrix during polymerization makes it more difficult for the excited molecule to relax to its twisted charge transfer state.[21] The redshift might be due to the increase in the polarity of the media after around 70% of the curing process, which makes the formation of the charge transfer state possible.

Smooth correlations were achieved between normalized LHIC ratios and the degree of curing percentages measured by DSC (Fig. 8). The results show that the LHIC ratio method provides a general method for monitoring and calibrating the curing of the phenolic polymers. For the Rütaphen

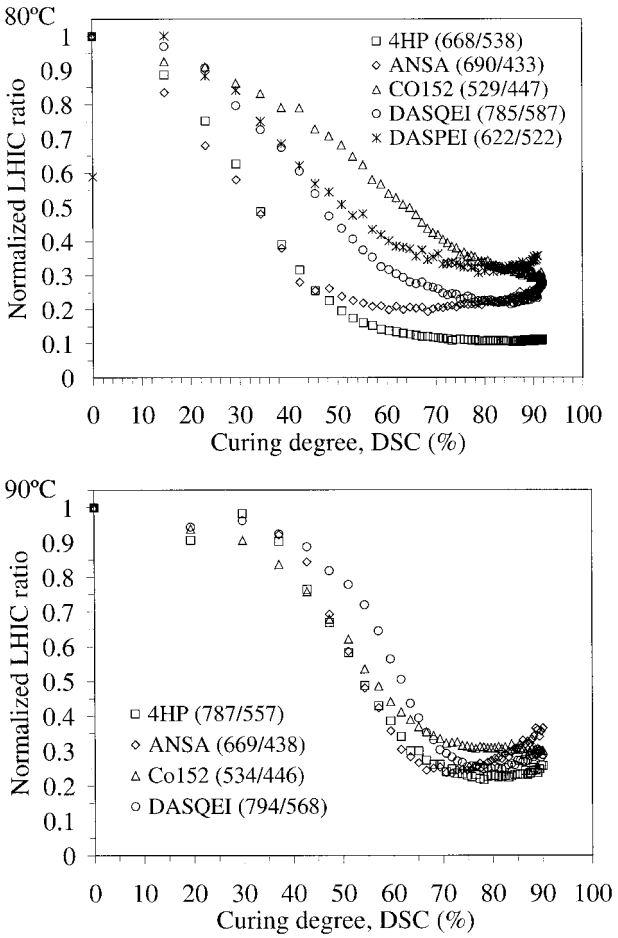

Figure 8 The correlation of the normalized LHIC ratios of the probes and the degree of curing percentage for the Rütaphen PL-2501 at 80 and 90°C.

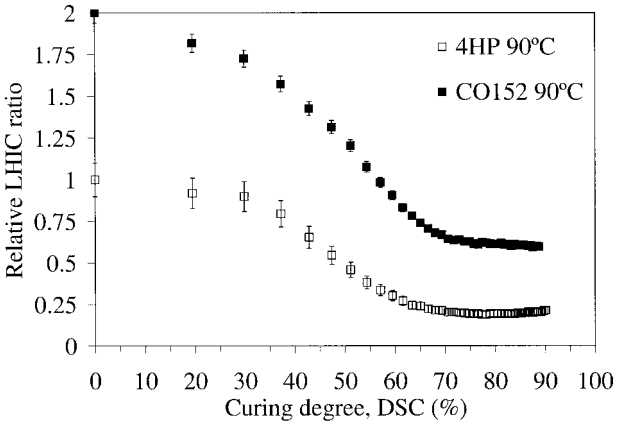

Figure 9 The reproducibility of the LHIC method for the Rütaphen PL-2501 at 90°C (3–7% error).

PL-2501 all probes are sensitive until around 70% of the curing process. The best correlation was obtained for CO152 and 4HP. During evaluation of the applicability of the LHIC ratio method with fluorescence probe technology, we found that the monitoring precision and reproducibility strongly depended on the magnitude and characteristics of the background fluorescence intensity, which can be due to the polymer or excitation light. It turned out that, for any monitoring to be possible, the fluorescence intensity of the probe incorporated into the polymer had to be higher than the background fluorescence at the monitored wavelengths. This can be controlled by the concentration of the probe and filtration of the excitation light. The reproducibility of the method for the phenolic resin Rütaphen PL-2501 was tested and the results are shown in Figure 9. There was 3–7% error for the LHIC ratio in our experiment for the Rütaphen PL-2501. If higher measurement precision is required, the concentration of the probe has to be increased proportionally. A part of this error can be due to a variation in the ratio of the starting materials. As the results show, the *in situ* curing profiles obtained with the LHIC method are precise enough for relative comparisons. Measurement with this method can be repeated and close results can be obtained; thus, the LHIC method is a reliable method for monitoring the curing process.

CONCLUSIONS

The results show that fluorescence spectroscopy is a quick, reliable, effective, and nondestructive measurement system for monitoring the curing process of phenolic resole resins. As the curing proceeds the emission maxima of the intrinsic fluorescence of the Phenolharz M1-0100-WD exhibited a few nanometers of redshift and quenching of intensity. A linear correlation between the fluorescence intensity of the emission maxima of Phenolharz M1-0100-WD at 80, 90, and 100°C and the curing degree were obtained. For phenolic resole resins without an emission band, such as the Rütaphen PL-2501, the degree of curing can be monitored with appropriate selection and concentration of the probe and the optimization of the monitoring parameters. A smooth correlation between the intensity ratios of the fluorescence intensities of the probes, which were selected from the wavelength ranges representing the lowest and highest intensity changes, and the curing degree of the Rütaphen PL-2501 was obtained. The fluorescence intensity ratio method eliminates the effect of intensity variations arising due to external factors, such as lamp intensity, optical alignment, probe location, excitation area, and temperature variation. The advantage of the LHIC ratio method is that it enables changes in the composition to be monitored throughout the curing process independent of the probe. Application of cure monitoring using the LHIC ratio method offers the possibility to precisely control the parameters of the curing process, makes *in situ* monitoring of the curing possible, and provides quantitative control of the quality and curability of the starting materials.

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