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Cure monitoring of epoxy resins by fluorescence quenching

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Summary

The effect of curing on the fluorescence intensity of 1,6-diphenyl-1,3,5-hexatriene (DPH) and 9,10-dimethylanthracene (DMA) was studied using two epoxide/amine systems. In the system diglycidyl ether of Bisphenol A (DGEBA)/1,3-diaminopropane the fluorescence intensity of DMA, I_f, increases with increasing conversion of epoxy groups; this is explained by means of a dynamic model of fluorescence quenching by dissolved molecular oxygen. Contrariwise, in the other system under study, DGEBA/poly(oxypropylene)diamine (Jeffamine ^{R} D-400), I_f of the DPH probe decreases, which is interpreted by using the model of static fluorescence quenching. Both effects are suggested for use in the cure monitoring of epoxy resins.

Introduction

The manufacture of polymer composites is accompanied by chemical and physical changes in the polymeric matrix. It is desirable that these changes should be adequately monitored and controlled during production. For this reason, nondestructive physical methods seem to be called for. Fluorescence techniques which monitor the change in the local viscosities of the system and are nondestructive by their nature, are particularly useful (1). For this purpose, measurements of fluorescence depolarization (2), excimer fluorescence (1,3), or fluorescence quenching (4) can be used, which are controlled by the diffusion of fluorescence molecules or of molecules of the quenching agent in the material. In addition, the method utilizing changes in the quantum yield of fluorescence of some probe molecules (the so called viscosity sensitive fluorescence probes) due to the hindering of internal rotations of chromophores accompanying the increase in the sample viscosity has been introduced by Louty (5) and Lévy (6). Changes in the quantum yield of fluorescence of reaction products of epoxide and diaminoazobenzene were also used (7).

This study deals with the effect of curing on the fluorescence intensity of fluorescence probes in two epoxide/amine systems. It is suggested to use the observed fluorescence intensity of the reaction mixture during curing.

Experimental

Epoxy resin: Diglycidyl ether of Bisphenol A (DGEBA) was purified by repeated recrystallization. DGEBA with epoxy equivalent weight 171 g/mol and functionality $f_n = 2$, had a weak

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emission band at 420 nm when excited at 340 and 375 nm. However, this emission was negligible at $\lambda > 435$ nm.

Amine hardeners: (i) 1,3-diaminopropane (DAP) analytical grade (Fluka) was used as received. The hardener had amino equivalent 19.0 g/mol H in amino groups, which gives $f_n = 3.90$. (ii) poly(oxypropylene)diamine - Jeffamine® D-400 (TEXACO) had an amino equivalent 114 g/mol H in amino groups, which gives $f_n = 3.85$.

Fluorescence probes: 1,6-diphenyl-1,3,5-hexatriene (DPH) and 9,10-dimethylanthracene (DMA)(Aldrich) were used as received These probes were dissolved in DGEBA by stirring at 323 K to a concentration of 1×10^{-5} mol/l.

Sample preparation: DGEBA with fluorescence probes was dissolved in Jeffamine® D 400 or DAP at 318 K, stirred for 5 minutes and then injected into reaction optical cells, which were closed up to avoid access of air. The reaction cell was made of a silicon rubber gasket sandwiched between two glass cover slides 0.2 mm thick. The initial molar ratio of amine hydrogens to epoxy groups was, $r_A = 1.1 (= 2 [NH_2] / [EPOXY])$.

Determination of epoxy groups: Near-infrared spectra were recorded with a Perkin-Elmer-Hitachi Spectrometer 340. The relative concentration of epoxy groups was calculated from the peak absorbance height at 2207 nm and compared with the peak absorbance height at 2138 nm taken as an internal standard (8).

Fluorescence intensity measurement: The fluorescence intensity was recorded with a fluorimeter of our own design. The light source was a quartz iodine lamp (150 W). The excitation wavelengths (375 nm for DPH and 405 for DMA) were selected by a grating monochromator (Jobin-Yvon H20 UV). The fluorescence intensity was recorded from the front surface illuminated reaction cell at 90° to the direction of the excitation beam and detected by a photomultiplier M12FQC 51 (Carl Zeiss, Jena). The excitation light was cut off by an edge filter (M. Griot GG 435).

Cure monitoring: The optical cells containing the measured epoxy/amine system were placed in a thermostated container with a preheated immersion liquid. The fluctuation of the reaction temperature was below ± 0.1 K. The sample was irradiated with the excitation light and the fluorescence intensity, I_f, was measured.

Time-resolved fluorescence measurements: Fluorescence lifetimes were determined from the intensity decays taken with an Edinburgh Instrument 299 T spectrofluorimeter.

Results and Discussion

a) System DGEBA/DAP: Fig.1 shows the dependences of relative changes in the fluorescence intensity, I_f, on the conversion of epoxy groups, ξ_E, for the probe DMA recorded during curing at 303, 308 and 313 K. After the initial plateau (c.5 min.), when the temperatures of bath and sample become equilibrated, I_f begins to increase monotonically with increasing conversion ξ_E, reaches its maximal values at $\xi_E > 0.6$ and remains virtually unchanged after that, due to the transition of the system into the glassy state, as discussed in greater detail below.

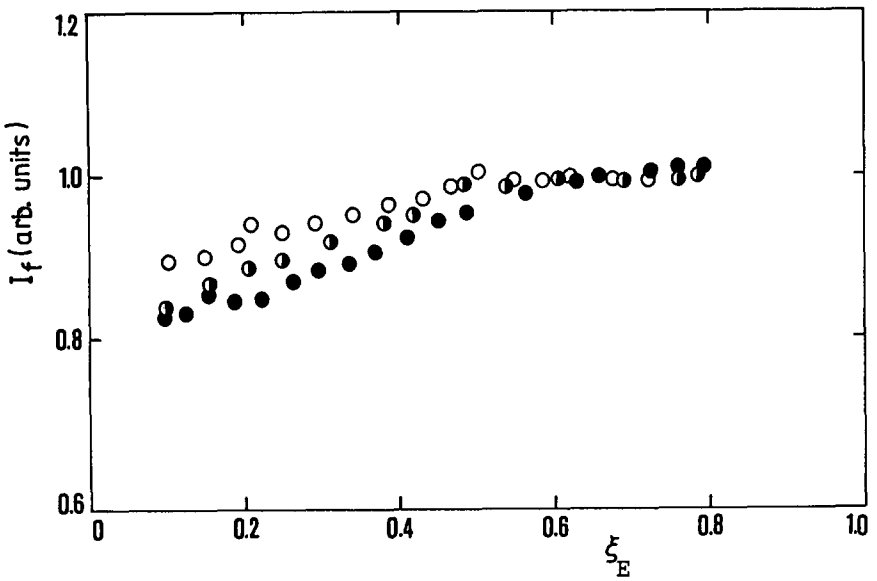

Fig.1 Dependence of the fluorescence intensity of the DMA probe on the conversion of epoxy groups ξ_E in the DGEBA/DAP system: reaction temperature $T_r = 303$ (o), 308 (◑) and 313 K (●).

The rise in I_f with ξ_E is typical of the dynamic quenching of fluorescence of probes with low-molecular weight quenching agents, controlled by translational diffusion (9). Experimental data can be adequately analyzed by using the Stern-Volmer relation (10). Under stationary conditions, we obtain

$$I_{f0}/I_f = 1 + k_Q[Q] , \qquad (1a)$$

where the rate constant

$$k_Q = 4\pi N_A \, p \, R_Q^3 \, (D\tau_{f0} + p\sqrt{D\tau_{f0}}) \qquad (1b)$$

and I_{f0} is the fluorescence intensity in the absence of the quenching agent, N_A is the Avogadro number, τ_{f0} is the mean lifetime of fluorescence in the absence of the quencher, p is the probability of nonradiative transition at the collision of the chromophore with the molecule of the quencher, R_Q is the interaction distance, D is the interdiffusion coefficient of chromophores and the quencher.

Two terms in brackets in relation (1b) express the dependence of I_f on D, and thus also on the local viscosity of the medium. The relative contribution of these terms depends on the magnitude of D. At $D\tau_{f0} \gg 1$ the first term is the decisive one, while at $D\tau_{f0} \ll 1$, usual for bulk polymers, the second term predominates ($\sqrt{D\tau_{f0}}$). For solid polymers and $k_Q(\xi_E)[Q] \ll 1$ (resulting from the fact that the changes in I_f are small on the whole), relation (1a) can be adjusted to

$$[I_f(1)/I_f(\xi_E)] - 1 = A(\sqrt{D(\xi_E)\tau_{f0}} - \sqrt{D(1)\tau_{f0}} \qquad (2)$$

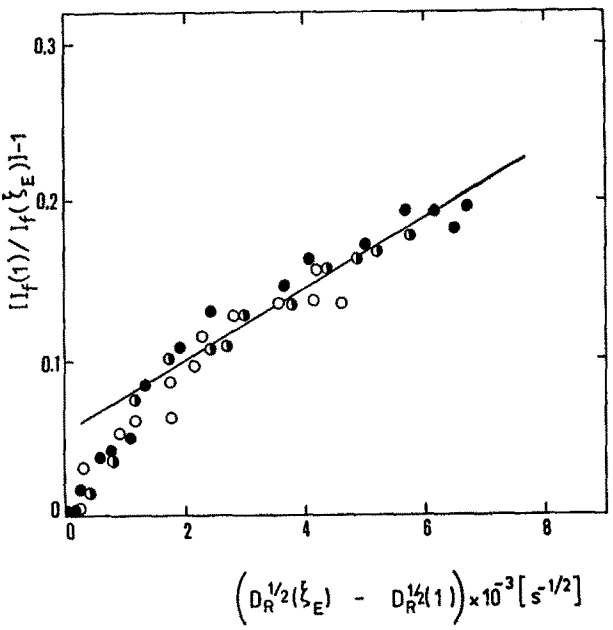

Fig.2. Dependence $[I_f(1)/I_f(\xi_E)]-1$ (data Fig.1) on $\sqrt{D_R(\xi_E)} - \sqrt{D_R(1)}$; T_r = 303(o), 308(◐) and 313 K (●)

where $A = 4\pi N_A p^2 R_Q$ = konst. independent of ξ_E. $I_f(\xi_E)$ therefore reflects changes in the translational diffusion coefficient D with ξ_E. Fig. 2 shows values $[I(1)/I(\xi_E)]-1$ taken from Fig.1 plotted as a function of the square root of the rotational diffusion coefficient D_R of the chromophore DMA probes measured during curing of the same reaction mixture. It can be seen in Figure 2 that at higher D_R values (lower conversion values) experimental points lie on a straight line. Deviation from such linear dependence can be seen at $\xi_E > 0.6$. where the glass transition temperature of the mixture, T_g, is comparable with, or higher than, the reaction temperature, T_r (cf. Table 1).

Table 1: Conversion values of epoxy groups ξ_E at which the glass transition temperature of the reaction mixture T_g reaches the reaction temperature of the mixture, T_r

T_r [K]	$\xi_{E,g}$
303	0.62
308	0.65
313	0.67

(a) T_g of the mixture was determined by DSC

In other words, in the rubberlike state of the mixture the relative changes of D and D_R are the same, differing only in the glassy state of the reaction mixture (D decreases more quickly with increasing ξ_E than D_R).

These experimental facts can be explained comparatively easily in terms of the free volume theory (11). In the rubberlike state of the polymer the molecular volume of both the quencher (we suppose that this is the dissolved O_2) and the fluorescence probes are smaller than the specific free volume of the polymer and therefore both diffusion processes (translational and rotational) are similarly affected by changes in the local viscosity of the medium during curing. The situation changes after transition into the glassy state, when the segmental mobility steeply decreases. Under these conditions basic differences between the rotational and translational diffusion of low-molecular weight compounds in macromolecular systems begin to be operative.

b) The DGEBA/Jeffamine D-400 system: The dependence of I_f of the DPH probe in the DGEBA/D-400 system on the conversion of epoxy groups ξ_E can be seen in Fig. 3. Unlike the DGEBA/DAP system, in which I_f was increasing with ξ_E, in this system the relative fluorescence intensity $I_f(\xi_E)/I_f(0)$ decreases monotonically during curing.

With respect to the discussion in section a), such drop in the intensity I_f cannot be due to the diffusion of the quenching agent. Moreover, as has been observed in the DGEBA/DAP system, the DPH probe shows a dynamic quenching effect with molecular

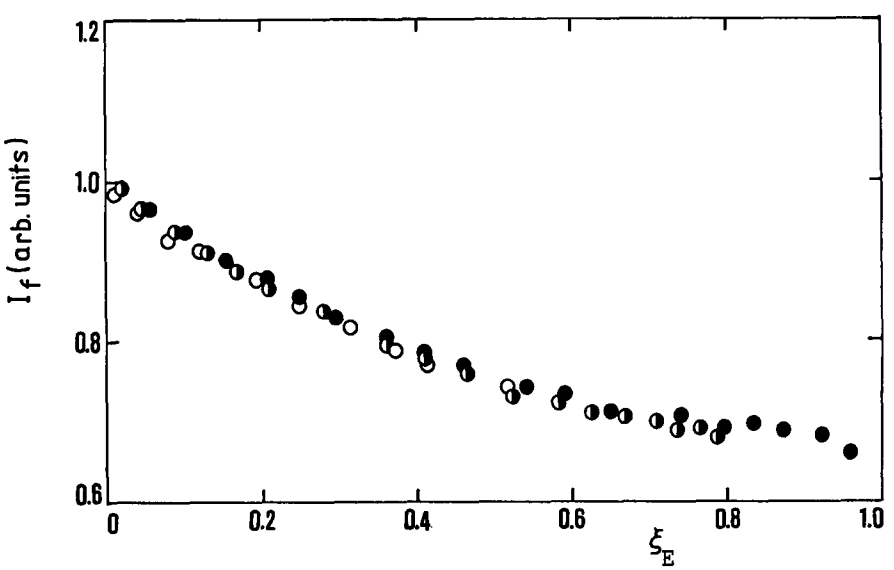

Fig.3. Dependence of the fluorescence intensity of the DPH probe on the conversion of epoxy groups ξ_E in the DGEBA/Jeffamine D-400 system; $T_r = 323$ (o), 343 (◑) and 363 K (●)

oxygen which is three times lower than that of DMA. As demonstrated by an analysis of experimental data, the observed changes in I_f can be explained and analyzed using a model of static quenching of the fluorescence, as suggested by Perrin (12). In this model the relative fluorescence intensity I_{f0}/I_f is an exponential function of the concentration of the quenching agent $[Q]$, i.e.

$$\ln(I_{f0}/I_f) = k_Q [Q] \quad , \tag{3}$$

where $k_Q = (4/3)\pi N_A R_O^3$, and R_O is the radius of the active sphere.

In the isothermal curing the intramolecular rate constants of nonradiative processes remain virtually unchanged, and hence R_O should be only slightly dependent on ξ_E. If we assume that the total quantities of the quenching agent in the sample do not vary during curing, then a change in the concentration $[Q]$ should be proportional to the change in density, ρ, of the cured mixture. Bearing in mind the known fact that in the rubberlike state and sufficiently far from the glass transition the density ρ of the reacting mixture is a linear function of conversion, $\rho = \rho_0(1 + \beta \xi_E)$ where ρ_0 is the density of the starting mixture and β is the coefficient of the conversion volume contraction, then by rearranging (3) we obtain

$$\ln(I_f(\xi_E)/I_f(0)) = -K \xi_E \tag{4}$$

where $K = (4/3)\pi N_A [Q_0] R_O^3 \beta$

In Fig.4, in which the dependence $\ln(I_f(\xi_E)/I_f(0))$ on ξ_E has been plotted, we can see a good fit between experimental data and the predicted model of static quenching (relation (4)) in the initial stage of the curing process, i.e. experimental points for $\xi_E < 0.4$ lie on a straight line.

Applicability of the model of static quenching can be further supported by measurement of the fluorescence lifetime τ_f. In the dynamic quenching model $\tau_f \approx I_f$, while for the static one τ_f is independent of I_f. For the system under study, τ_f was found to be 4.7 ± 0.1 ns at the beginning of the curing process ($\xi_E < 0.1$), and τ_f was found to be 5.4 ± 0.1 ns at $\xi_E = 0.95$, which means only a small change in the fluorescence lifetime, even in an opposite direction.

By analogy with poly(vinylmethyl ether), where a static quenching of the fluorescence of anthracene due to oxygen atoms of ether groups has been observed, the same groups of Jeffamine D-400 could be the quencher in the system under study (13). Accepting this hypothesis, the concentration $[Q]$ can be determined as 7.0 mol/l. From the slope K read off from the straight part in Fig.4 and using relation (4), we can estimate the magnitude of R_O, if β is known. Using $\beta = 0.057$, calculated from the densities of the starting components of the reaction mixture $\rho_0 = 1.075$ g/cm^3 and the density of the cured material $\rho(\xi_E = 1) = 1.136$ g/cm^3, we obtain $R_O = 0.85$ nm, i.e. a value which is in a very good agreement with the published data for characteristic distances of the electron-electron exchange interaction ($R_O \approx 1$ nm) (9).

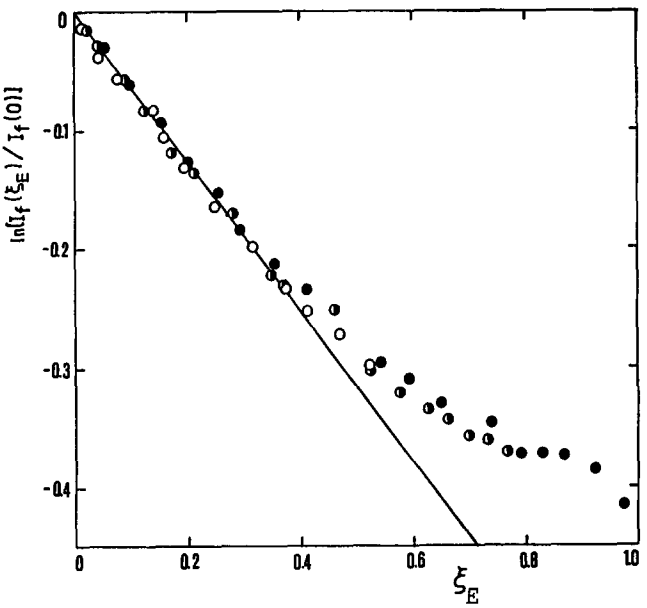

Fig.4. Dependence of $\ln[I_f(\xi_E)/I_f(0)]$ on ξ_E (data Fig.3); T_r = 323(o), 343 (●), and 363 K (●).

Deviations from the linear dependence observed in Fig.4 for $\xi_E > 0.4$ could be due to the nonlinear dependence of the density of the mixture on ξ_E for these conversions, for which however independent experimental findings are missing.

Conclusion

It can be said, in conclusion, that the observed changes in I_f can be used in the cure monitoring of epoxy resins. In the the DGEBA/1,3-diaminopropane/DNA system the rise in the intensity I_f reflects changes in the local viscosity of the mixture. The measurement can also reflect small changes in the reaction temperature (by 5 K in this case). In the DGEBA/poly(oxypropylene)diamine/DPH system the drop in the intensity I_f is proportional to the change in the density of the cured material. It is of interest that also small density changes produce comparatively large changes in the fluorescence intensity.

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