Continuous UV Cure Monitoring and Dielectric Properties of Photocross-linked Epoxy–Acrylate Resins*

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SYNOPSIS

The changes in viscosity of epoxy–acrylate resins during the photocross-linking process have been monitored continuously. The curing curves show change of shape and a distinct peak especially at high intensities. The intensity dependence of gel time follows a superlinear power law of the type $t_p \alpha I^{-1.6}$ rather than the $\frac{1}{2}$ power law. The dielectric relaxation studies on these photocross-linked films having different compositions of epoxy and n-butyl methacrylate reveal a particular composition range in which various dielectric parameters pass through critical values. These various findings have been explained on the basis of phase separation taking place during the UV curing process but at a submicron level leading to a very small domain size. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

On-line cure monitoring of thermosets has been receiving considerable attention in recent years and its importance has been realized in the areas of advanced composites, structural adhesives, and industrial coatings.[1-3] It has become an integral part of testing new formulations and specifying optimum curing conditions for the product. Although a few attempts have been made in the past to study the photocuring process of polymers using different techniques such as infrared spectroscopy,[4] dilatometry,[5] gel fraction measurements,[6] nuclear magnetic resonance,[7] and other physical methods,[8] these have been carried out on "postpolymerization" or sometimes on an "interrupted photoexposure" basis. Such studies can give information only on a broad basis about the general curing behavior and, in fact, in some cases, even this may be erroneous since thermal cycling (as in DSC, DMA, and relaxation spectroscopy) immediately after photo-irradiation can

cause further cross-linking in the process of characterization itself. Further, no information on viscosity and gelation—which are directly related to molecular weight—is available on a continuous basis from these techniques. We have carried out for the first time continuous measurements of viscosity during the photopolymerization and cross-linking of epoxy–acrylate resins using ultraviolet (UV) irradiation and a vibrating probe rheometer. Epoxy–acrylate resins have been chosen for these studies because they constitute important photocross-linkable systems, finding a variety of applications in optical fiber coatings, topcoats for metal containers, UV curing inks, as well as printed circuit boards.[9,10] Our studies revealed the complex nature of the photocuring process: its dependence on radiation intensity and composition of the formulation. These studies coupled with dielectric relaxation spectroscopy have given indications to various steps involved in the curing process and these results are presented in this article.

EXPERIMENTAL

Actocryl-400, an aromatic epoxy-diacrylate resin based on diglycidyl ether of bisphenol A (DGEBA)

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supplied by Ancomer, Manchester, UK, was used as the main matrix. This polymer can be polymerized/cross-linked by photo as well as by thermal initiation in combination with other low molecular weight acrylates.[11] In the present case, n-butyl methacrylate (nBA) was used as a comonomer and/or cross-linker and it was added in various proportions of 10–80% by weight. The photoinitiator was dimethoxyphenylacetophenone (Irgacure 651, Ciba Geigy) and its concentration was 5% by weight of the total resin matrix. The initiator was first dissolved in nBA to which the Actocryl resin was added and mixed under low illumination. This was poured into a specially designed transparent cell used for viscosity measurements under photoirradiation. The experimental setup is schematically represented in Figure 1. The cell consists of thin microscopic glass slides stuck together with a spacer glass slide (1.0 mm) using araldite and stored overnight to ensure complete cross-linking. Lack of leakage and absence of dissolution of the adhesive was tested with a number of solvents. The cell containing the photocurable formulation was clamped firmly from the sides to the base plate, and the probe, flattened SS wire (0.6 mm thick), was allowed to vibrate in it freely. This assembly was illuminated from all sides using front reflecting mirrors and aluminum foil. Particular precaution was taken to ensure that no shadow region due to the probe was present. The irradiation source was a 200 W air-cooled medium-pressure mercury lamp (Osram, Germany) provided

with a water filter, neutral density filter, etc., mounted on an optical bench. The area of illumination was more than twice the size of the cell. Details regarding viscosity/gel time measurement using a Strathclyde rheometer and dielectric monitoring of the cured films were same as reported elsewhere.[12–16]

RESULTS AND DISCUSSION

The viscosity of the curing formulation (derived from the amplitude of oscillation of the probe) was monitored at intervals of 5 s immediately after the start of continuous exposure. Figure 2 shows the typical curing curves obtained at six different intensities for a composition containing an Actocryl: nBA ratio of 60 : 40 with 5% initiator. Curves 1–6 correspond to an increase of intensity from 1 to 1.5, 2, 3, 4, and 5 times the original, respectively. There are many interesting features to be noted from these measurements: (a) There is an induction period for the start of polymerization that depends on intensity; (b) as the intensity is increased, the shape of the curing curve changes from smooth to a stepped one; (c) there is an appearance of a peak just after the rapid rise in viscosity, especially at high intensity; and (d) there seems to be a threshold value of intensity only above which the curing proceeds to completion or the highest value of viscosity is attained.
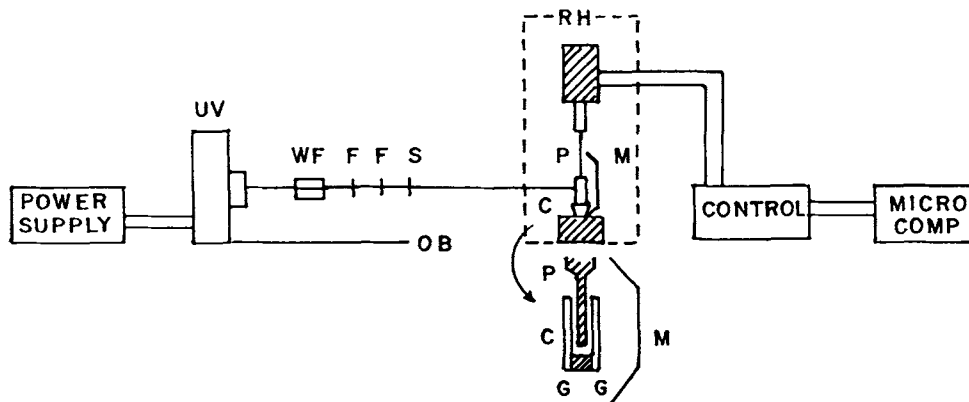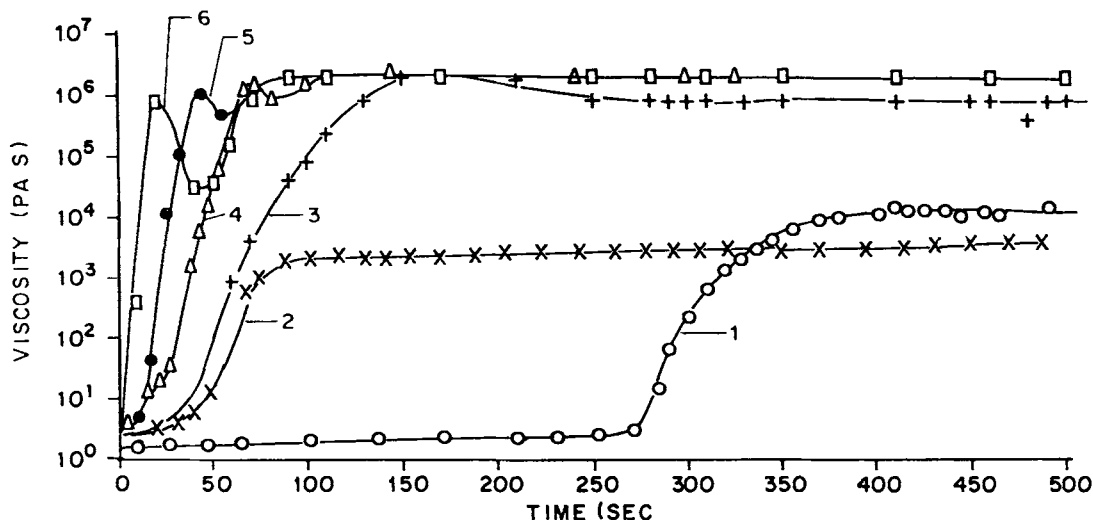
CONTINUOUS UV CURE MONITORING

Figure 1   Experimental setup for continuous UV cure monitoring showing (UV) radiation source, (WF) water filter, (F) neutral density filer, (S) slit/shutter, (OB) optical bench, (RH) strathclyde rheometer, (P) probe, (C) cell, (M) front reflecting mirror, and details of the cells: P, 0.6 mm thick 3 mm/wide; G–G distance, 1.0 mm.

UV CURE MONITORING A400-nBA,5% INITIATOR

Figure 2 Curing curves for the epoxy–acrylate resin (60/40), 5% initiator at various intensities. Curves 1–6 correspond to increase of the relative intensity of 1.

To understand these various results, one has to first look into the mechanism and kinetics of the photopolymerization/cross-linking process. The various steps involved in photocuring are the (i) absorption of light by the photoinitiator, (ii) generation of free radicals, (iii) initiation of polymerization and oligomer formation, and (iv) formation of the cross-linked product. Some authors have described the kinetics of these processes as follows[17–19]: Typically, the photoinitiation rate (R_P) is given as

$$R_P = \phi R_{absorp} = 2.303\phi\epsilon[S]I_0 10^{-\epsilon l}$$

$$\simeq 2.303\phi\epsilon[S]I_0 \quad \text{for small thicknesses} \quad (1)$$

where ϕ is the quantum yield for the initiator; ϵ, the absorption coefficient at the incident wavelength; $[S]$, its concentration, I_0, the incident light intensity; and l, the thickness. However, it is known that absorbed oxygen inhibits the process of initiation of polymerization by scavenging the generated free radicals. If $[H]$ is the inhibitor concentration, then we have

$$[H] = [H_0] - R_i t \quad (2)$$

Thus, the onset of polymerization would take place at $[H] \simeq 0$ or from eq. (1) and (2):

$$t_{onset} = [H_0]/\{2.303\phi\epsilon[S]I_0\} \quad (3)$$

Now considering that the usual free-radical polymerization kinetics operates after the initiation step, one can derive the rate of polymerization as
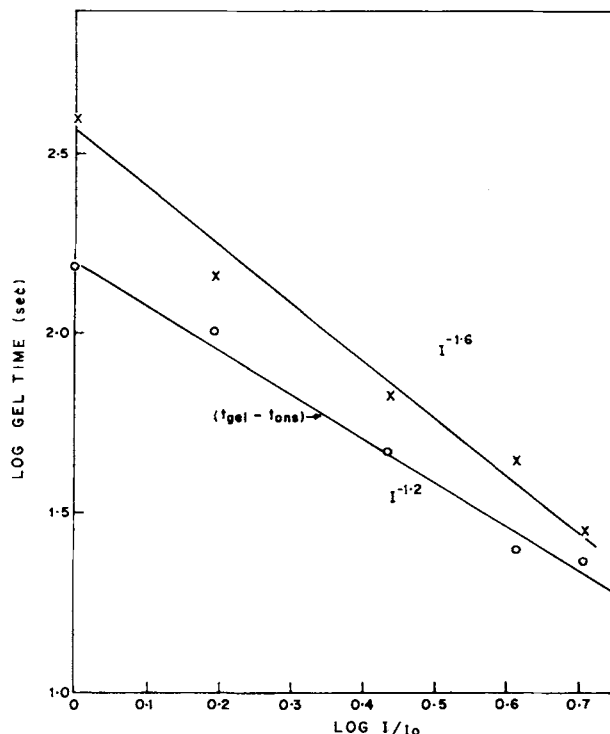

Figure 3 Intensity variation of gel time and same after correction for onset time.
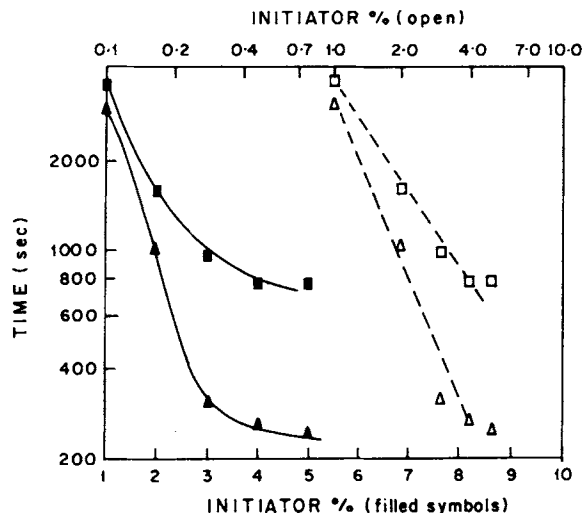
INITIATOR % (open)

Figure 4 Dependence of gel time on initiator concentration in thermally cured epoxy-acrylate resin (60/40).

$$-\frac{dM}{dt} = (k_p^2/k_t)^{1/2}R_i^{1/2}[M]$$

$$= (k_p^2/k_t)^{1/2}\{2.303\phi_s\epsilon[S]I_0\}^{1/2}M \quad (4)$$

where the various symbols have their usual meaning. Equation (4) on integration yields

$$\log(M/M) = (k_p^2/k_t)^{1/2}\{2.303\phi_s\epsilon SI_0\}^{1/2}t \quad (5)$$

This brief discussion of the photopolymerization process suggests that the time to attain an upper limiting value of viscosity should be dependent on intensity as

$$t_{\text{peak}} = A[I_0]^{-1/2} \quad (6)$$

It has been suggested that the above should be corrected for the onset time in order to observe a $\frac{1}{2}$ power dependence.[20] To confirm the same, a plot of $\log t_{\text{gel}}$ vs. $\log I$ as well as $\log(t_{\text{gel}} - t_{\text{onset}})$ vs. $\log I$ was made as shown in Figure 3. In both cases, the graph shows much stronger intensity dependence, $t_{\text{peak}} \propto I^{1.2}$ or $I^{-1.6}$, than expected from the above equations. This suggests that the process of photocuring in the present case does not follow a simple mechanism and/or the kinetics given above. It may be of interest to mention here that even in the case of thermal curing of epoxy-acrylates we have observed that gel time depends on the initiator concentration (peroxide for thermal case) as I^n, where $n = 1.6$–1.8 rather than 0.5 (see Fig. 4 and Ref. 15). These observations suggest that the curing of epoxy-acrylate involves additional processes such as radical trapping, phase separation, or spinoidal decompo-
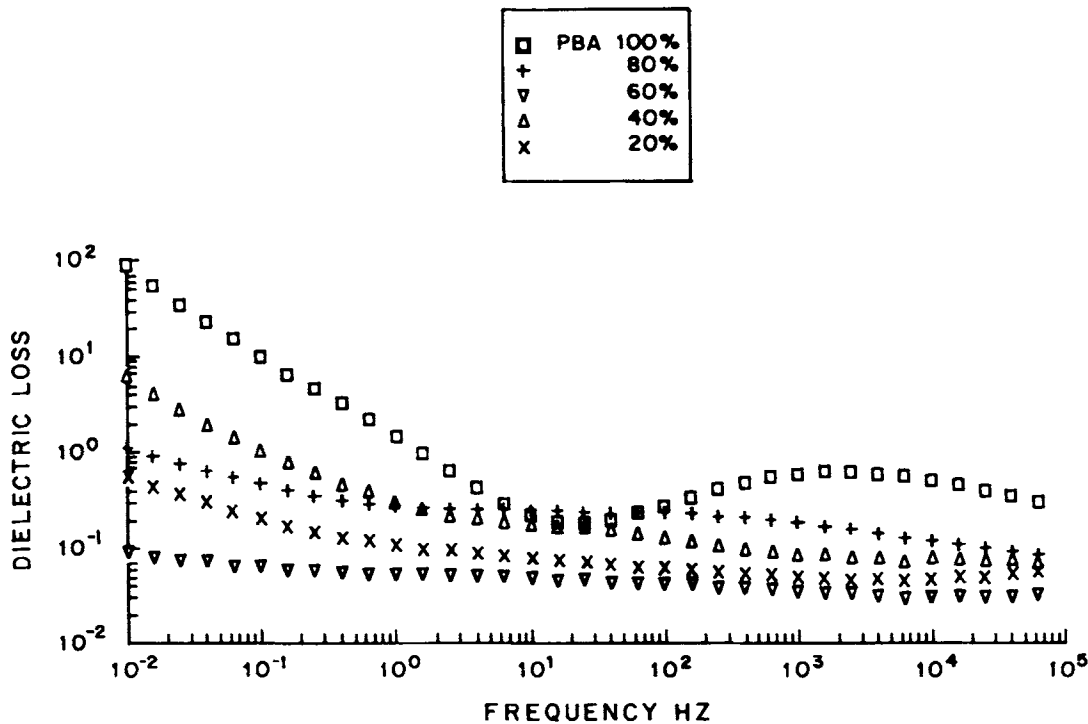
□	PBA	100%
+		80%
▽		60%
△		40%
x		20%

Figure 5 Dielectric loss spectrum for photocross-linked epoxy-arylate resin at 330 K for different compositions. Initiator concentration 5% and irradiation intensity corresponding to curve 6 of Figure 2.
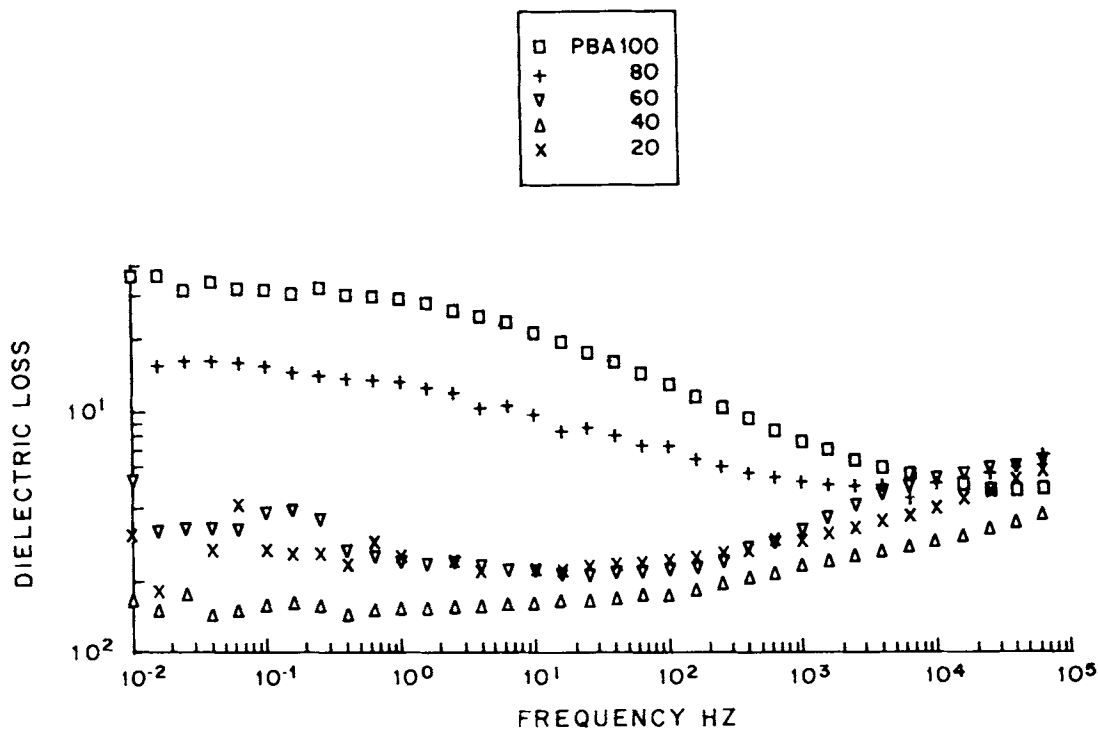
Figure 6   Dielectric loss spectrum for photocross-linked epoxy–arylate resin at 280 K for different compositions. Initiator concentration 5% and irradiation intensity corresponding to curve 6 of Figure 2.

Figure 7   Dielectric loss spectrum for photocross-linked epoxy–arylate resin at 220 K for different compositions. Initiator concentration 5% and irradiation intensity corresponding to curve 6 of Figure 2.
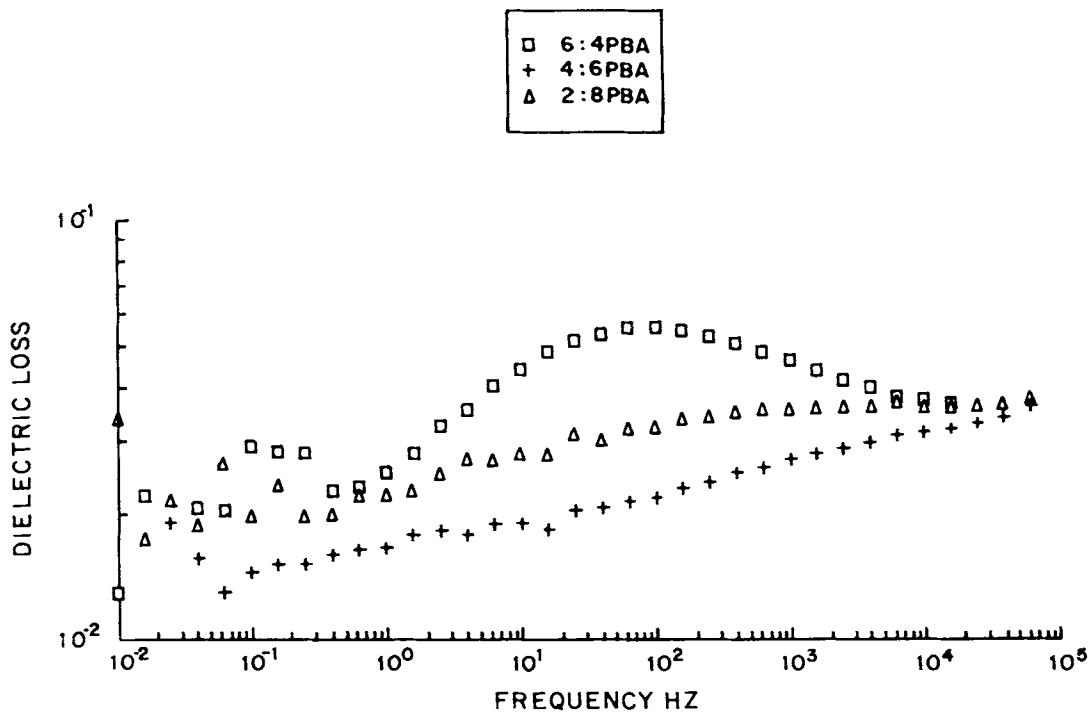
sition. The occurrence of a peak in the curing curve strongly suggests the possibility of phase separation.[21]

Further studies were carried out to investigate the aspect of phase separation that would reflect on the dielectric and optical properties of the films.[22,23] The dielectric relaxation of these films having different compositions, i.e., nBA content of 20–100%, was studied over a wide range of temperatures (150–400 K) and frequencies (10^{-2}–10^5 Hz). Typical dielectric loss spectra in which prominent differences are observed are indicated in Figures 5–7 for temperatures of 330, 280, and 220 K, respectively. A large number of such data was obtained for other temperatures as well, but is not shown here. These various results can be consolidated in the form of a relaxation map as shown in Figure 8, which is a plot of $\log f_m$ vs. $1/T$, where f_m is the frequency, and T, the temperature at which the relaxation peak appears. The salient features that emerge from these are that (i) there are mainly two relaxation peaks observed in the range of frequency and temperature studied, (ii) the strength of the relaxation peak depends on the nBA content of the formulation, and (iii) the peak position shifts with composition. The high-temperature peak corresponding to the α-re-

laxation that arises from the glass transition process is seen to shift to the high-temperature side with increase in epoxy content. However, there appears to be a critical composition at which the highest temperature for α-relaxation is obtained. Since the glass transition temperature increases with degree of cross-linking, the high-temperature shift in the α-transition may be understood in terms of the optimal number of cross-links obtained at the critical composition. The β-relaxations observed at low temperatures (< 250 K) also shows large compositional dependence. In fact, the β-process appears to be more sensitive to composition than does the α-relaxation. There is a large shift in its peak position toward the low-temperature side as well as a decrease in its activation energy, especially for the composition of 40% nBA. For comparison, the β-process of thermally cured epoxy–acrylate (90% BA) is also indicated in Figure 8, and it is interesting to note the large difference in the temperature region in which it appears for the two cases.

The effect of composition on the dielectric properties was studied with an expectation that if phase separation is occurring during curing, then it would become more distinct by changing the relative composition of the two phases. Figure 9 shows collec-
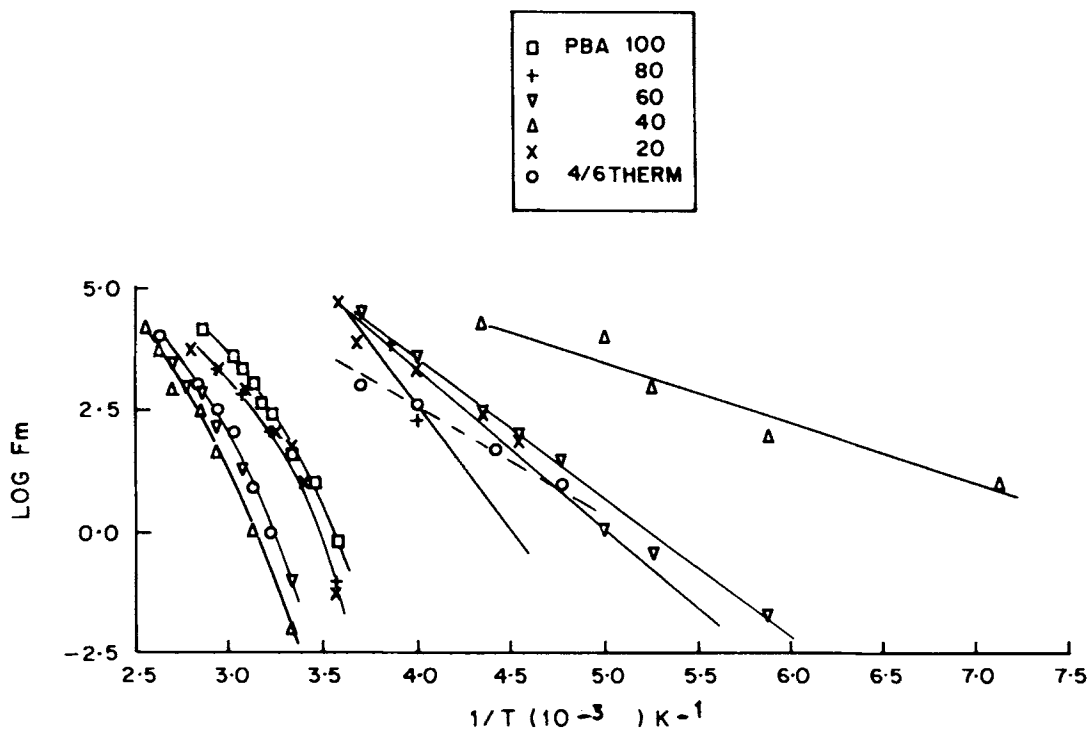
□	PBA	100
+		80
▽		60
△		40
x		20
o	4/6THERM	

Figure 8 Dielectric relaxation map of photocross-linked epoxy arylate resins showing α- and β-relaxation regions. The β-relaxation of thermally cured (60/40) resin is also indicated.
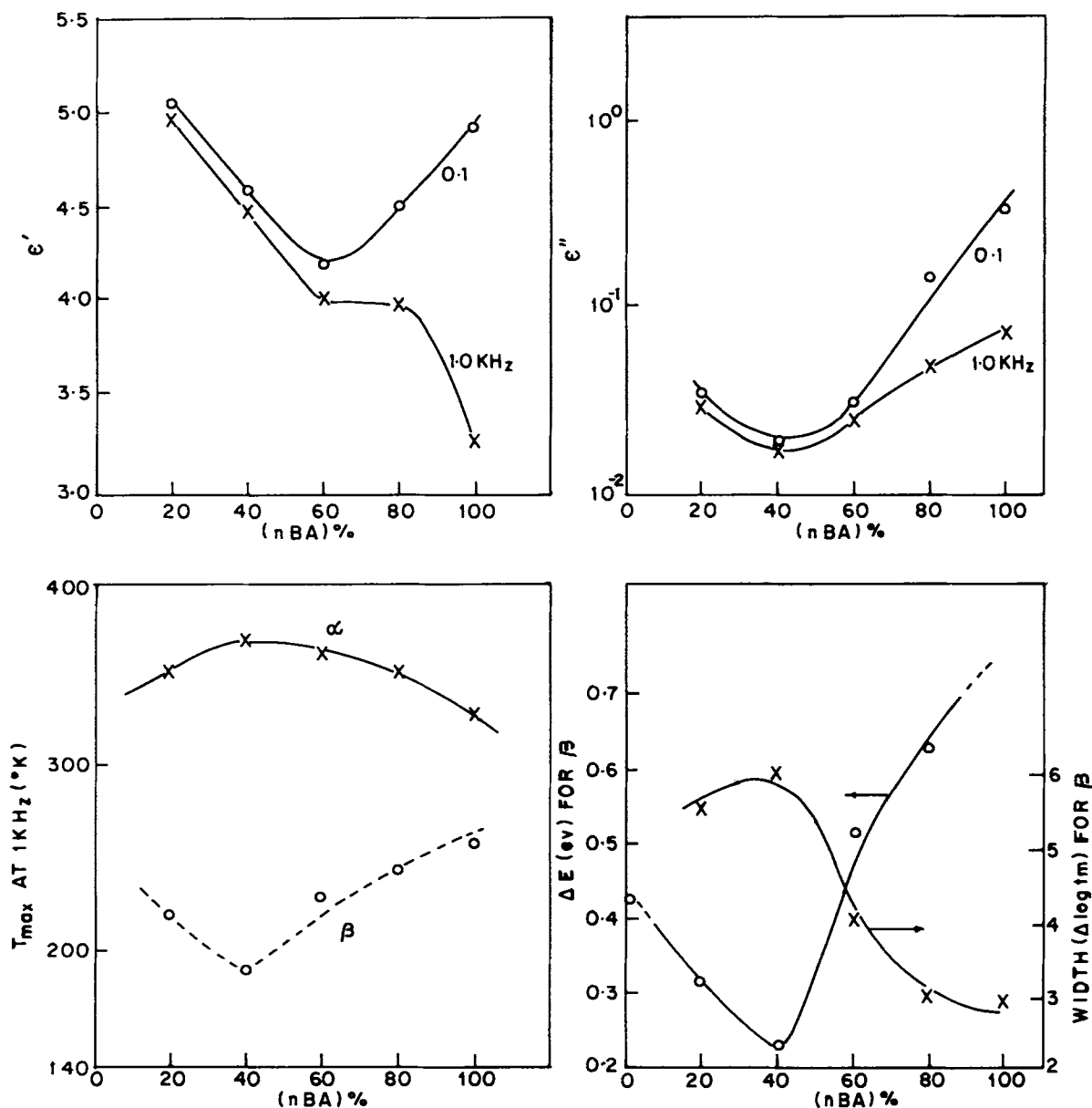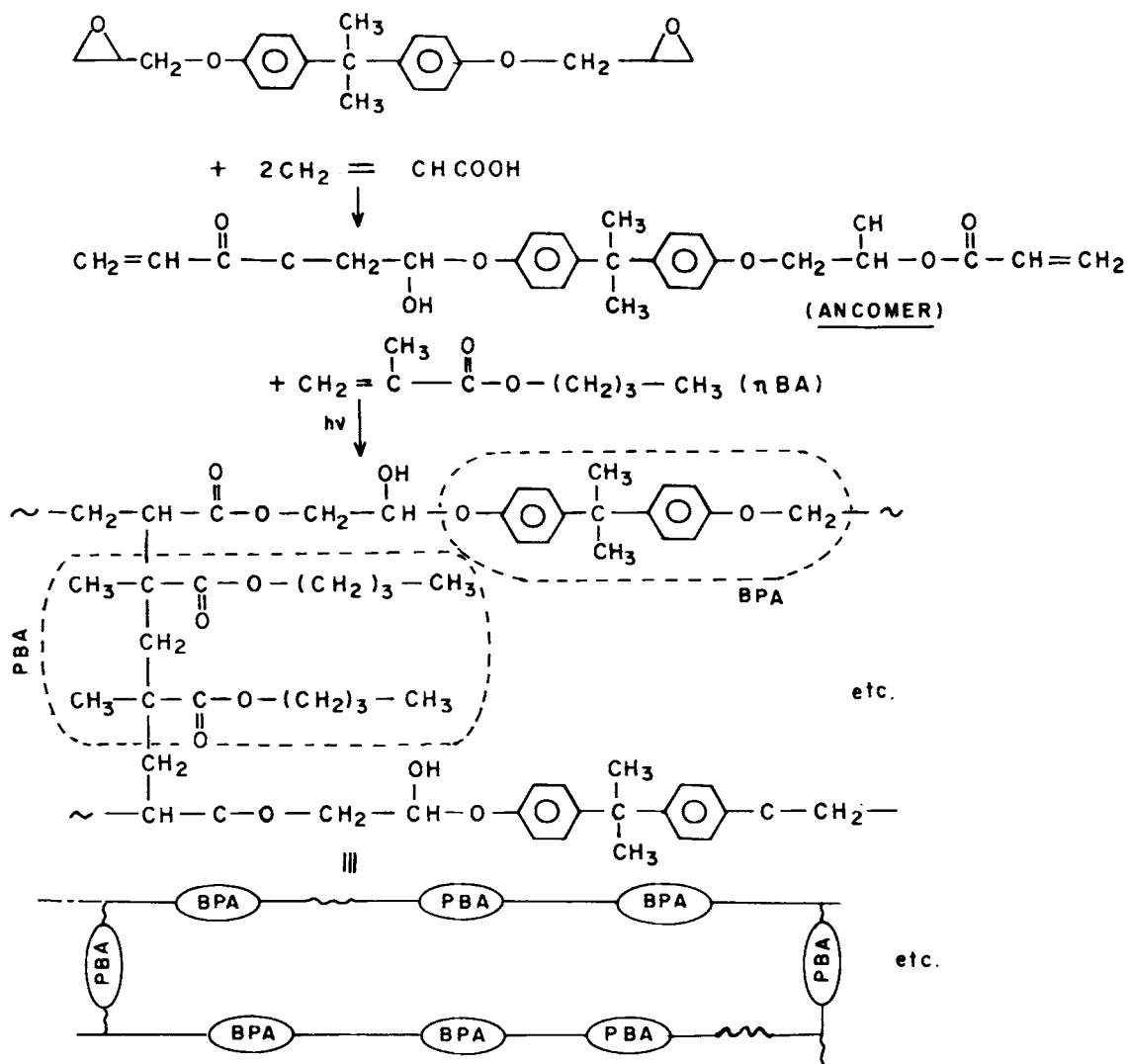
Figure 9   Various dielectric parameters of photocross-linked epoxy–arylate resins as a function of composition.

tively the effect of composition on various dielectric parameters especially for the β-process. It is evident from these graphs that a composition in the midregion of 40% nBA and 60% epoxy appears to be a critical one. At higher nBA content, the dielectric dispersion is quite large due to flexibility of the molecules, whereas it is narrow at low nBA contents due to a closer, tight, and rigid epoxy network. A minimum in the T_{max} of the β-peak and its activation energy is also noticed at the same composition. Some authors [24-26] investigated the β-damping peak by dynamical mechanical loss measurements in thermally

cured epoxy with diamines and observed a large shift, a change of shape, and its broadening with increase of the curing temperature. They have attributed these to increase in the cross-link density as well as formation of nodular points: highly cross-linked areas separated by a loose network. In the present case, such a morphology would be inherent since there are two types of processes taking place simultaneously, viz., chain extension (polymerization of nBA or DGEBA-CO-nBA) and cross-linking. The morphology of the film would be governed by relative rates of the two processes (Scheme I).

SCHEME — I

$CH_2=CHCOOH$ ... reactions

$+ 2CH_2 = CHCOOH$

(ANCOMER)

$+ CH_2 = C(CH_3)-C-O-(CH_2)_3-CH_3$ (nBA)

$h\nu$

BPA

PBA

III

etc.

BPA ~~~ PBA — BPA

PBA   PBA

BPA — BPA — PBA ~~~

etc.

To investigate the phase morphology, these films were examined by optical polarizing microscopy and scanning electron microscopy. As such, these photocured films are optically clear and transparent for all compositions, suggesting that the phase domain size is quite small (of the order of 0.5 μm or less). Also, both the phases can have very close refractive index values so that there is no optical contrast. To increase the contrast, these films were soaked in a dilute (0.2%) solution of Eosin red dye in acetone for 0.5 h and then washed. Since the dye is expected to penetrate preferentially in acrylate-rich domains, this would increase the contrast. Figure 10 shows the micrograph of the film so treated and the two-phase morphology is evident from the same. However, it may be mentioned here that this type of morphology could be observed by this technique in nBA-rich samples only. Further work is in progress on morphological investigations on photocrosslinking.

SUMMARY AND CONCLUSION

Continuous UV cure monitoring of the epoxy–acrylate resins shows that the photocross-linking process involves several events occurring simultaneously. Phase separation is a distinct possibility, especially at a high intensity of radiation. Such finer details of the UV curing process have been distinctly brought out by the above studies.

It may be of interest to mention that the type of
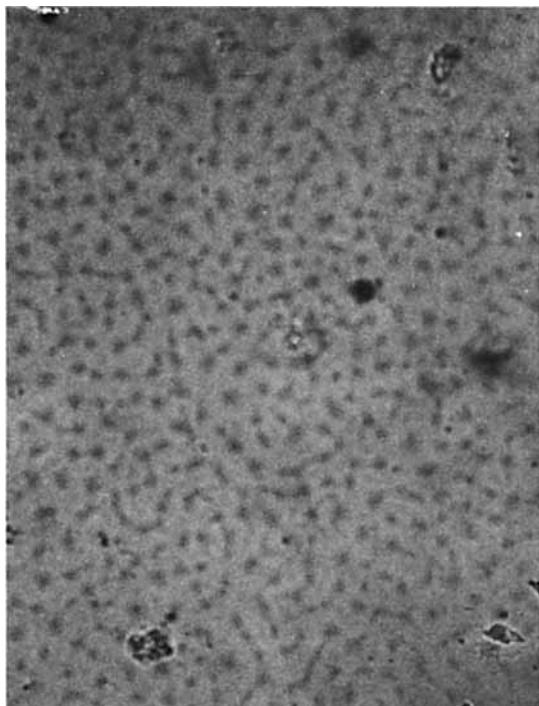
200x

Figure 10 Photomicrograph of (40/60) epoxy–arylate resin after photocuring and then exposing to dye solution.

morphology and network formed at high intensity and short exposure time is quite different from that of low intensity and long exposure time. Such differences can be explained on the failure of the reciprocity law for exposure. Based on present studies, it seems that phase separation may be a more important factor to be considered for noting such differences.

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