

Distribution of Onium Salt Photoinitiators in a Two-Phase Epoxy System

KATHLEEN L. COVERT and DAVID J. RUSSELL*

Systems Technology Division, IBM, 1701 North Street, Endicott, New York 13760

SYNOPSIS

A phase-separated epoxy blend containing a sulfonium salt cationic photoinitiator was studied. The onium salt was found to be preferentially soluble in one of the resins of the system. Scanning electron microscopy and microprobe analyses were done to determine the concentration distribution in the phases and the results compared to a model based on liquid extraction distribution coefficient behavior. Finally, the photolithographic behavior of various blends of the epoxy resins is discussed and the results compared to the behavior predicted by the photoinitiator distribution. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The cationic photopolymerization of polymers, especially epoxies, is becoming an increasing portion of the UV-curable film market.¹⁻³ Photolysis mechanisms, polymerization mechanisms, and performance data for cationic initiators have been previously discussed.^{4,5} Recently, cationic photopolymerization with onium salts has been used for photolithographic imaging of epoxy systems.^{6,7}

Onium salt photoinitiators have been reported to have different solubilities in reactive monomer systems.³ Recently, a systematic study of the solubility of triphenylsulfonium hexafluoroantimonate was done in different polymers.⁸ Scanning electron microscopy (SEM) and DSC analyses of the films revealed evidence that different polymers were saturated at different onium salt loadings.⁸

Phase separation of polymer blends has been under investigation recently because of an increase in desirable properties, especially toughness.^{9,10} Some recent work has focused on the toughening mechanisms for epoxies containing a thermoplastic discontinuous phase.^{11,12}

In many cases, it is desirable to have additives in a polymer system, such as antioxidants or curing

agents. As in the case of the onium salts, these additives may demonstrate different solubilities in various polymers. Billingham et al.¹³ used SEM to characterize the concentration distribution of additives and impurities across crystalline domains formed in amorphous polypropylene. Additional work by Billingham et al.¹⁴ demonstrated that the solubility of phenolic antioxidants was dependent on the structure of the antioxidant, the temperature, and the polymer.

More recently, Kulich and Wolkowicz studied the distribution of antioxidants in a rubber-modified acrylonitrile-butadiene-styrene polystyrene system.¹⁵ They reported that the distribution of the photoinitiator was dependent on the solubility parameter of the additive and the polymer (calculated from the structures). Varying the polarity of the continuous phase polymer by changing the styrene-to-acrylonitrile ratio changed the solubility of the additives in the polymer.

In photolithography, typically, a photosensitive polymer film is exposed to actinic radiation patternwise through some type of artwork having transparent and opaque areas. In negative-acting resist systems, such as a combination of epoxy resins and onium salts, polymerization occurs where the light is absorbed by the resist film, and no reaction takes place under the opaque areas of the artwork. The two areas of polymerized resins and unpolymerized resins have differential solubilities in various solvents. After exposing the resist film, the im-

* To whom correspondence should be addressed.

age is developed, typically by spraying the film with a solvent that washes the unpolymerized material away, leaving behind a negative image of polymerized resist. Several good introductions to photolithography have been written, and additional information can be found elsewhere.^{16,17}

In light of the above, one might expect an onium salt photoinitiator in a two-phase epoxy system to exhibit preferential solubility in one of the phases. A model system consisting of two resins was studied. One of the resins, EpiRez SU-8, is an octafunctional bisphenol A epoxy. This resin, in conjunction with cationic onium salt photoinitiators, has shown rapid photospeeds with photogellation occurring at low exposur doses. The other, phenoxy resin PKHC, is a relatively high molecular weight condensation product of epichlorohydrin and bisphenol A. This resin has a very low epoxy content and therefore a slow photospeed. However, PKHC is flexible, tough, and a good film former. The onium salt photoinitiator, UVE 1014, is a mixture of several onium salts.⁵ The structures for some of the components are shown in Figure 1.

Preliminary work with formulations containing SU-8 and PKHC suggested that different combinations of SU-8 and PKHC might offer versatility in cationic photoimaging formulations. However, it was observed that the resin blends exhibited phase

separation, and during the solvent develop step, it was further observed that one of the resins was being preferentially washed away by the developer solvent (γ -butyrolactone). In addition to there being an uneven distribution of available epoxy functionality due to the separation of the two resins, preliminary microprobe analyses suggested that there was an uneven distribution of the sulfonium salt photoinitiator. Furthermore, it was determined that the resin phase determined to be the SU-8 had a higher initiator concentration. Thus, the low epoxy content and the low initiator content of the predominantly PKHC phase would explain the preferential solubility of the PKHC phase during the solvent develop step. However, the observed differences in the solvent washout after imaging showed that there was not as tremendous a difference as the differences in the epoxy and initiator content might suggest.

A simple model based on liquid-liquid solvent extraction was proposed. Equation (1) describes the concentration distribution coefficient for a solute X distributed between two immiscible liquid phases¹⁸:

$$D_c = \frac{[X] \text{ phase 1}}{[X] \text{ phase 2}} \quad (1)$$

Typically, eq. (1) describes the distribution of an solute between an organic and aqueous phase during an extraction. This relationship should be valid over a reasonable difference in the volumes of the two phases. If the volumes of the phases are known, then the mass distribution coefficient can be calculated using eq. (2), where V_1 and V_2 are the volumes of phases 1 and 2, respectively¹⁹:

$$D_m = \frac{[X]_1 V_1}{[X]_2 V_2} \quad (2)$$

Combining eqs. (1) and (2) yields eq. (3), where $D_c = D_m$ if $V_1 = V_2$:

$$D_m = D_c \frac{V_1}{V_2} \quad (3)$$

It was speculated that the distribution of the photoinitiator might follow eq. (1) for several ratios of resins in the mixture, where the initiator would distribute unevenly between the two resins based upon its preferential solubility in the SU-8 resin. Once the distribution coefficient was determined, the mass and concentration of the initiator could be estimated for each phase in a variety of mix ratios.

To test this model, several mixtures of SU-8 and

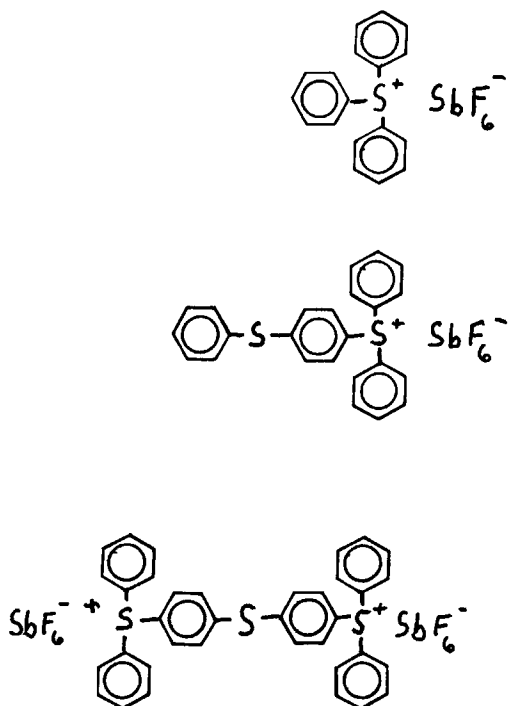


Figure 1 Onium salts in UVE 1014.

PKHC were mixed, and 3 pph UVE 1014 sulfonium salt photoinitiator was added. Films were cast from the solutions, cured, and examined for phase separation. Where phase separation was observed, WDS analysis was done to determine the concentration of Sb, S, and F in the two phases. The data were used to test the validity of the proposed model.

EXPERIMENTAL

Resins

SU-8 was obtained from Rhone-Poulenc (Louisville, KY), and the phenoxy resin PKHC, from Union Carbide (Danbury, CT). Both resins were used without further purification and were predissolved in propylene glycol monomethyl ether acetate (PGMEA, Aldrich Chemical Co., Milwaukee, WI). Triphenylsulfonium hexafluoroantimonate photoinitiator, UVE 1014, was purchased from General Electric (Schenectady, NY).

Sample Preparation

The resin mixtures were obtained by weighing known amounts of the resin solutions. UVE 1014 was added by weight to a concentration of 3%. The solutions were mixed using a magnetic stirrer. The SEM samples were prepared by casting films on glass slides, air drying for 15 min, and baking at 125°C for 15 min. The samples were exposed from both sides to 3 J of UV energy using a high-pressure mercury arc lamp (Tamarak Scientific Co., Anaheim, CA) and baked at 100°C for 4 h. The resin surface was sputter-coated with copper, and the sample was cut in half, potted, and ground smooth. Examining the cross section ensured that the bulk concentrations, rather than the surface concentrations, were measured. The images were prepared by coating the solutions on copper-clad laminates using an R-K Print Coat wound wire rod drawdown apparatus (R-K Print-Coat Instruments Ltd, Litlington, UK). The films were air-dried for 20 min and then oven-dried for 10 min at 125°C. The films were exposed

to 2 J through a diazo artwork and a Stauffer 21-step step tablet (Stauffer Graphic Arts, South Bend, IN). The films were then baked at 125°C for 15 min to advance the polymerization, followed by a solvent develop step using a Riston A-Processor (DuPont, Wilmington, DE) containing γ -butyrolactone sprayed for 90 s at 15 psi.

SEM/Microprobe Analyses

A JEOL Model JXA-733 microprobe was used for EDS and WDS analysis. Table I shows the parameters used during the analyses. All samples were carbon-coated prior to analysis. BSE photographs were taken at 20 keV and 13–30 nA.

RESULTS AND DISCUSSION

Polymer Blend Morphology

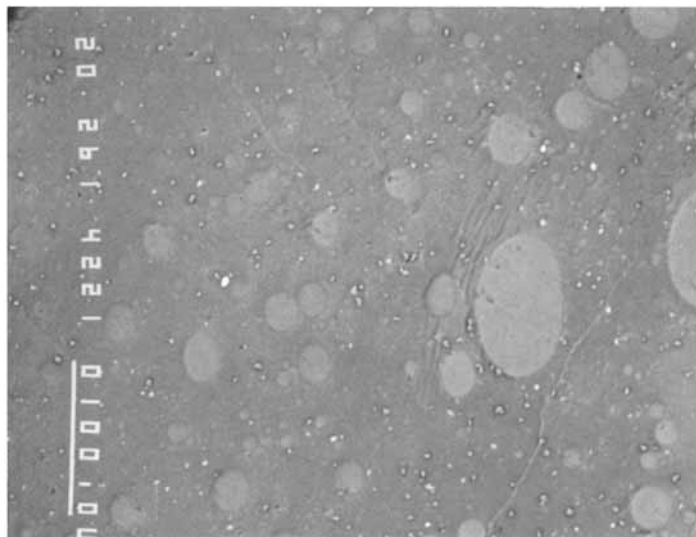
Preliminary experiments with a formulation containing a blend of SU-8 and PKHC with a triphenylsulfonium hexafluoroantimonate photoinitiator exhibited phase separation. In that formulation, the data suggested that the initiator was preferentially soluble in the SU-8 phase of the blend.

The BSE photographs of Figures 2–6 show that all of the ratios of these two resins in this work exhibited phase separation. BSE photomicrographs of the SU-8 and PKHC resins are shown in Figures 7 and 8. The samples of the SU-8 and PKHC resins appear homogeneous.

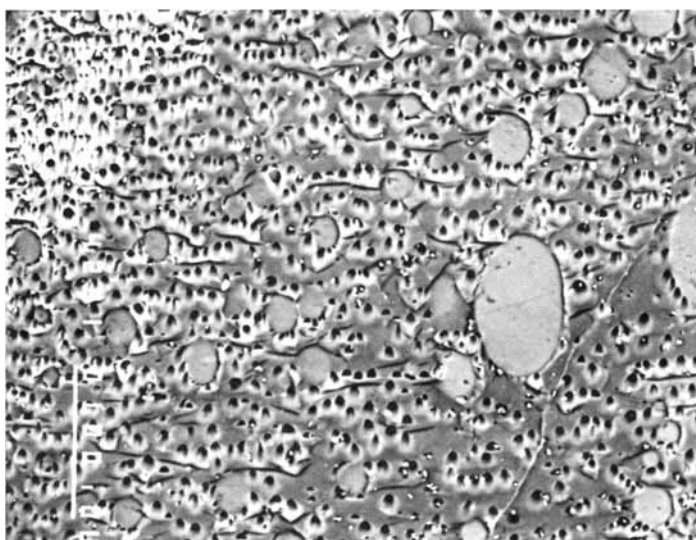
Figure 2 shows BSE photomicrographs of the 20 : 80 SU-8 : PKHC blend. The BSE technique shows areas containing high atomic weight elements as being brighter. Figure 2 shows bright spheres of a discontinuous phase contained in a darker matrix. The relative proportions of the two phases and the contrast supports the hypothesis that the discontinuous phase is predominately SU-8 enriched in photoinitiator. As the concentration of SU-8 is increased, the morphology changes as shown in Figure 3 for 40 : 60 SU-8 : PKHC. For this sample, there are regions appearing to contain a discrete SU-8

Table I Parameters Used in the WDS Analyses of the Samples

Element	<i>E</i> (keV)	Series	Spectrometer	Std	Wavelength (Å)	Background (A)	Volts (keV)	Current (nA)	ZAF
S	2.308	K	PET	Fe2S	172.01	±4	12	20	1.091
Sb	3.605	L	PET	Sb	110.11	±4	12	20	1.390
F	0.667	K	STE	LiF	92.93	+8, +15	12	20	2.791



BSE 260x 15nA
20WT% SU8 - 80WT% PKHC with INITIATOR



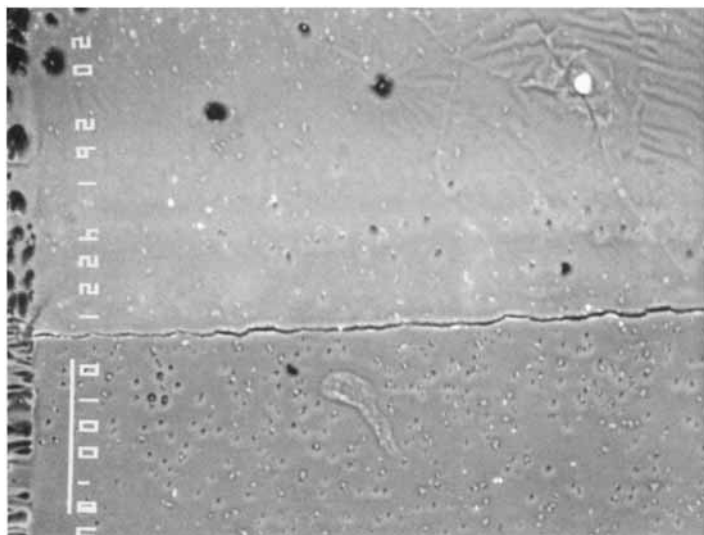
BSE 260x 30nA
20WT% SU8 - 80WT% PKHC with INITIATOR

Figure 2 20 : 80 SU-8 : PKHC.

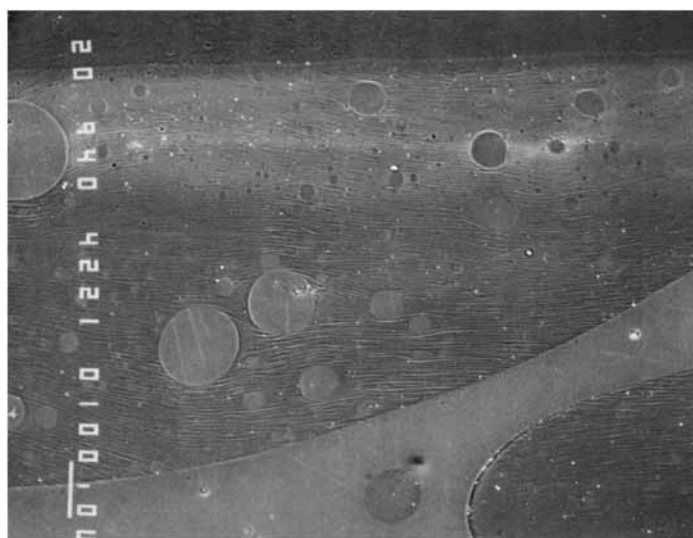
phase in a PKHC matrix, but there are also regions where the discontinuous phase appears to be PKHC in a continuous phase of SU-8. As the SU-8 content of the blend is increased from 40 : 60 SU-8 : PKHC to 80 : 20 SU-8 : PKHC, the appearance of both regions, SU-8 dispersed in PKHC and PKHC dispersed in SU-8, are still obvious (Figs. 3-6). Since the resin blends were cast from solution, it can be assumed that they started as a homogeneous mixture and phase-separated upon drying. The inversion of

the phases within a single sample is most likely dependent upon the relative concentrations of the two resins on a microscale upon drying, which is not surprising when the two resins are in nearly equal concentrations.

The incompatibility of these two resins was at first surprising due to the similarity of the common bisphenol A repeating unit. Furthermore, the solubility maps of both resins as determined by ASTM method D3132 (Ref. 20) had considerable overlap.



BSE 260x 13nA
50WT% SUB - 50WT% PKHC with INITIATOR



BSE 94x
40WT% SUB - 60WT% PKHC with INITIATOR

Figure 3 40:60 SU-8:PKHC.

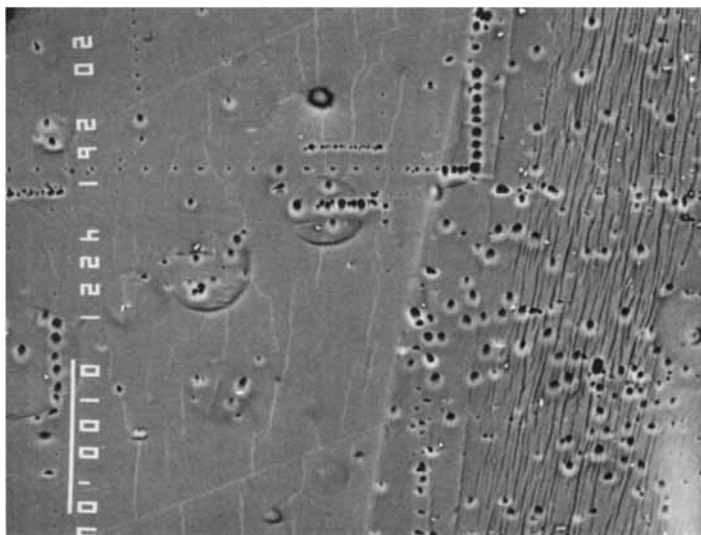
Figure 4 50:50 SU-8:PKHC.

However, from the solubility map, a wide range of total solubility parameters could be obtained for each resin.

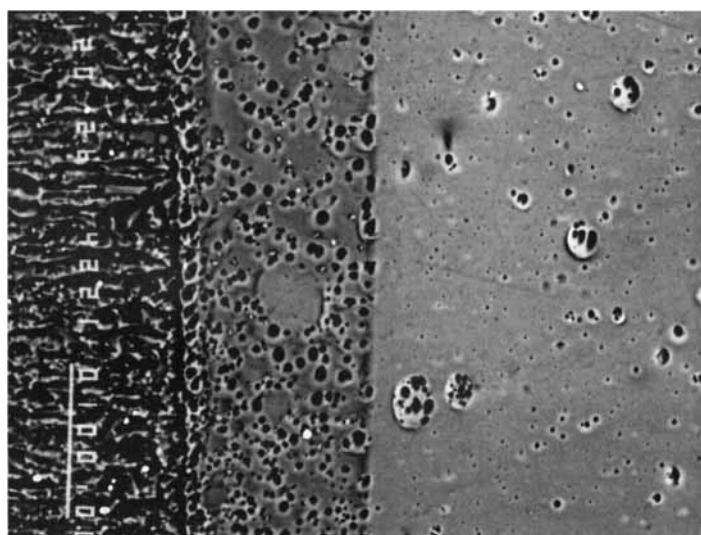
The solubility parameter and the compatibility of the two resins were calculated using the method described by Krause.²¹ The solubility parameter was calculated using the group molar attraction constants. The solubility parameters calculated for SU-8 and PKHC were 9.0 and 10.1, respectively, which

are in the range determined by the ASTM method.²⁰ Using these data, the interaction parameter was calculated to be 0.22 for SU-8 and PKHC.

The critical interaction parameter, used to determine whether a blend of polymers might be compatible, was also calculated.²¹ For the SU-8 and PKHC blend, the critical interaction parameter was calculated to be 0.012. Since the interaction parameter is much larger than the critical interaction pa-



BSE 260x
80WT% SUB - 20WT% PKHC with INITIATOR



BSE 260x
60WT% SUB - 40WT% PKHC with INITIATOR

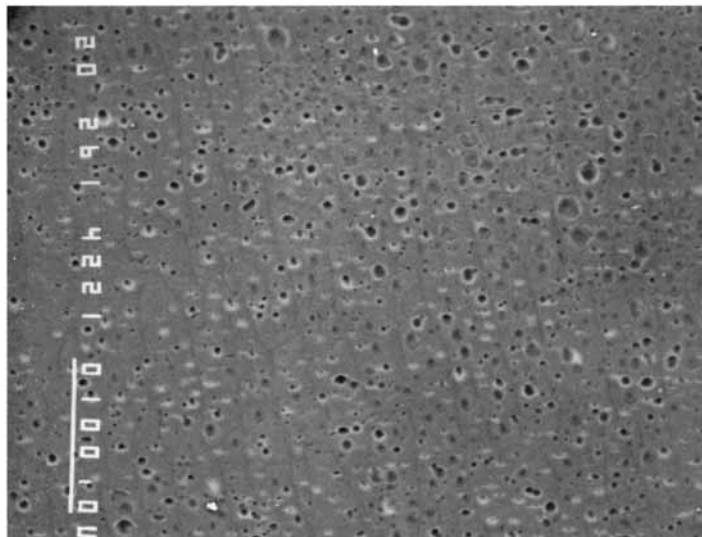
Figure 5 60 : 40 SU-8 : PKHC.

Figure 6 80 : 20 SU-8 : PKHC.

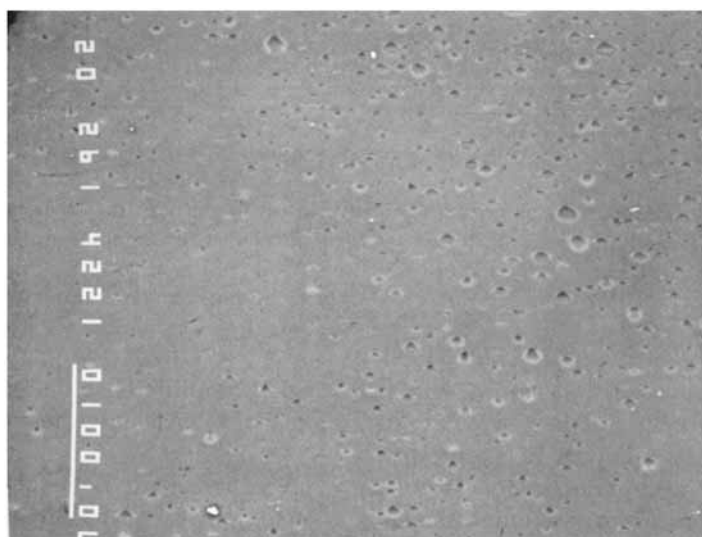
parameter, the blend is predicted to be incompatible, at least at some proportions.²¹

Characterizations of blends of PKHC with low molecular weight diglycidal ether of bisphenol A (DGEBA) resins have not shown evidence of phase separation.²² Previous characterization of SU-8 resins has demonstrated that a wide range of molecular weight components are present, including some

DGEBA.^{7,23} Calculating the critical interaction parameter for the high molecular weight fraction of SU-8 and for the DGEBA fraction yields 0.0043 and 0.17, respectively. The critical interaction parameter for the high molecular weight fraction is again much lower than the calculated interaction parameter. However, even though the critical interaction parameter for the DGEBA fraction is lower



BSE 260x
100 WT% SU8 with INITIATOR



BSE 260x
100 WT% SU8 with INITIATOR

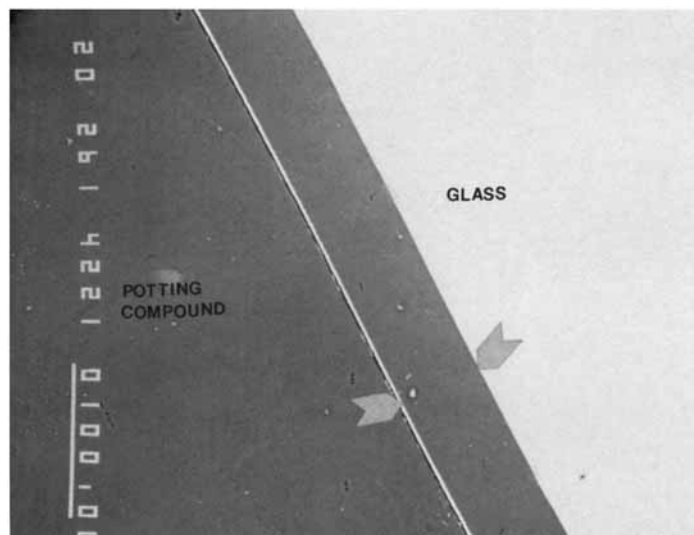
Figure 7 100% SU-8.

than the calculated interaction parameter, the difference is most likely negligible in view of the assumptions made and other factors that are not taken into account for the calculations.²¹ Also, no attempt is made here to compensate for the polydispersity of the PKHC resins used. Thus, the calculated compatibilities for SU-8 and PKHC suggest that SU-8 and PKHC are incompatible, but some of the lower molecular weight oligomers of SU-8 may indeed be

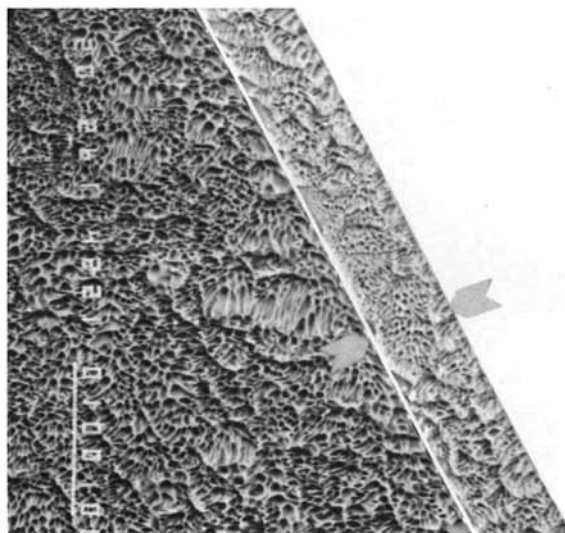
miscible in the PKHC. This is in agreement with the data for DGEBA resins and PKHC.

Microprobe Analysis

Monte Carlo analysis predicted that the beam penetration into the sample at 12 keV would be ca. 5 μm and the BSE efficiency would be only approximately 4%. Therefore, attempts to determine the



BSE 260x 10nA
100 WT% PKHC with INITIATOR



BSE 260x 30nA

Figure 8 100% PKHC.

Sb content of the features in the samples were run at 80 nA, but resulted in severe degradation of the samples. Subsequent determinations were done at 20 nA and scan times of 640 s.

It was observed during analyses that some features of the samples were more prone to degradation than were others. Further observations showed that the SU-8 sample was resistant to degradation, but the PKHC sample was still significantly degraded at the low current density used. It was further observed that the areas resistant to degradation cor-

related with the bright features from the BSE photomicrographs (Figs. 2-8). This again supports the hypothesis that some of the features are predominately SU-8-enriched in photoinitiator.

The BSE photomicrographs and the observed degradation of the sample enabled qualitative determinations of the composition of the phases in the samples to be made. However, the sample degradation was found to interfere with the determination of the Sb. Compared to the background, the Sb concentration tended to increase during the counting

time; this was more apparent with samples containing predominantly PKHC. It was believed that the organic polymer material burned away more rapidly in the beam, thus resulting in an artificially high Sb concentration.

It was hypothesized that the organic portion of the photoinitiator molecule would degrade at the same rate as would the polymer matrix. Monitoring the S response would then be a way of determining differences in the changing rates of response for the Sb and the organic matrix. The correction factor (X) is the ratio of the S-to-Sb response for the sample to the theoretical S-to-Sb response (determined to be 0.42) as given in eq. (4):

$$\frac{(S/Sb)}{0.42} = X \quad (4)$$

For each determination, the corrected Sb concentration was obtained by multiplying the determined Sb concentration by the correction factor (X). The correction was applied to the F determinations also and resulted in better precision between the Sb and F values for duplicate determinations within a feature of a given sample.

The Sb-to-F ratio determined by the microprobe analysis also varied from sample to sample and was significantly larger than the theoretical value. It was speculated that the carbon background response might be interfering, since the F signal was small. The Sb-to-F response ratio for the single-component systems of SU-8 and PKHC were very reproducible, but different from the theoretical value and from each other. The Sb/F values for the SU-8 and PKHC samples were 0.41 and 0.55, respectively.

This difference was again assumed to be due to the relative stability of the polymers, since differences in beam-induced degradation had been observed during analysis. Therefore, the relative differences in the Sb/F ratios were believed to be due to the resin composition of a particular feature, e.g., no feature was either pure SU-8 or PKHC, but rather a mixture of the two in some proportion. This is consistent with the calculated interaction parameters based on the solubilities as discussed above. It is assumed that the composition of each feature may be unique, and therefore the data generated by probing an area is not assumed to be representative of the whole phase.

A correction factor (R) was calculated to account for the different resin composition within a sample feature. Starting with eq. (5) for the ratios of the

Sb/F ratios for the pure resin samples, the Sb/F ratio for PKHC is normalized to 1:

$$(Sb/F)_{\text{sample}} = \frac{(Sb/F)_{\text{SU-8}}}{(Sb/F)_{\text{PKHC}}} (R) \quad (5)$$

Rearranging eq. (5) allows R to be calculated using eq. (6), which shows that the correction is the ratio of the (Sb/F) ratios for the sample to the SU-8:

$$R = \frac{(Sb/F)_{\text{sample}}}{(Sb/F)_{\text{SU-8}}} \quad (6)$$

In this case, the Sb/F ratio in the feature is proportional to the SU-8 concentration of the feature. Since the Sb/F ratio for the pure SU-8 sample is taken to be indicative of pure SU-8, then R is the fraction of SU-8 in the feature analyzed. Again, if the PKHC is normalized to 1, the weight fraction of SU-8 is equal to $[SU-8]/[PKHC]$. This results in a way to estimate the amount of SU-8 in each feature analyzed for each sample. In fact, the calculated ratio qualitatively correlates with the BSE photomicrographs, where the features containing the highest fraction of SU-8 appear brightest (due to the high Sb content).

Models

The original model proposed for a system consisting of two phase-separated resins and a photoinitiator distributed between them was based on liquid-liquid extraction [eq. (1)]. The wide variety of features contained in the samples made it somewhat difficult to calculate the antimony concentration distribution coefficient (D_c) for all the analyses. As an example, a plot of D_c (where phase 1 is SU-8 and phase 2 is PKHC) for the top area of the samples is shown in Figure 9. Theoretically, the slope should be 0; however, a slope of -1.1 is obtained. This shows that the distribution of the Sb between the two phases changes as the fraction of SU-8 increases, with a trend toward less Sb in the spheres at higher SU-8 concentrations in the blend.

The mass distribution coefficients were calculated for the data in Figure 9 and are plotted logarithmically in Figure 10 for the different samples. Figure 11 shows the theoretical plot of $\text{Log}(V_s/V_p)$ (where V_s and V_p are the volume fraction of SU-8 and PKHC, respectively) vs. the fraction of SU-8. The respective plots produce eqs. (7) and (8):

$$\text{Log } D_m = 1.695f(\text{SU-8}) - 0.68 \quad (r = .956) \quad (7)$$

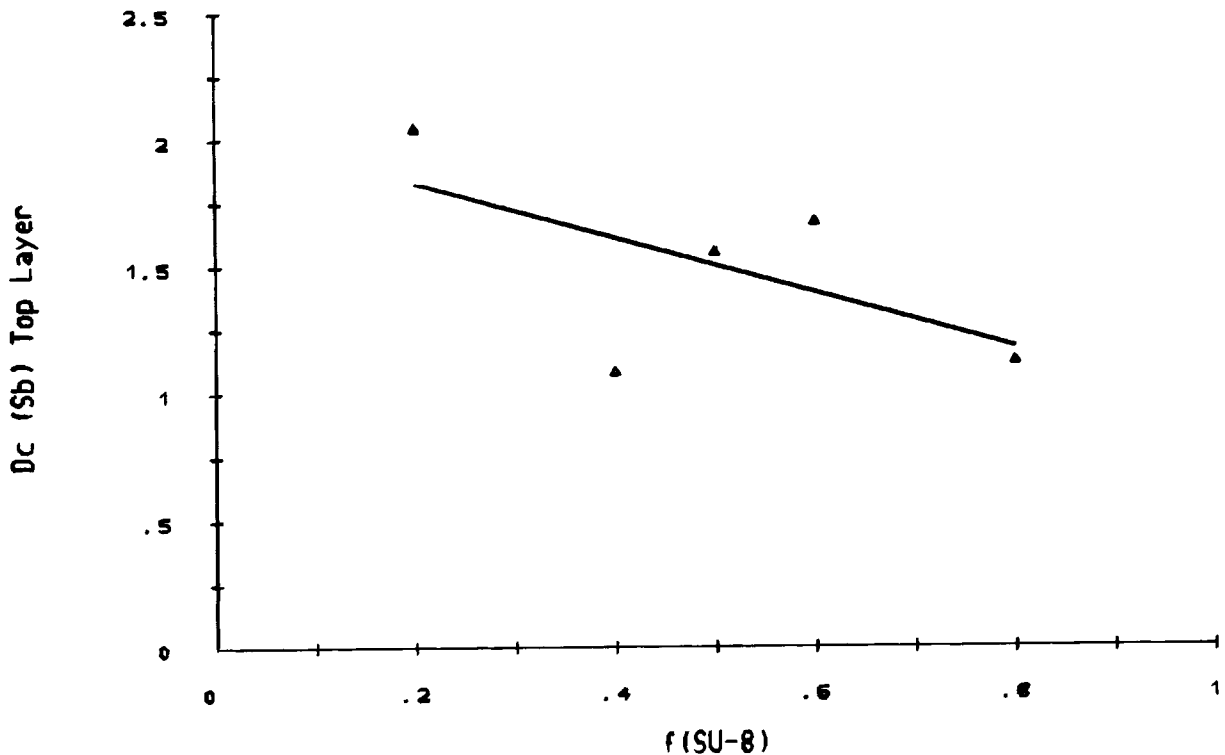


Figure 9 Concentration distribution coefficient of Sb vs. weight fraction of SU-8 in the top area of the sample.

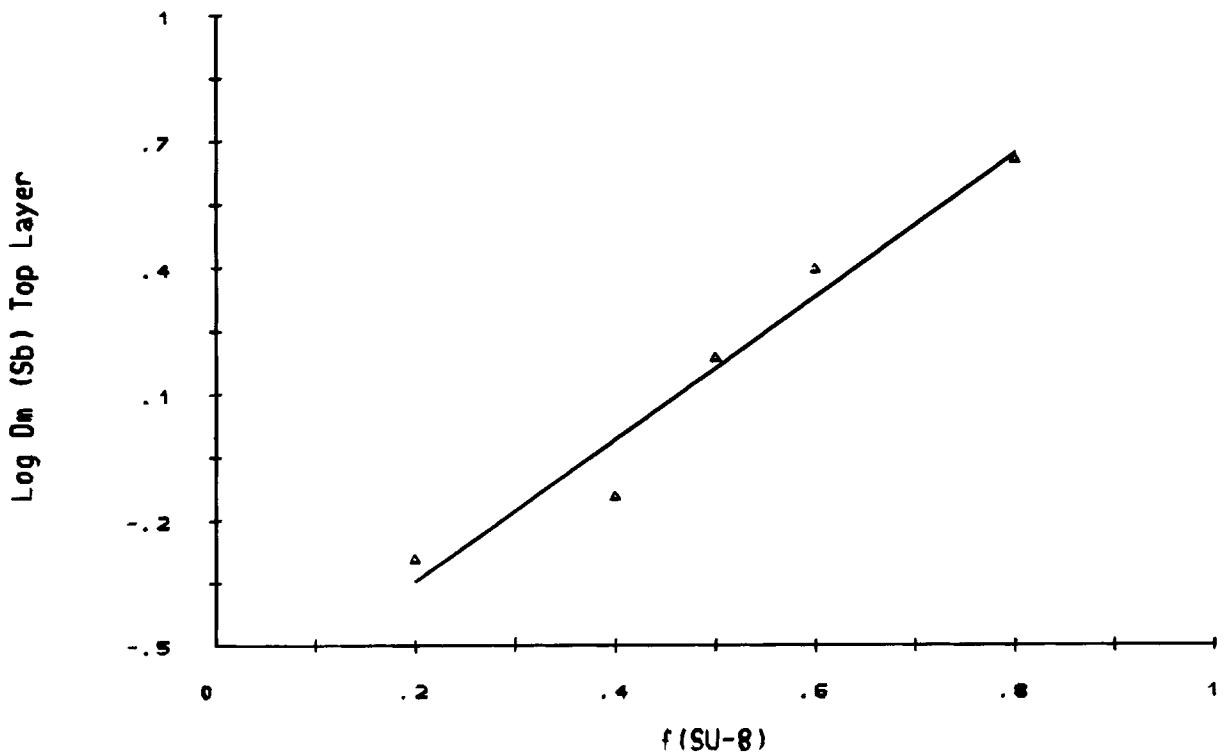


Figure 10 Log of the mass distribution coefficient of Sb vs. weight fraction of SU-8 in the top area of the sample.

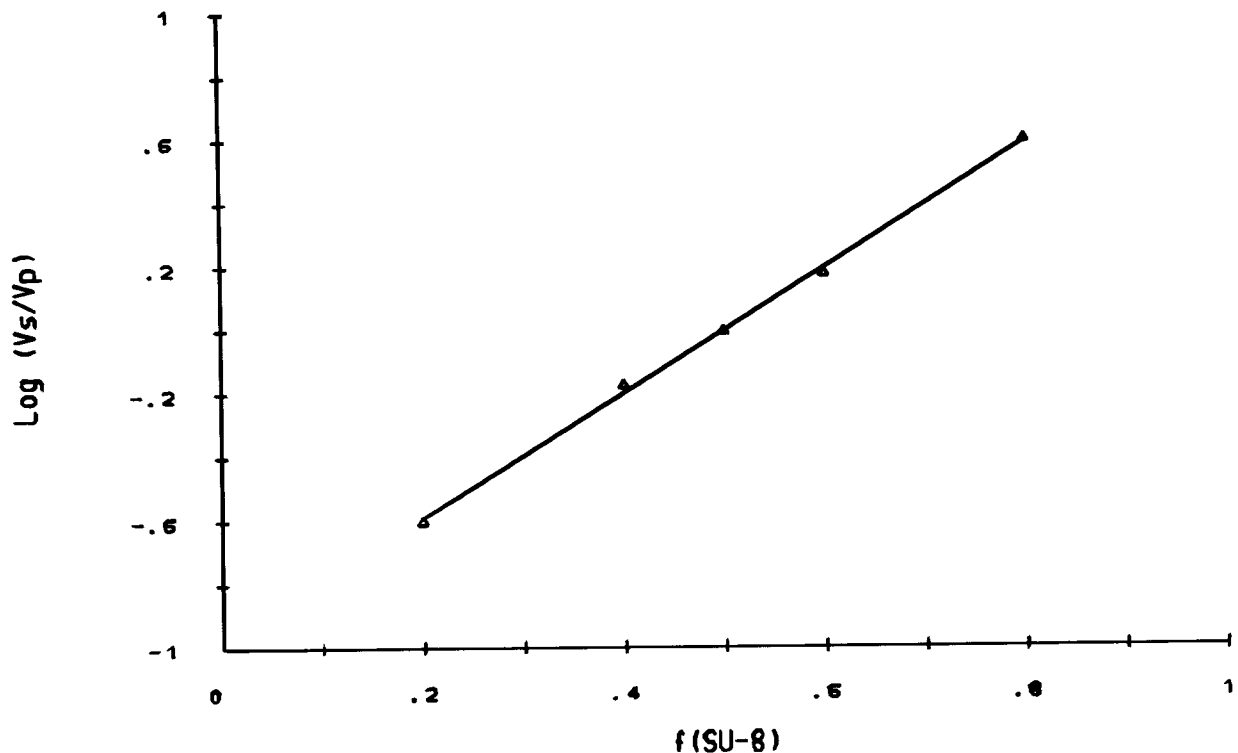


Figure 11 Log SU-8-to-PKHC-mix-volume ratio vs. weight fraction of SU-8 in the sample.

$$\text{Log}(V_s/V_p) = 1.98f(\text{SU-8}) - 0.99 \quad (r = .999) \quad (8)$$

Again, if the D_c for each sample was the same, then the slopes of the two equations would be the same [see eq. (3)]. This again suggests that the D_c changes with the fraction of SU-8, in agreement with the observation of Kulich and Wolkowicz that the distribution changes as the polymer composition changes.¹⁵

The calculated ratio of SU-8/PKHC for the spheres probed in the tops and bottoms of each sample were plotted as a function of the fraction of SU-8 in Figures 12 and 13. Each sample location (top vs. bottom) shows a negative slope for the data, suggesting that as more SU-8 is added to the polymer blend less SU-8 is contained in the spheres. This may be a consequence of the different solubilities of the different molecular weight fractions of the SU-8.

The above data suggest that the fraction of SU-8 varies for different features in each sample, e.g., is independent of the ratio of the two resins in the blend. It also is noted that the Sb concentration in the spheres decreases as the SU-8 content of the spheres decreases. This suggests that the Sb content is dependent on the SU-8 content in the spheres.

The relationship between the Sb concentration and the SU-8 concentration was further explored. For each spot probed in each feature of the blend, the total Sb concentration is determined, and the mass of the SU-8 and PKHC are calculated from the ratios using eq. (6):

$$(C_t)(M_t) = (C_s)(M_s) + (C_p)(M_p) \quad (9)$$

Assuming the Sb concentration is dependent on the SU-8 content of the feature, eq. (9) is essentially a mass balance for the analysis of the feature, where C_s and C_p are Sb concentrations in the SU-8 and PKHC, respectively; M_s , the mass of the SU-8; M_p , the mass of the PKHC in the feature; C_t , the determined Sb concentration (by microprobe); and M_t (total mass), equal to the $M_s + M_p$. For the ratio [SU-8]/[PKHC], M_p can be normalized to 1 so that [SU-8]/[PKHC] is equal to the wt % of SU-8 (M_s). Substituting in eq. (9) gives

$$(C_t)(M_t) = C_s f[\text{SU-8}] + C_p \quad (10)$$

Since $M_t = M_s + M_p$,

$$(C_t)(1 + f[\text{SU-8}]) = C_s f[\text{SU-8}] + C_p \quad (11)$$

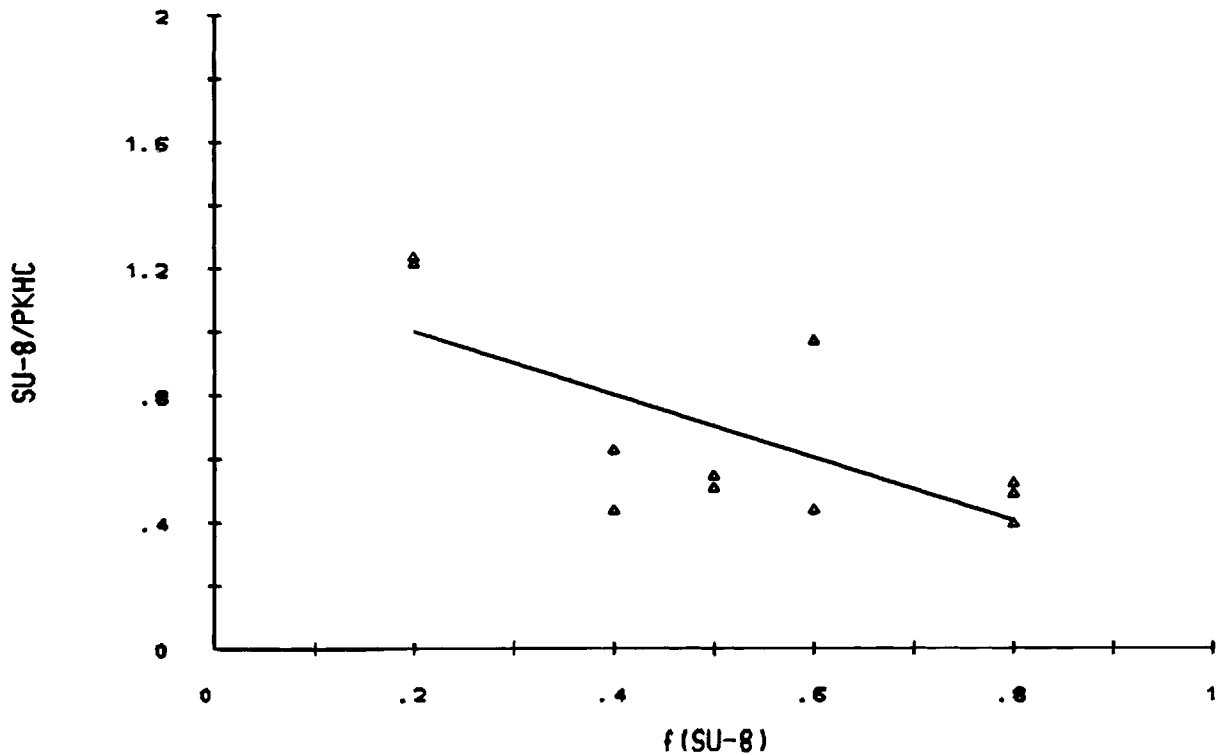


Figure 12 Epoxy resin ratio (top layer spheres) vs. weight fraction of SU-8 in the sample.

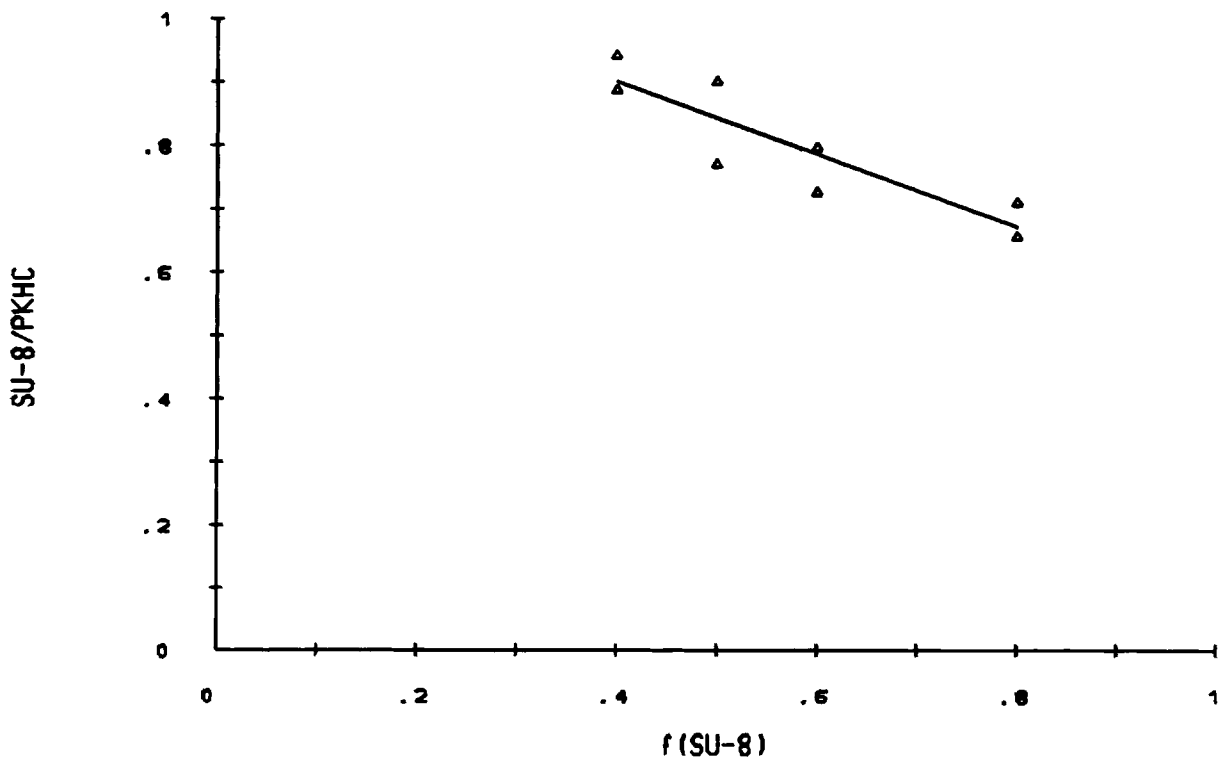


Figure 13 Epoxy resin ratio (bottom layer spheres) vs. weight fraction of SU-8 in the sample.

A plot of $(Ct)(1 + f[\text{SU-8}])$ as a function of $f[\text{SU-8}]$ for the results obtained from each of the determinations for all the features of the samples is given in Figure 14. From the results can be calculated the equation

$$(Ct)(1 + f[\text{SU-8}]) = 1.64f[\text{SU-8}] + -0.17 \quad (r = .871) \quad (12)$$

Theoretically, C_p cannot be negative and is assumed to be 0. Also, since the original photoinitiator concentration gives an S_b concentration of 0.6, at an $[\text{SU-8}]/[\text{PKHC}]$ ratio of 1 (SU-8 = PKHC), $C_p = 1.20$. The value of 1.47 determined from the plot and eq. (12) is in fair agreement.

These results suggest that the S_b concentration in a feature is dependent on the SU-8 concentration of that feature. No S_b is found for features with low SU-8 concentrations. Note that in Figure 14 the wt % of SU-8 plotted is for all features probed and is not interchangeable with the wt % (fraction) in the sample blend.

Lithography

The photospeed of each resin blend containing 3% photoinitiator is given in Figure 15 for an exposur dose of 2000 mJ/in.². The PKHC resin is considered

fairly unreactive due to the low epoxy content and results in a step held of 2. Adding 20–40% SU-8 increases the step to about 9–10, which represents about a 16× increase in photospeed. Further increasing the SU-8 content to 50% and above gives a 256× increase in photospeed (a step of 18), the same photospeed as SU-8 alone.

In Figure 2, the BSE photomicrograph of the 20 : 80 SU-8 : PKHC blend, phase domains considered to be SU-8, by virtue of the relative concentration and the BSE results, are seen. Yet, there is a significant photospeed increase, which could occur only if some of the highly reactive SU-8 was present in the continuous phase. Increasing the SU-8 to 40% does not change this, but at the 50% SU-8 level, the blend takes on the reactive characteristics of 100% SU-8 resin with respect to the photospeed. This suggests that at SU-8 concentrations of 50% or greater there is sufficient epoxy functionality so that the epoxide content is not the limiting factor in the polymerization reaction. Here, the continuous phase either contains a sufficient amount of SU-8 or is the SU-8-rich phase.

CONCLUSIONS

Blends of a highly functionalized reactive epoxy of medium molecular weight (SU-8) and a high

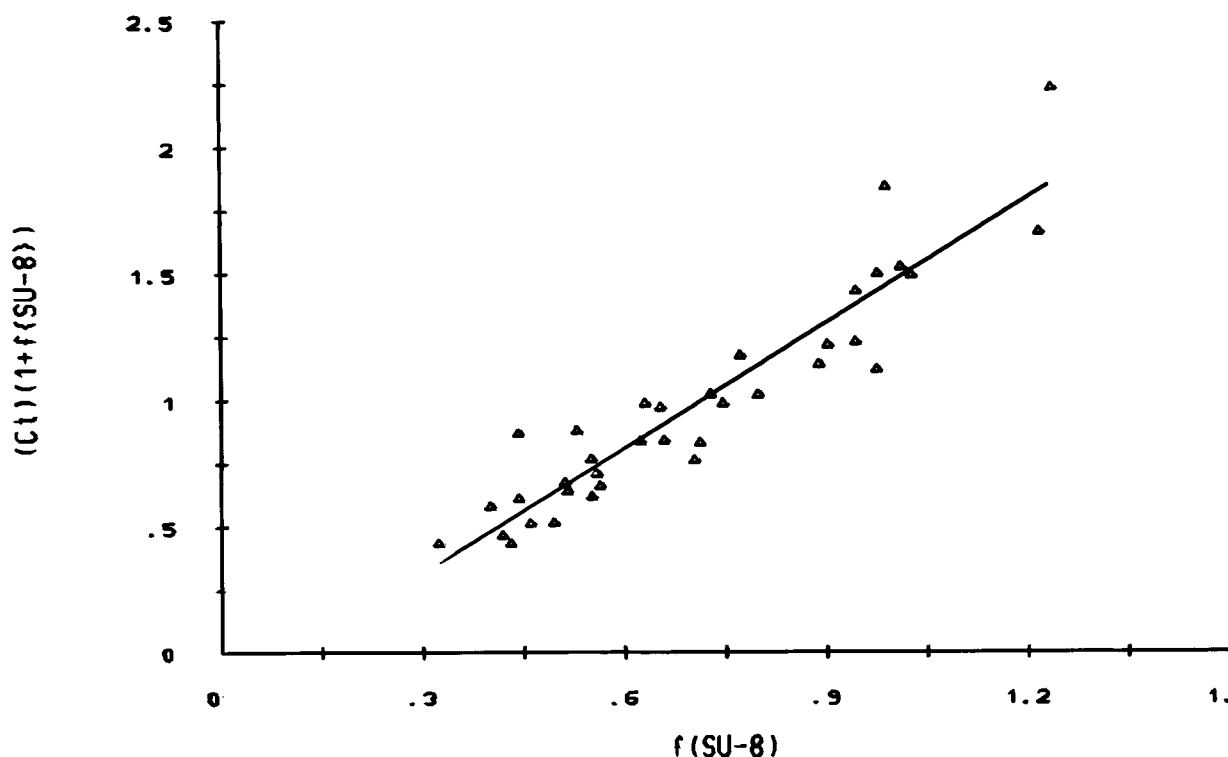


Figure 14 Relationship of determined S_b concentration vs. normalized epoxy resin ratio.

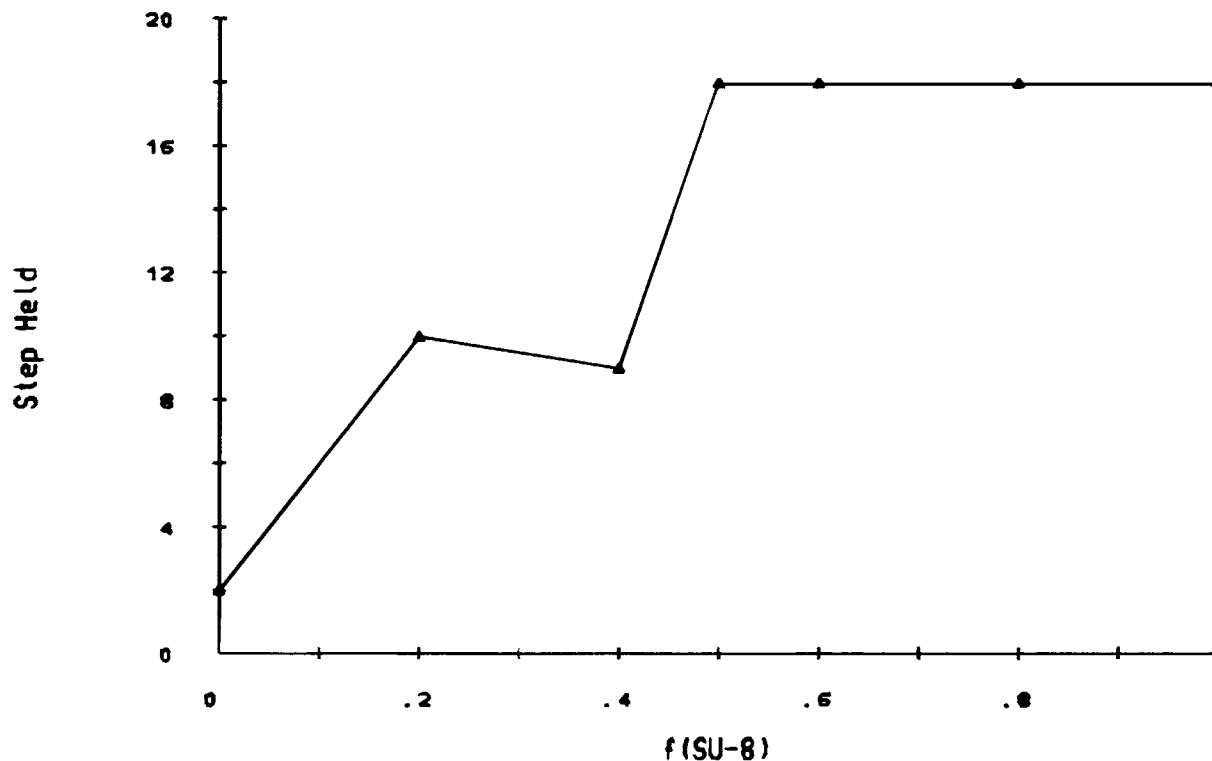


Figure 15 Photospeed of resin blends.

molecular weight low-reactivity phenoxy resin (PKHC), with 3% by weight of a cationic sulfonium salt photoinitiator added to the blends, were studied using microprobe analysis and photolithography. The distribution of the photoinitiator was determined and compared to a simple model based on liquid-liquid extraction theory.

BSE photomicrographs showed that the two resins phase-separated in all the blends studied. Sample degradation during microprobe analysis indicated that the phase domains did not contain individual resins from the blend, but contained varying amounts of both resins. Compatibility calculations based on calculated solubility parameters predict that some of the low molecular component of the SU-8 should be soluble in the PKHC resin. Calculated SU-8 : PKHC ratios based on differing Sb : F ratios from the microprobe analysis support the observations that each feature contains a unique SU-8/PKHC ratio that was independent of the blend ratio. Plots of the SU-8/PKHC ratios in the discontinuous phase showed that the concentration of SU-8 in the spheres decreases as the concentration of SU-8 in the blend increases. Photolithography of the resin blends showed that even at low SU-8 concentrations a significant amount of SU-8 was present in the continuous phase.

The BSE photomicrographs and the observed degradation of the sample features during analyses suggested that the phase domains that had a high SU-8 content were enriched in photoinitiator. Measurements of the concentration distribution coefficient (D_c) for the photoinitiator revealed that the D_c changed as the fraction of SU-8 increased; in fact, the D_c decreased as the SU-8/PKHC decreased, indicating that initiator concentration correlates with the SU-8 concentration. This is not surprising since composition of the two phases used to calculate the D_c are changing also. Finally, a plot relating the Sb concentration to the weight of SU-8 yields a relationship that shows that the photoinitiator concentration is very dependent on the SU-8 concentration.

In summary, a two-phase polymer blend, containing a photoinitiator with different solubilities in each phase, was studied. The range of molecular weights of the resins results in each phase domain containing a different ratio of the two resins. Because of this, the photoinitiator does not evenly distribute between the two phases according to a simple partition model. Instead, the concentration of initiator in a phase domain is somewhat random and dependent on the concentration of SU-8 in that phase domain.

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