Controlling Photoimaging of Epoxies by Blending to a Specific Molecular Weight

DAVID J. RUSSELL, *IBM Systems Technology Division,*
1701 North Street, Endicott, New York 13760

Synopsis

An epoxy formulation developed for a photoimaging application was found to exhibit poor clean-out in the developing solvent depending on the lot of one of the base resins. Size exclusion chromatographic (SEC) analysis of the residual material showed it to be a high molecular weight (M_w) fraction of the base resin EpiRez SU-8. The resin was fractionated, and it was demonstrated that removing the high M_w fraction from the formulation enhanced its developability. Lower M_w versions of this resin were evaluated and found to be unsuitable. However, blending one of these resins (EpiRez SU-6) with the SU-8 resulted in a formulation that exhibited excellent developability. Mathematical relationships were calculated that enabled blends to be made, resulting in a defined molecular weight regardless of the lots of resins used.

INTRODUCTION

Photolithography has been widely used in the electronics industry for the manufacture of printed circuit boards and solid-state devices. The basic principle of photolithography is to utilize light-induced reactions to change the solubility of a polymeric material in a developer solvent. There are several texts that serve as a good introduction to lithography and the materials used.[1,2]
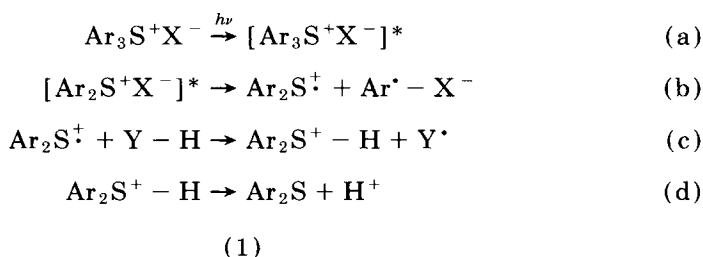
Photolithography, using a negative acting photoresist, typically involves the process flow outlined here: The photoresist is applied as a thin film on a substrate such as an epoxy–glass prepreg board or a prepreg board with copper laminated as the outside layers. A phototool such as a diazo or silver halide film or an emulsion-coated glass is placed on the resist film. The phototool is patterned with areas that are transparent to actinic radiation and other areas that are opaque. Upon exposure to actinic radiation of a sufficient expose dosage, those areas of the photoresist under the transparent portions of the phototool undergo polymerization. The areas unexposed do not react. Following exposure, the resist is developed. This typically involves spraying the resist with a solvent or solution in which the unexposed (unpolymerized) resist is soluble but the exposed (polymerized) resist is not. In this fashion, the image on the phototool is transferred to the resist and the substrate upon which the resist is applied. Subsequent processing could be done to etch away underlying copper in those areas where the resist is developed away, solder the copper that is exposed, etc.

In the imaging process outlined here, the develop step is extremely important. One must choose a solvent in which the unpolymerized resist is readily soluble. However, the solvent must not be aggressive enough to attack the polymerized material. In fact, one of the requirements for a developer solvent is that it be a minimal solvent for the resist.[3] Other chemical considerations include the

kinetics of the dissolution and the boiling point of the solvent.[3] Several processing parameters such as the temperature, spray nozzle configuration, spray pressure, and residence time in the developer can influence the results obtained in the imaging process.[4,5] Minimizing these can reduce the tendency of the solvent to swell the crosslinked portions of the resist. In fact, in many cases the physical action of the developing tool is of prime importance, especially when the developer is a marginal solvent.

One of the characteristics of an underdeveloped resist is incomplete clean-out at the foot of the resist.[4,5] Incomplete clean-out can range from this residual material at the foot of the resist to patches of residual resist remaining in the line channels and dissolved resist material redepositing on the surface of the resist. Also, some swelling of the resist may occur if the solvent can readily diffuse into the polymerized resist.[6] The choice of solvent can have a significant influence on the quality of the clean-out and the amount of residual resist, or scum, left in the line channels.[3,6]

A variety of chemistries may be employed in the formulation of photocuring films. Recently, much work has been done on the use of cationic curing of epoxies using onium salt chemistry.[7] The use of cationic systems enables photoimaging materials based on epoxy resins to be formulated. These materials have advantages over conventional systems employing acrylates polymerized using free radical chemistry such as no oxygen sensitivity during expose and stable shelf lives, and the final cured properties of epoxy resins for applications in speciality systems. The photopolymerization of epoxies typically involve a mixture of resins containing epoxide groups (oxirane rings) and a photoinitiator, which undergoes photodecomposition to produce a bronstead acid. One proposed mechanism for the photodecomposition of a triarylsulfonium salt is shown in Scheme 1.[7]

$$Ar_3S^+X^- \xrightarrow{h\nu} [Ar_3S^+X^-]^* \tag{a}$$

$$[Ar_2S^+X^-]^* \rightarrow Ar_2S^{+\cdot} + Ar^{\cdot} - X^- \tag{b}$$

$$Ar_2S^{+\cdot} + Y - H \rightarrow Ar_2S^+ - H + Y^{\cdot} \tag{c}$$

$$Ar_2S^+ - H \rightarrow Ar_2S + H^+ \tag{d}$$

$$(1)$$

In this scheme, the triarylsulfonium salt photolyzes to form a radical cation that abstracts a proton from a doner to eventually yield a proton. This proton can open an oxirane ring to directly link two epoxide groups, as shown in Scheme 2.

$$(2)$$
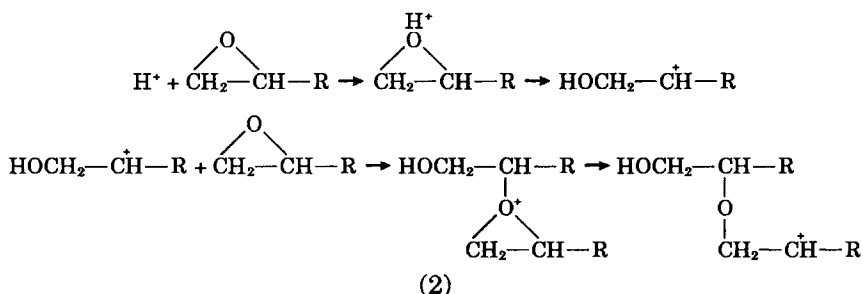
Propagation of this reaction results in a higher degree of crosslinking of the epoxy monomers. In many systems, the degree of polymerization can be controlled to some extent by the concentration of photoinitiator, the expose dose, and a controlled heating of the system following exposure.

Although cationic curing of epoxies has been used extensively for UV-curable coatings,[7,8] little has been published on the use of cationic chemistry in photolithography. Several examples of cationically cured photoimagable materials are listed in Refs. 9–12.

When processing a cationic resist system, the same factors applicable to a conventional resist must be considered. Among these is the optimization of the imaging process to yield the best resolution capabilities of the system. Some of these factors may be dictated by the chemistry of the system, such as the expose dose required to polymerize the resist to the desired level. Other factors, such as the choice of the developer solvent, may be defined by outside factors including environmental considerations, safety hazards, and compatibility with existing processes.

When formulating a photoresist, especially when properties such as flexibility, toughness, softening point, etc. are important, it is extremely useful to possess knowledge of the molecular weight distribution of the polymer system. In fact, properties such as those mentioned here are related to the molecular weight of the polymer.[13] Another property that is affected by molecular weight is the polymer solubility, which generally decreases with increasing molecular weight.[13,14]

Size exclusion chromatography (SEC) is one of several techniques that can be used to determine the molecular weight of a polymer.[14] There are several good general references such as one written by Yau, Kirkland, and Bly[13] that serve as introductions to SEC. In addition to the generation of the values of M_n, M_w, M_w/M_n, and M_z that describe the distribution, valuable information can be obtained by comparing the distributions contained in the chromatograms.[13] Recent advances in high-performance SEC has shown that this technique is applicable to small molecules,[15] including epoxy resins and mixtures thereof.[16]

In this work, a negative acting epoxy-based photoresist system employing cationic chemistry, A2, was formulated for a specific application. The process that was to be used included developing in 1,1,1-trichloroethane (known as methyl chloroform or MCF). This solvent proved to be a marginal solvent for developing A2. It was discovered that different lots of A2 developed differently, specifically with respect to the amount of scum left in the line channels. Several processing variables such as expose dose, developing time, temperature, and spray pressure were explored, but no set of parameters were found that completely eliminated this problem. Having exhausted the possibilities from an engineering aspect, some fundamental material properties, specifically differences in the molecular weight distributions, were investigated in an effort to establish a process for this material.

EXPERIMENTAL

Solvents. Tetrahydrofuran (THF), methylethyl ketone (MEK) HPLC grade (Burdick and Jackson, Muskegon, MI).

Standards. Polystyrene, M_w 35,000, 9000, 2000, and 800 (Supelco, Inc., Bellefonte, PA).

Resins. EpiRez SU-8, EpiRez SU-3, EpiRez SU-6 (Hi-Tek Polymers, Inc., Louisville, KY).

Equipment

HPLC. A Perkin-Elmer Series 4 pump was used with a model LC-85B variable wavelength detector operating at 279 nm and a Perkin-Elmer model LC-25 refractive index detector (thermostated at 30°C with a circulating water bath). A Perkin-Elmer ISS-100 autosampler was used for sample injection. A Perkin-Elmer model AFC-1 fraction collector was used in the prep scale experiments. A Perkin-Elmer model 3600 data station with Chromatographics 2 and GPC 5 software was used for data acquisition and processing.

Columns. *Analytical:* Toya Soda TSK 3000 HXL, 2500 HXL, and 1000 HXL column preceded by a TSK guard column (Varian Assoc., Sunnyvale, CA). These columns have a 5-μm particle size and pore sizes of 1500, 500, and 40 Å, respectively. *Prep-scale:* 2.5 cm ID $\times$ 120 cm Styrogel column of 1000 Å pore size (Waters Associates, Milford, MA).

Mobile Phase. Tetrahydrofuran, HPLC grade, was used without further purification (Burdick and Jackson, Muskegon, MI).

Procedure. *Analytical:* All compounds and standards were prepared as solutions in THF at an approximate concentration of 5 mg/mL. THF was used at 0.7 mL/min for the mobile phase. A 25-μL volume was used for each injection. *Prep:* SU-8 was prepared as a 12% solution in THF. THF was the mobile phase at 7.0 mL/min. A 1.0-mL sample size was injected. Fractions were collected and the solvent evaporated until several grams of fractionated SU-8 were isolated.

RESULTS AND DISCUSSION

An epoxy formulation was developed for a photoimaging application. The formulation consisted primarily of SU-8 octafunctional resin with several lower molecular weight additives. The molecular weight distribution of the formulation A2 is shown in Figure 1, and the lot of SU-8 used for the initial batch of A2 in Figure 2. The molecular weights (M_w) of the A2 and SU-8 were 5100 and 6060, respectively.

Preliminary process definition was done with A2. As part of the imaging process, parameters associated with the developing of the uncrosslinked resin system were optimized to give the best contrast and sidewall profile using MCF as the developer solvent. A SEM photo showing a typical, developed line channel is shown in Figure 3(a).

A subsequent production lot of the material was made. However, upon processing the material using the established conditions, poor clean-out of the unexposed areas was experienced. This "scumming" was observed in the developed out line channels and along the foot of the resist, and poor sidewall profiles were encountered as seen in Figure 3(b). Samples of patterned A2 were rinsed with MEK upon which it was observed that the MEK removed all visible scum without attacking the surface of the polymerized material. A chro-
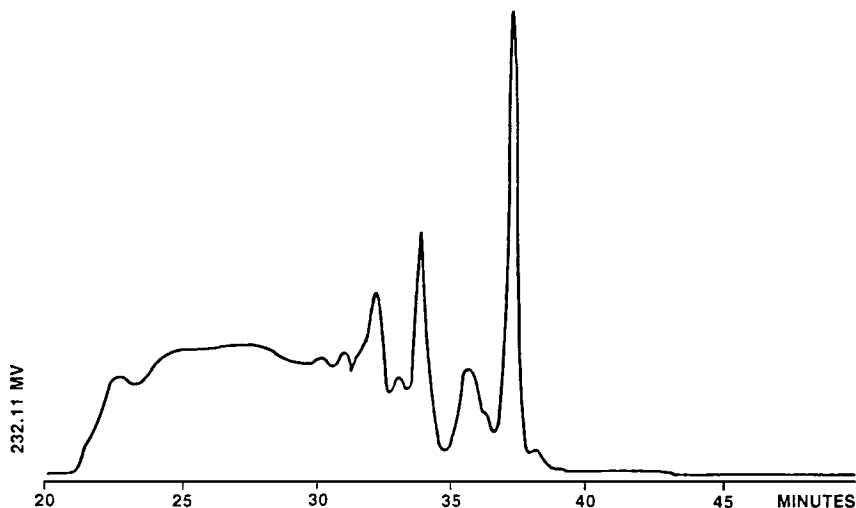
Fig. 1.   Molecular weight distribution of A2, original lot.

matogram of the MEK rinse is shown in Figure 4. A significant increase in the amount of the high molecular weight material can be seen. Upon examination of the lot of SU-8 used to manufacture lot 2 of the formulation, it was obvious that an increased amount of the high molecular weight shoulder was present [Fig. 5(a)]. The M_w's of the second lot of A2 and the SU-8 used in its manufacture were about 6900 and 8870, respectively. Subsequent lots of A2 seemed to display this scumming to differing degrees of severeness.

Several lots of the SU-8 used to make A2 were obtained and characterized by SEC. The molecular weights ranged from 6060 to 8870. Also apparent was the difference in the relative amount of the high M_w shoulder as can be seen
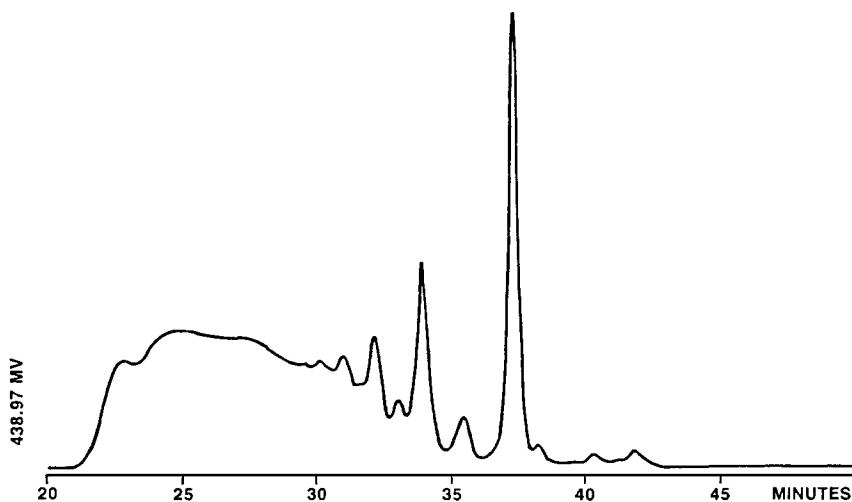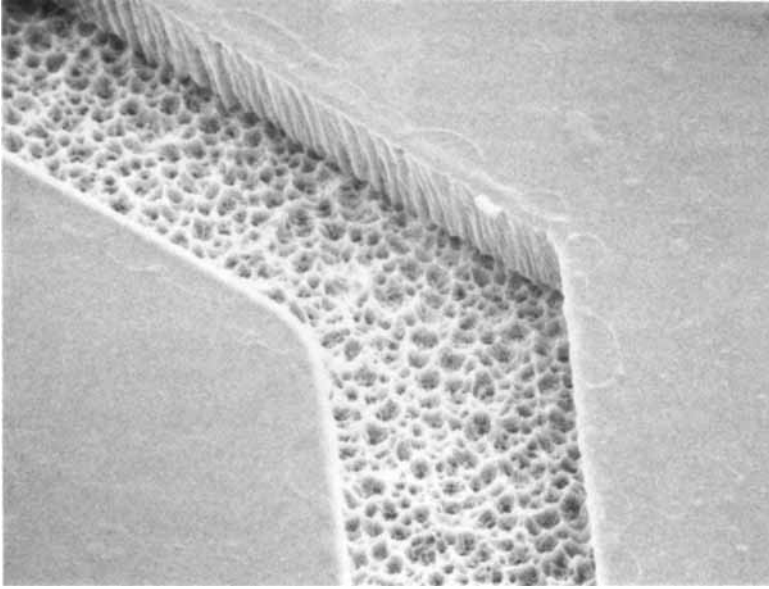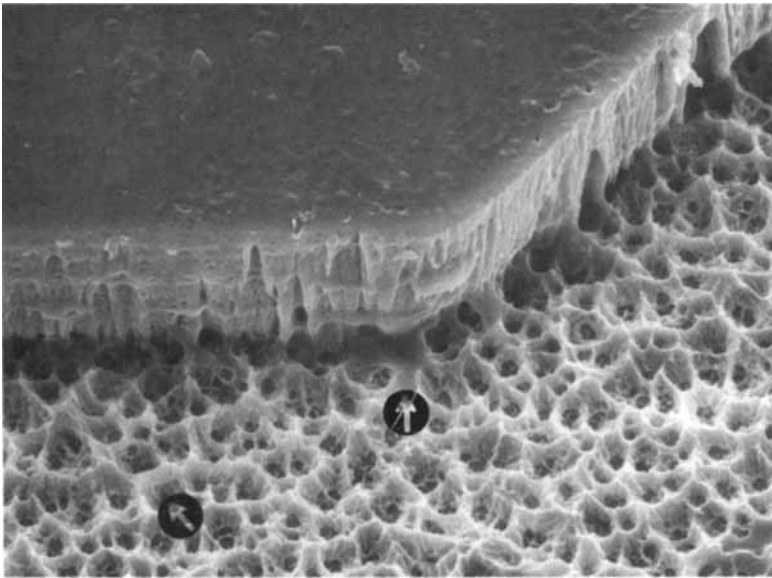

Fig. 2.   Molecular weight distribution of SU-8 lot 2.

A) CLEAN LINE CHANNEL, GOOD SIDEWALL

B) POORLY DEVELOPED LINE CHANNEL WITH POOR SIDEWALL AND RESIDUAL RESIST (SCUM).

Fig. 3.   Developed line channels: (a) Resist with intermediate amounts of high molecular weight resin; (b) resist with an increased fraction of high molecular weight material present.
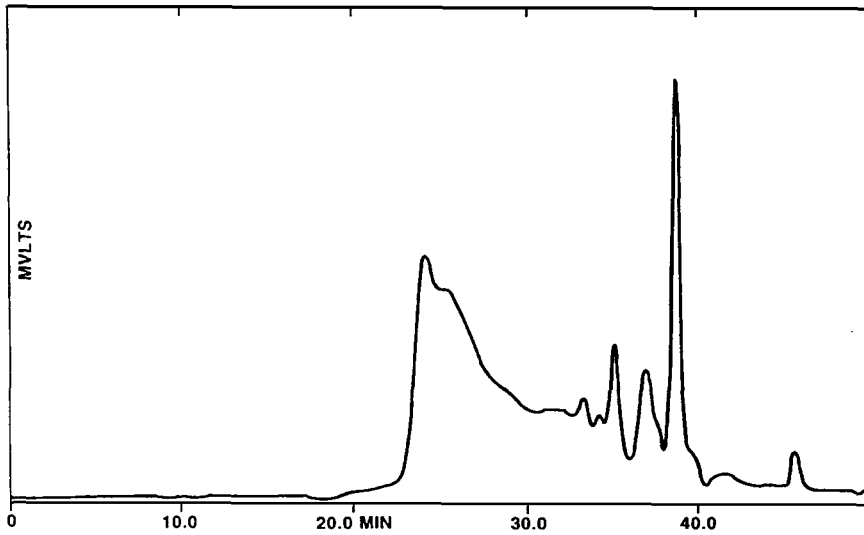
Fig. 4.   Molecular weight distribution of scum.

by comparing Figures 2 and 5(a). Imaging experiments indicated that there was a correlation between the amount of high molecular material present in the A2 and its ability to develop clean in MCF.

A semiprep GPC was set up and the SU-8 resin with the most amount of high M_w material [Fig. 5(a)] was fractionated to eliminate the high M_w shoulder [Fig. 5(b)]. Several grams of the fractionated material were collected and a trial formulation was made in the lab. Although some material properties were affected by removing all of the high M_w end of the distribution, it developed cleanly in MCF.
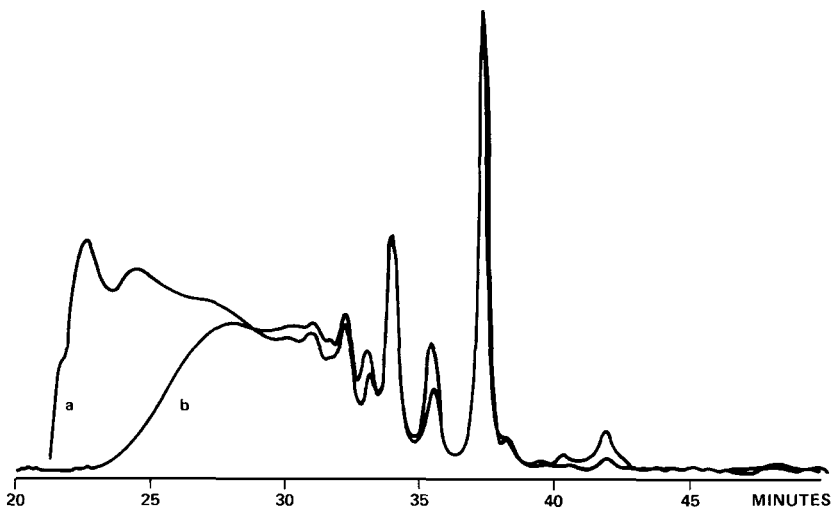

Fig. 5.   Molecular weight distribution of SU-8 lot 4: (a) unfractionated, (b) fractionated.

The fact that there appears to be a differential solubility between the high molecular weight fraction of the resin and the lower molecular weight fractions is not totally surprising, especially when the solvent is known to be a marginal one. In general, the effect of molecular weight on a polymer's solubility is minor compared to the chemical nature of the polymer but, nevertheless, plays a role.[14] Larger molecules, in addition to being less soluble than a smaller molecule in a given solvent, may also be kinetically slower to dissolve.[14] These interactions, however, plus the dependency on the specific configuration of the developer tool used, make it difficult to predict these results even if the solubility of the polymer system in the solvent is known.

The conclusion was made that some, but not all, of the high M_w material needed to be removed; or, more importantly, the relative amount of the high M_w material had to be controlled to enable consistent processing, as the developing of A2 seemed especially sensitive to variations in the high M_w material. Samples of additional materials with the same basic octafunctional epoxy novalak structure but differing molecular weights were obtained. It was thought that one of these might serve as a replacement for the SU-8 in the A2 formulation. Upon examining the size exclusion chromatogram of SU-3 [Fig. 6(a)], it was seen that, although there was far less high molecular weight material present, the amount relative to the bulk of the material (excluding the large amount of the diglycidyl ether of bisphenol A present at a retention time of 37.5 min) was similar to the original lot of SU-8. Indeed, when several blends of SU-8 and this SU-3 were characterized, no differences in the relative amounts of high M_w shoulder to the bulk could be discerned. The chromatogram of the SU-6 material obtained [Fig. 6(b)] looked essentially identical to the fractionated SU-8 [Fig. 5(b)] and resulted in similar properties when used as a replacement in A2.

Since it was felt that the basic properties were controlled by the bulk of the SU-8 (e.g., the medium M_w material) but influenced by the high M_w shoulder,
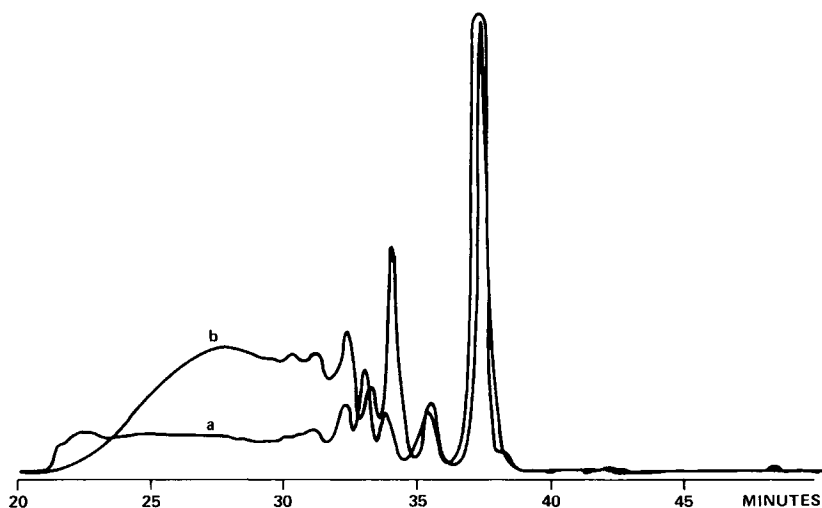

Fig. 6.   Molecular weight distribution additional octafunctional epoxies: (a) EpiRez SU-3, (b) EpiRez SU-6.

several blends of SU-8 and SU-6 were evaluated. Figure 7 shows the chromatograms of some select blends. This approach showed promise as a method to obtain the relative ratio of high to medium M_w material needed to enable a tight control of the process. In fact, it can be seen that the chromatogram of the blended material in Figure 7(c) strongly resembles the original lot of SU-8 used (Fig. 2).

Additional lots of SU-6 were obtained. The molecular weights ranged from 2700 to 3940, and none of the high M_w shoulder material was detected in any of the samples. Initial experiments done by trial and error using blends of different lots of SU-8 and SU-6 showed that good results were obtained with a certain amount of the high M_w shoulder present. At that point a method for controlling the M_w and predicting the amount of each resin in the blend was needed. Several things were tried. These included plotting the peak height (normalized) of the high M_w shoulder as a function of the fraction of SU-8, plotting the ratio of the normalized peak height to the medium molecular weight material as a function of the fraction of SU-8, and plotting the M_w as a function of the percent SU-8 in the blend. Although plots of the high M_w peak height gave a smooth curve with a high correlation, the best results were obtained by plotting the M_w as a function of the percent SU-8.

A plot of the M_w of several blends of an SU-8 lot and an SU-6 lot is displayed in Figure 8. A linear plot is obtained resulting in

$$M = 38.37S + 3950 \qquad r = 0.9997 \tag{1}$$

where M is the resulting molecular weight and S is the percent SU-8. Similar results were obtained using other lots of SU-8 and SU-6 in blends.

Several lots of blended material were evaluated for performance. Since the process was developed using the original lot of A2, it was desired to duplicate this lot during production. A plot of the molecular weight of a given lot of A2,
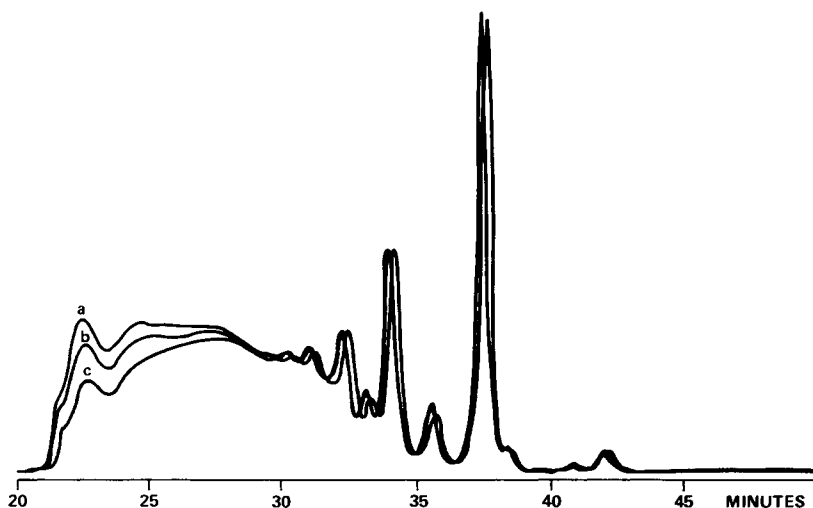

Fig. 7. Molecular weight distribution of blends of SU-8 and SU-6. (a) 80 : 20 SU-8 : SU-6; (b) 70 : 30 SU-8 : SU-6; (c) 60 : 40 Su-8 : SU-6.
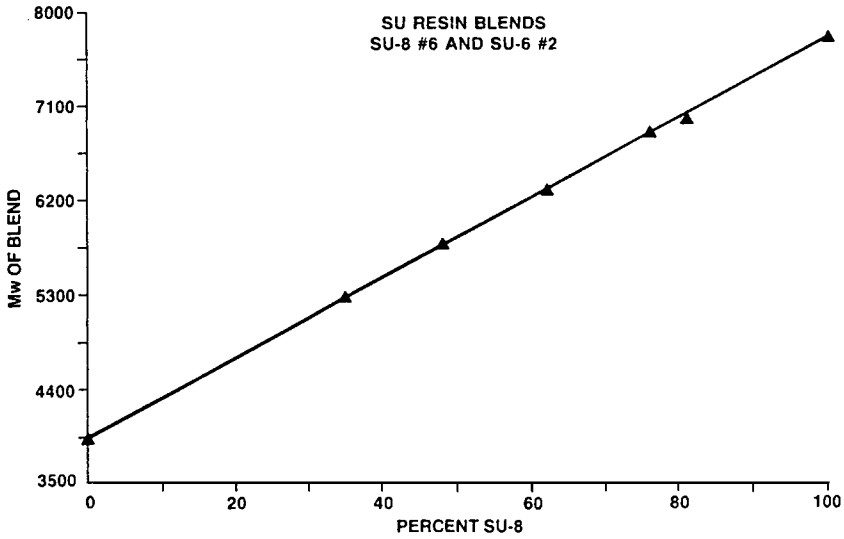
Fig. 8.   Plot of the molecular weight of the blend as a function of the percent SU-8.

as a function of the molecular weight of the SU-8 used in that lot, is graphed in Figure 9 and yields

$$M_{A2} = 0.69\,M + 910 \qquad r = 0.9974 \qquad (2)$$

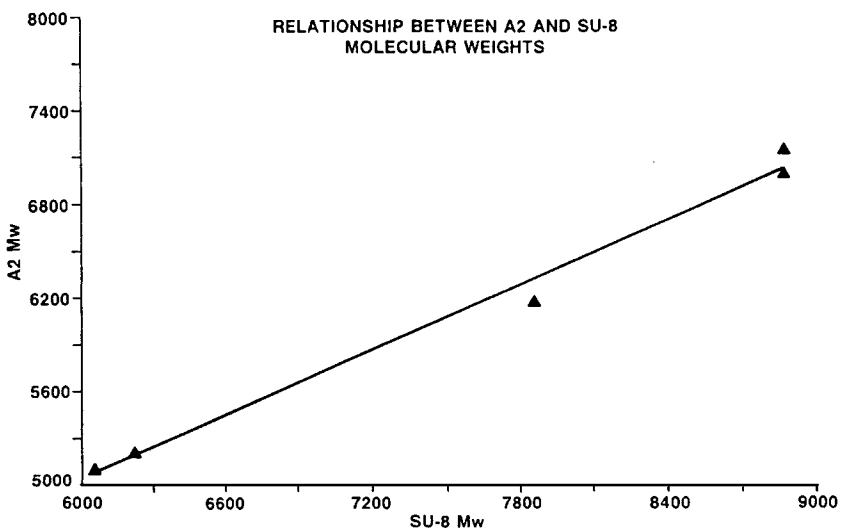where M_{A2} is the molecular weight of the A2 formulation and M is as defined in Eq. (1).

Fig. 9.   Plot of the molecular weight of A2 as a function of the molecular weight of SU-8.

With these relationships established, blends could be made to duplicate the original lot of A2. The M_w of the original lot of A2 (5100) is substituted for M_{A2} in Eq. (2), and the value of M calculated. Then a series of sample blends are made using the production lots of SU-8 and SU-6 available and the M_w's of the blends determined and plotted to obtain a relationship similar to Eq. (1). Using the value for M determined by Eq. (2) allows the proper percentage of SU-8 to be used. Figure 10 shows a dual plot of chromatograms of the original lot of A2 with a lot made with a blend of SU-8 and SU-6 as already described. Although minor differences can be seen between the chromatograms, the amount of the high M_w shoulder compared with the rest of the material is virtually identical. In fact, other blends were calculated to yield higher and lower M_w lots of A2 to explore the process windows and set limits on the specifications for the A2 material.

CONCLUSIONS

A formulation containing a high percentage of an octafunctional epoxy novalak resin (SU-8) was developed for a photoimaging application and was found to leave scum upon developing in 1,1,1-trichloroethane. Subsequent characterization by size exclusion chromatography showed that the developing process was particularly sensitive to the molecular weight of the material, especially the amount of a high M_w shoulder. An additional resin (SU-6) having a lower M_w and none of the high M_w shoulder material was blended with the SU-8. The resulting formulation exhibited good clean development. Relationships were developed relating the M_w of the formulation to the M_w of the blend used; consequently, formulations could be made to specific molecular weights to ensure processability. This method might be adopted to control other processing properties that are sensitive to molecular weight in other formulations for other applications.
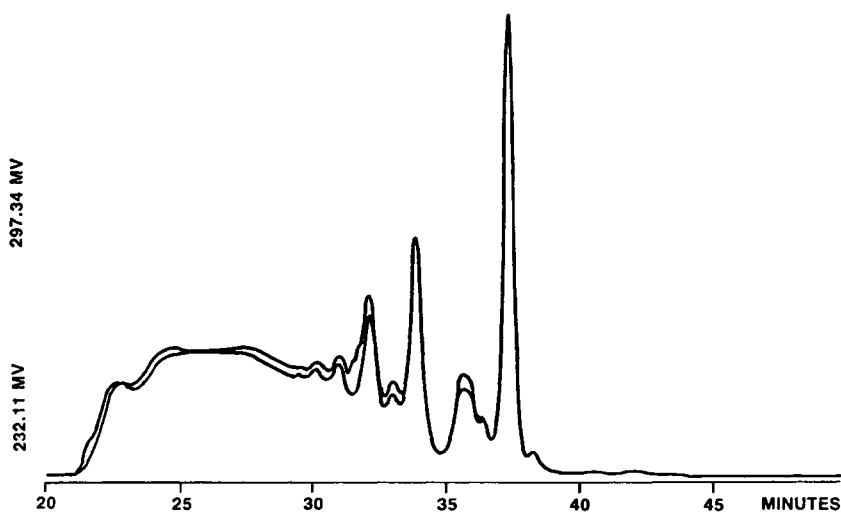

Fig. 10.   Molecular weight distributions of the original lot of A2 and a blend.

References

1. W. S. DeForest, *Photoresist Materials and Processes,* McGraw-Hill, New York, 1975.

2. L. F. Thompson, C. G. Wilson, and M. J. Bowden, Eds. *Introduction to Microlithography,* American Chemical Society, Washington, DC, 1983.

3. A. E. Novembre, L. M. Masakowski, and M. A. Hartney, *Polym. Eng. Sci.,* **26,** 1158 (1986).

4. J. F. Lucas, "Predicting Performance of Dry Film Photo Resist by Analysis of the Resist Sidewall," in *Proceedings of the Printed Circuit World Convention II,* Sheraton Hotel, Munich, June 9–12, 1981.

5. M. I. Gurian, "Reliable Fine Line Wet Processing," in *Proceedings of the Technical Program,* National Electronics Packaging and Production Conference, Anaheim, CA, February 25–27, 1986.

6. L. F. Thompson and M. J. Bowden, "Resist Processing," in L. F. Thompson et al., Eds., *Introduction to Microlithography,* American Chemical Society, Washington, DC, 1983, p. 161.

7. J. V. Crivello, "Photoinitiated Cationic Polymerization," in *UV Curing: Science and Technology,* S. Peter Pappas, Ed., Technology Marketing Corporation, Norwalk, CT, 1978.

8. *Proceedings of Radtech '88—North America,* New Orleans, April 24–28, 1988, RadTech International, Northbrook, IL, 1988.

9. P. Dickenson and M. Ellwood, U.S. Patent 4,548-890, Oct 22, 1985.

10. S. Newman, U.S. Patent 4,708,925, Nov. 24, 1987.

11. J. V. Crivello, U.S. Patent 4,193,799, Mar 18 1980.

12. J. V. Crivello, U.S. Patent 4,108,747, Aug 22, 1978.

13. W. W. Yau, J. J. Kirkland, and D. D. Bly, *Modern Size-Exclusion Liquid Chromatography,* Wiley-Interscience, New York, 1979.

14. F. W. Billmeyer, Jr., *Textbook of Polymer Science,* Wiley-Interscience, New York, 1984.

15. A. Krishen and R. G. Tucker, *Anal. Chem.,* **49,** 898 (1977).

16. D. J. Russell, *J. Liq. Chromatogr.,* **11**(2), 383 (1988).