High-Contrast, High-Sensitivity Aqueous Base-Developable Polynorbornene Dielectric

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ABSTRACT: The impact of multifunctional epoxy-based additives on the crosslinking, photolithographic properties, and adhesion properties of a tetramethyl ammonium hydroxide developable, polynorbornene (PNB)-based dielectric was investigated. Three different multifunctional epoxy additives were investigated: di-functional, tri-functional, and tetra-functional epoxy compounds. The tetra-functional epoxy crosslinker enhanced the UV absorbing properties of the polymer at 365 nm wavelength. It was found that the epoxy photo-catalyst could be efficiently activated without a photosensitizer when the tetra-functional epoxy was used. The polymer mixture with additional (3 wt %) tetra-functional epoxy crosslinker and without a UV sensitizer showed improved sensitivity by a factor of 4.7 as compared to a polymer mixture containing the same number of equivalents of non-UV sensitive epoxy with a UV sensitizer. The contrast improved from 7.4 for the polymer mixture with non-UV absorbing epoxy and a UV sensitizer to 33.4 for the new formulation with 3 wt % tetra-functional epoxy and no UV sensitizer. The addition of the tetra-functional epoxy crosslinker also improved the polymer-to-substrate adhesion, which permitted longer development times, and allowed the fabrication of high-aspect-ratio structures. Hollow-core pillars were fabricated in 96-µm thick polymer films with a depth-to-width aspect-ratio of 14 : 1. The degree of crosslinking in the cured films was studied by nanoindentation and swelling measurements. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Photosensitive polymer dielectrics materials are valuable in micro-electro-mechanical systems (MEMS) and microelectronics packaging.[1–5] The critical attributes of polymer dielectrics include mechanical properties, ease of processing, dielectric constant and loss, thickness range, and photosensitivity. Numerous photosensitive and nonphotosensitive polymers have been developed for various MEMS and microelectronics applications.[4,6–12] Dielectrics based on a polynorbornene (PNB) backbone are of interest because PNB has a low dielectric constant, low moisture uptake, and a high glass transition temperature.[3,13,14] Epoxy-based PNB polymers are useful in electronic packaging because they have excellent adhesion to substrates and modest cure temperatures.[3] The acid catalyzed activation of epoxy groups is an efficient way to induce epoxy ring opening and crosslinking to enhance the physical properties.[6]

Previously, an epoxy crosslinked, aqueous-base developed, PNB dielectric (Avatrel 8000P) was introduced for packaging applications.[3,10] Avatrel 8000P has straightforward processing parameters, high mechanical strength, and good thermal stability.[3] As

shown in Figure 1, the fluorinated alcohol and carboxylic acid groups on the PNB backbone provide solubility in aqueous base during developing and crosslinkable sites for the multifunctional epoxy additives.[3,10] The epoxy-based crosslinking of PNB can be initiated by an acid catalyst. This reaction has been studied with numerous epoxy systems.[12,15–17] The photo-initiated reaction is one that leads to the formation of a three-dimensional cross-linked network.[18–20] During exposure to ultraviolet (UV) radiation or elevated temperature, the photoacid generator (PAG) decomposes to form a protic acid (HX).[21,22] The acidic proton reacts with lone pair electrons on the epoxide oxygen, leading to epoxy ring opening and the formation of a hydroxyl group and a carbocation. Crosslinking occurs when the carbocation reacts with either a pendant carboxylic acid group of a neighboring polymer chain to form an ester linkage[23] or with a second epoxy ring to form a polyether linkage.[19]

PNB and epoxy mixtures can be made photosensitive by inclusion of a PAG to catalyze the epoxy ring-opening reaction. Raeis-Zadeh et al., have shown that the addition of a tetra-functional epoxy crosslinker, tetraphenylol ethane tetraglycidyl ether (4-EP), to the
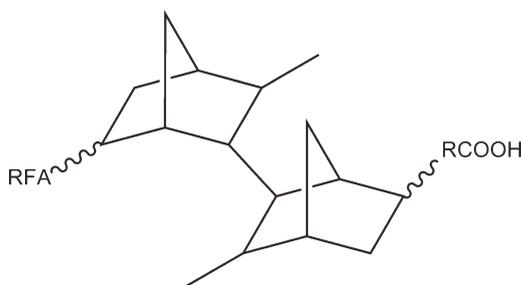
Figure 1. The chemical structure of the polynorbornene polymer (Avatrel 8000P).

PNB-PAG-epoxy mixture improves the crosslinking and photodefinition.[10] The addition of TPEGE resulted in high contrast, high sensitivity, excellent adhesion, and the ability to make high-aspect-ratio features. High contrast (γ) formulations ($\gamma = 24.2$) were patterned by developing in aqueous-base when 4-EP was added to the PNB polymer mixture. The contrast of the polymer was obtained by measuring the film thickness after developing as a function of exposure dose.[3,10] The contrast is defined by eq. (1).[24]

$$\gamma = \frac{1}{\log_{10}\frac{D_{100}}{D_0}} \quad (1)$$

where D_{100} is the minimum exposure dose where none of the photo-defined material is removed after exposure and developing at a fixed developing time, and D_0 is the maximum exposure dose where all of the polymer is soluble and removed during developing.

High-fidelity, hollow-core structures with aspect-ratios of 13 : 1, and vertical side-walls were fabricated in thick films.[10] The PNB formulation with additional 4-EP showed comparable mechanical strength and residual stress to SU-8, a commonly-used negative-tone epoxy-based dielectric. The elastic modulus and hardness were reported as 2.8 and 0.17 GPa, respectively, for the fully crosslinked films.[10] The elastic modulus of SU-8 is 3.3 GPa.[3] The hardness (H) was defined as the applied load per unit area of indentation, as given by eq. (2).[25]

$$H = \frac{P_{\max}}{A(h_c)} \quad (2)$$

where $P_{\max}$ is the maximum load and, $A(h_c)$ is the projected contact area for an indenter, and h_c is estimated for a geometrical constant (ε) by using the Oliver and Pharr model, eq. (3).

$$h_c = h_{\max} - \varepsilon\frac{P_{\max}}{S} \quad (3)$$

The results showed that the incorporation of a small quantity of 365 nm, UV absorbing 4-EP to Avatrel 8000P resulted in efficient energy absorption and transfer to the PAG resulting in epoxy activation and crosslinking. However, the UV sensitizer used in the Avatrel 8000P formulation does not participate in polymer crosslinking and remains in the polymer film as a low-molecular-weight additive. Such additives, which do not become part of the final polymer matrix, can result in inferior proper-

ties compared to purer formulations. In this report, a new approach to creating higher sensitivity photosensitive formulations with superior photodefinition properties without noncrosslinking additives has been found. We improved the polymer crosslinking and photodefinition properties by replacing the sensitizer and epoxy additive package with 365-nm absorbing 4-EP. The results are compared to previously reported formulations, in which a noncrosslinking additive was used as the UV absorbing sensitizer.[10] Also, the effect of similar multifunctional epoxy-based crosslinkers on the physical and photochemical properties of the PNB-based dielectric was investigated so as to enhance the resolution, aspect-ratio, adhesion, and photo-speed of the formulation. These epoxy crosslinkers, which have the same phenol groups resulting in UV absorption at 365 nm as in 4-EP, have different functionalities. The structures of the epoxy-based crosslinkers used in this study are shown in Figure 2, and are identified as 4-EP, 3-EP, and 2-EP hereafter.
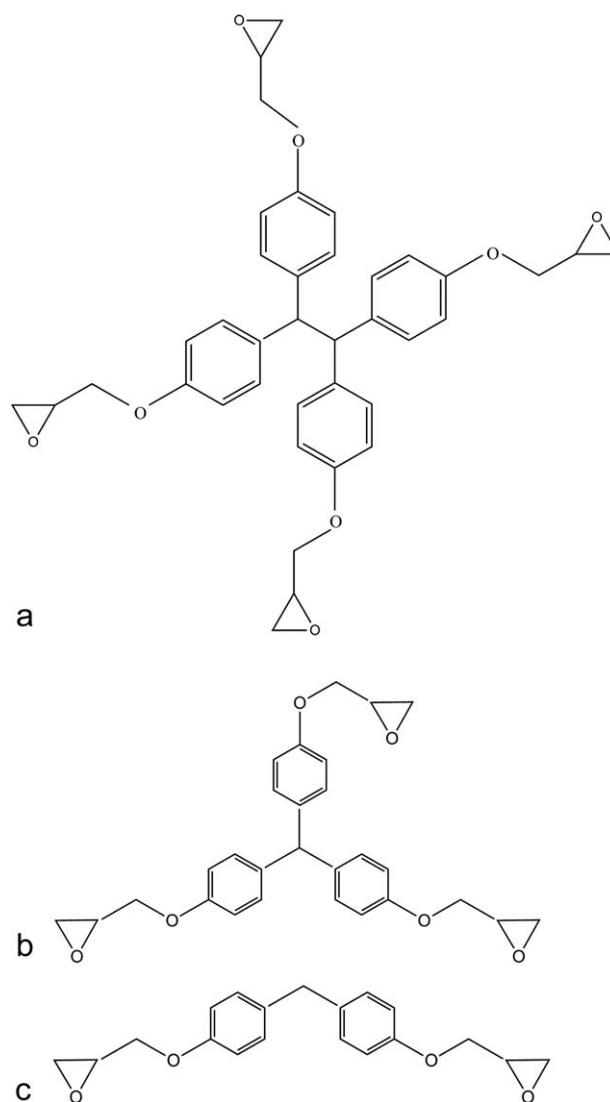

Figure 2. (a) The chemical structure of tetraphenylol ethane tetraglycidyl ether, 4-EP (b) triphenylol methane triglycidyl ether, 3-EP (c) bisphenol F diglycidyl ether, 2-EP.

Table 1. Polynorbornene Formulations

Polymer formulation	Title
Base polymer (Avatrel 8000P)	BF
BF with no CPTX	BC
BF with supplementary 1 wt % 4-EP	A
BC with supplementary 1 wt % 4-EP	B
BC with supplementary 3 wt % 4-EP	C
BF with supplementary 1 wt % 2EP	D
BF with supplementary 1 wt % 3EP	E

EXPERIMENTAL

The functionalized PNB polymer (Avatrel 8000P) was provided by Promerus LLC (Brecksville, OH). The polymer mixtures were formulated by mixing the PNB polymer, multifunctional epoxy crosslinkers, an UV radiation sensitizer, a PAG, and an adhesion promoter in propylene glycol monomethyl ether acetate (PGMEA) solvent. 1-chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) was used as a photosensitizer.[20,26] PGMEA, CPTX, and epoxy-based crosslinkers were purchased from Aldrich Chemical. A summary of the formulations made with the multifunctional epoxy crosslinkers tetraphenylol ethane tetraglycidyl ether (4-EP), triphenylol methane triglycidyl ether (3-EP), and bisphenol-F diglycidyl ether (2-EP) are listed in Table 1. The epoxy crosslinkers were dissolved in PGMEA and ball-milled with the PNB resin for 72 h. For the thick-film samples, the polymers were spin-coated on <100> silicon wafers using a CEE 100CB Spinner at 1000 rpm for 30 s producing about 40 μm thick films. The films were soft-baked at 100°C for 10 min in an oven (air ambient) to remove the residual solvent. The effect of exposure dose was studied using a variable-density optical mask (Opto-line International Inc.). Contact printing was used to evaluate the aspect-ratio of the photo-defined structures. UV exposures were performed using a Karl Suss MA-6 Mask Aligner with a 365-nm filter. The samples were postexposure baked in an oven at 100°C for 8 min. The thin-film samples (25 μm) were spin-coated at 1500 rpm for 30 s. Polymers were both soft-baked and postexposure baked at 100°C for 5 min on a hotplate. The exposed films were developed using Shipley MF-319 [0.26N tetramethyl ammonium hydroxide (TMAH)] developer. After developing, the films were cured in a nitrogen-purged furnace at 160°C.[11] The temperature was ramped at 5°C/min and held at the temperature for 1 h. The furnace was allowed to cool slowly to the ambient temperature by natural convection.

The film thickness was measured after the postexposure bake with a Veeco Detak profilometer. Solid samples were dissolved in PGMEA. The swelling of thick-film samples was evaluated using an Ohaus Voyager Pro balance with readability of 0.0001 g and linearity of ±0.0002. Quasistatic nanoindentation was performed on thin-film samples with a Triboindenter nano-indenter (Hysitron, Minneapolis, MN). The indenter was located on an antivibration table and enclosed in an acoustic housing. A Berkovich tip was loaded to 7500 μN in 10 s, held for 10 s, and unloaded to 250 μN in 2 s. To minimize the impact of the substrate on the indentation results, the maximum force was chosen so as to indent less than 5% of the film thickness, which was 25 μm. Additionally, to exclude edge effects, an array of points was indented in the center of the samples. The maximum drift rate of the experiments was set to 0.1 nm/s and was determined over a period of 40 s. The curvature of the Berkovich tip was between 250 and 970 nm. The Oliver-Pharr model was used to analyze the load-depth curves.[3] The hardness was obtained from eq. (2) and the reduced modulus was extracted from the 20 to 95% portion of the unloading curve. To mitigate the effect of thermal drift, the first data points were discarded so that the average hardness and modulus only included indents above 500 nm.

A 1 wt % solution of 3-aminopropytriethoxy silane (3-APS) in ethanol (90% ethanol) was applied on the substrate surface in all experiments to enhance the film-to-substrate adhesion. The solution was spin-coated at 300 rpm for 10 s followed by a higher-speed spin at 1500 rpm for 20 s. To remove excess ethanol, the samples were baked at 130°C for 15 min on a hotplate. A 15 s ethanol rinse was used to remove excess material.

RESULTS AND DISCUSSION

Previously, it has been shown that the addition of as little as 1 wt % of 4-EP significantly improved the photodefinition properties of Avatrel 8000P. The contrast improved from 7.37 for Avatrel 8000P [identified as the base formulation (BF)] to 24.2 for the formulation with the addition of 1 wt % 4-EP (formulation A). Additionally, 4-EP showed high UV absorptivity at 365 nm. The sensitivity of the polymer was enhanced by a factor of 3.7 by the addition of 1 wt % 4-EP. In BF, CPTX, a noncrosslinking UV absorber, was used as the photosensitizer. Additives such as CPTX, which do not become a part of the final polymer matrix, reside within the final polymer structure and can result in property degradation as compared to purer formulations. In this work, the feasibility of using 4-EP, which is a tetra-functional crosslinker with a high UV absorptivity, was investigated as the only UV absorber in the polymer mixture. New formulations with 1 wt % 4-EP (formulation B) and 3 wt % 4-EP (formulation C) (no CPTX) were investigated. The sensitivity and photodefinability of the polymers were compared to those of BF and formulation A. The mechanical properties and the degree of moister uptake of the formulations were studies to determine the effectiveness of using 4-EP as the photosensitizer and crosslinker on the properties of the cured films.

Contrast experiments were performed to compare the contrast and sensitivity of the formulations. The contrast curves for formulation B and C are shown in Figure 3. The addition of 4-EP increased the developing time for the polymer. The developing time for BF was 3.00 min, while the developing time for formulation B and C were higher at 4.30 and 4.50 min, respectively. These results show that, 4-EP improved the polymer-to-substrate adhesion and also affected the solubility of the unexposed film in the aqueous-base developer. The increased adhesion and longer developing time with formulation B and C is because of higher degree of epoxy ring opening and resulting reaction with the surface. That is, in the presence of 4-EP, epoxy rings are fully reacted, improving the polymer-to-substrate adhesion.
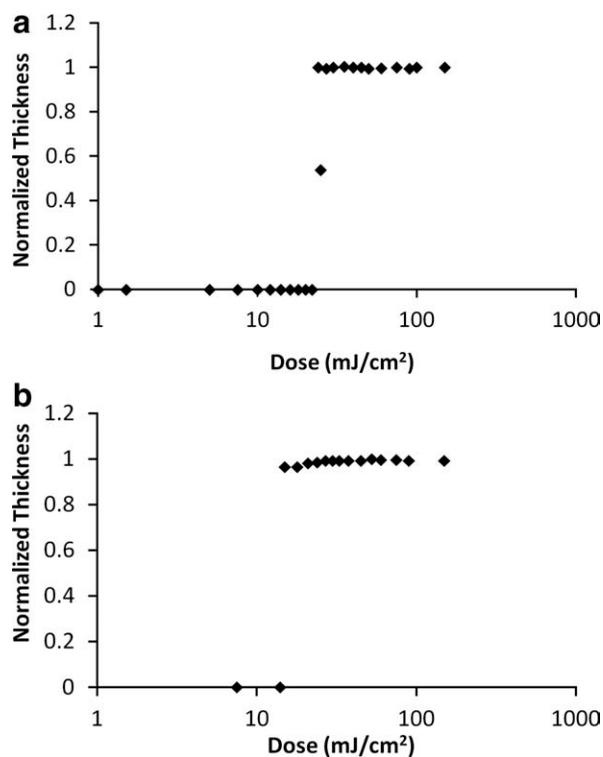
Figure 3. Contrast curve for (a) formulation B, (b) formulation C.

Additionally, 4-EP resulted in fractional epoxy ring opening after spincoating and baking (soft-bake and PEB). This effect was investigated previously in unexposed samples using FTIR spectroscopy where it was shown that some of the epoxide rings had reacted, resulting in some degree of crosslinking in the unexposed regions after the 100°C postexposure bake.[10] These effects were only observed in the presence of 4-EP, showing that 4-EP significantly improved the polymer adhesion characteristics and affected the polymer dissolution behavior.

Photosensitivity is one of the critical characteristics of a photoresist or a permanent dielectric. Upon the absorption of UV radiation within the polymer film, PAG activates and produces an acid within the polymer film, catalyzing the epoxy ring opening reaction, which leads to polymer crosslinking. In BF, the UV absorption was increased by adding CPTX as the sensitizer to the polymer formulation. In this case, energy transfer occurred between the sensitizer and the PAG, creating the acid catalyst. As shown in Figure 3(a), structures were patterned with formulation B at doses as low as 16 mJ/cm^2, which is an extremely low value compared to the D_{100} value for BF, 66 mJ/cm^2. This improvement in the sensitivity for the mixture containing 4-EP, compared to BF, is attributed to greater interaction between the UV sensitizer and the acid catalyst. That is, although 4-EP has less UV absorptivity as compared to CPTX (used in BF), it is more effective than CPTX because once it absorbs UV radiation and activates the PAG (via energy transfer), the epoxy functionalities are guaranteed to be within close proximity of the photogenerated acid.

Formulation B showed slightly higher sensitivity as compared to formulation A (16 mJ/cm^2 for formulation B compared to 18 mJ/cm^2 for formulation A). One reason could be the more

effective energy transfer between 4-EP and PAG (compared to that of CPTX and PAG) since CPTX does not participate in polymer crosslinking and remains in the polymer film as a low molecular weight additive. The same effect was observed in formulation C [Figure 3(b)]. The sensitivity of formulation C improved compared to that of BF and the D_{100} value deceased from 66 mJ/cm^2 for BF to 14 mJ/cm^2 for formulation C. It can be concluded that the addition of 4-EP to the polymer in the absence of CPTX results in more efficient energy transfer and creation of the acid catalyst (compared to the use of CPTX as a sensitizer), which results in greater crosslinking.

To further investigate the effect of 4-EP on the photodefinability of the polymer, contrast values were calculated from the slope of the line connecting D_0 to D_{100}. As it can be seen from Figure 3(a), the addition of 1 wt % 4-EP to BF in the absence of CPTX significantly improved the contrast. The contrast value increased from 7.37 for BF to 26.5 for formulation B. Commonly used photoresists have been reported to have a contrast of 2 to 3,[27–29] and the contrast for high-contrast chemically amplified photoresist ranges from 6 to 10.[30–32] This improvement in contrast of the polymer is due to the addition of 1 wt % 4-EP and omission of CPTX. The addition of 4-EP resulted in more effective crosslinking within the polymer because of its higher functionality (four epoxy units/molecule) compared to the di- and tri-functional crosslinkers in BF. 4-EP has a greater chance of crosslinking two or more PNB polymer strands. This should result in greater crosslinking and lower solubility at low exposure doses (closed to D_0 where not all the epoxy has reacted), and improved contrast. We also note that photosensitive materials with higher sensitivity, e.g., 4-EP formulations, also generally have higher contrast.

Contrast experiments were also performed for formulation C, which had a higher 4-EP concentration. As shown in Figure 3(b), the addition of 3 wt % of 4-EP further improved the polymer contrast resulting in an extremely high value of 33.4. This contrast value is one of the highest contrast values reported for photosensitive materials in the literature. This improvement in contrast is due to the same reasons mentioned earlier: achieving a critical degree of crosslinking at lower doses, higher epoxy functionality for the crosslinker, and higher sensitivity of the polymer due to the addition of 4-EP. These results show that the addition of 4-EP to BF as the UV sensitizer significantly improved the polymer crosslinking, contrast, and photosensitivity.

The ability to fabricate high-aspect-ratio features is a function of the contrast, sensitivity, and adhesion characteristics of the photosensitive material. Since formulations B and C showed significant improvement in these parameters compared to BF, the ability to fabricate high-aspect-ratio features was investigated and compared to that of BF. For this work, hollow-core structures were chosen since they are difficult to fabricate due to the restricted transport of the developer into the spatially restricted core of the structure compared to the transport of the developer to the outside of the structure. Thick films were photopatterned at an exposure dose of 100 mJ/cm^2, at 365 nm, with formulation B resulting in 39 μm tall, hollow-core, triangular-shaped structures. Double coating was performed for formulation C, which resulted in 97 μm thick films. Because of the improved polymer-to-substrate adhesion with 4-EP, the unexposed
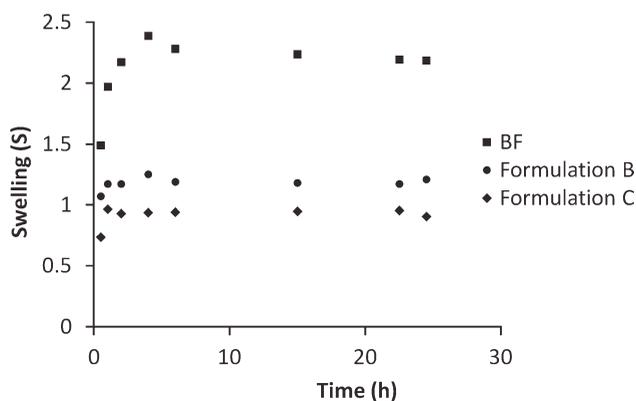
Figure 4. Influence of 4-EP on swelling of a fully crosslinked cured polymer.

polymer film at the center of the structure were fully dissolved before delamination occurred at the outside edge of the polymer structure. Hollow-core features with 3 μm diameter openings were fabricated in 39 μm thick films using formulations B. Hollow-core features with 7 μm diameter openings were fabricated in double-coated, 97 μm thick films using formulations C. The resulting aspect-ratio for formulation B was 13 : 1, while that of formulation C was 14 : 1. To confirm complete development of the center core region of the structure for the formulations with additional 4-EP, copper was electroplated in the hollow core portion of the film after a 2 min plasma (RIE) descum. If the polymer was not fully developed from the center core, electroplating would not occur. It was concluded that the center core of the structures was fully developed because copper electroplating occurred in the center region of structures patterned with both formulation B and C. As shown previously, the highest aspect-ratio achieved for BF in 39 μm films was 5 : 1. Fabrication of higher aspect-ratio structures with BF required longer developing time to fully develop the center core, which led to film delamination and lifting. Thus, only formulations with the additional 4-EP crosslinker had sufficient adhesion, contrast, and sensitivity to produce features with an aspect-ratio of greater than 13 : 1. It can be concluded that the use of 3 wt % 4-EP with no CPTX resulted in higher contrast, sensitivity, film-to-substrate adhesion, and aspect-ratio (formulation C).

To study the effect of 4-EP on the crosslink density and mechanical properties of formulations B and C, the reduced modulus and hardness of these formulations were compared with those of BF using nanoindentation. Previously, Avatrel 8000P formulations showed slight degradation of the polyether linkages between the epoxy crosslinkers at cure temperatures above 160°C.[33] This decomposition mechanism has been studied for similar PNB systems by Chiniwalla et al.[19] In this study, all samples were tested after a 160°C cure for 1 h. BF, formulation B, and formulation C had a reduced modulus of 2.80, 2.84, and 2.86 GPa, respectively. The hardness values for BF, formulation B and formulation C were 0.13, 0.14, and 0.14 GPa, respectively. These results show that 4-EP resulted in a slight improvement in the mechanical properties. Also, there were no apparent negative changes to the film by adding 4-EP. All films were

relatively crack resistance and showed good adhesion to the substrate as discussed previously.

To investigate the actual degree of crosslinking, swelling experiments were performed. A lower degree of crosslinking will result in greater solvent absorption and swelling.[34] Swelling tests were performed in PGMEA after a final cure at 160°C for 1 h. The mass of each sample was measured at eight different times during a 24 h swelling period. The percent increase in weight was calculated from eq. (4), as shown in Figure 4. Each data point is the average of four measurements, and the standard deviation was less than 0.0003.

$$S = \frac{W_t - W_0}{W_0} \qquad (4)$$

where S is the swelling, W_t is the weight of sample swollen with solvent at time t, and W_o is the sample weight in dry state.[35,36]

As shown in Figure 4, the sample weight increased with the swelling time. The sample weight of BF significantly increased compared to that of the formulations with additional 4-EP. These observations agree with the previous results discussed above. The degree of swelling decreased from 2.1 for BF to 1.2 and 1.0 for formulations B and C, respectively. The degree of swelling was greater for BF because it had a lower molar epoxy content than the other formulations, resulting in a lower crosslink density and higher water uptake. The addition of the 4-EP crosslinker to the polymer increased the degree of crosslinking between the epoxy and the polymer reaction sites, especially in the case of formulation C.

It was shown that the addition of 4-EP to BF improved the polymer photosensitivity and photodefinability. To study the effect of having the UV absorbing moiety within the epoxy crosslinker (compared to non-UV absorbing epoxy with added sensitizer), new formulations were made with 2-EP and 3-EP, which have negligible UV absorption compared to 4-EP. 2-EP and 3-EP compounds have similar structures to 4-EP, except for
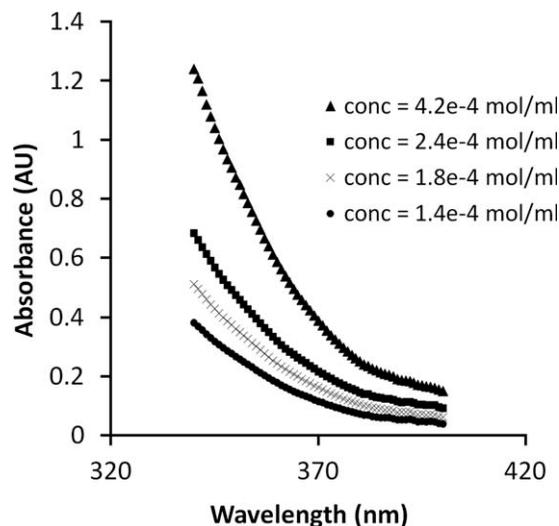

Figure 5. Changes in UV–vis spectrum of dilute solution of 3-EP in PGMEA from 200 to 600 nm.
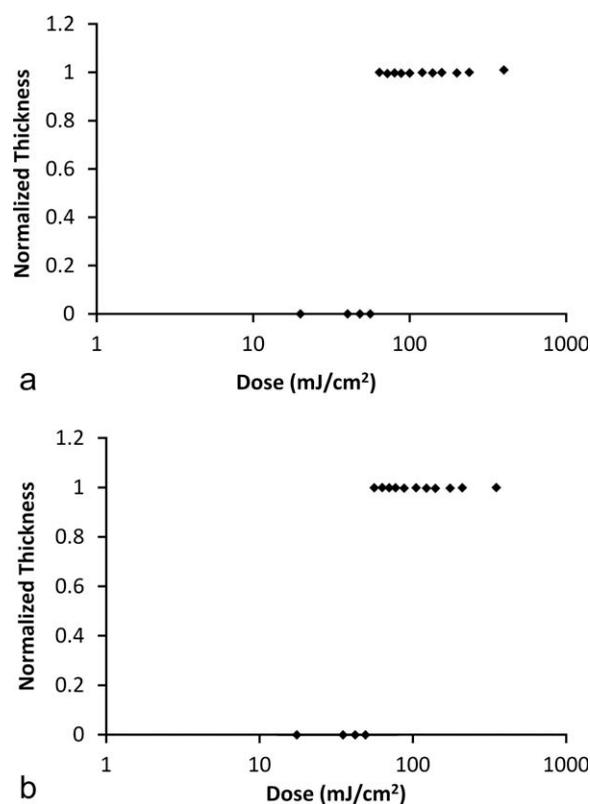
Figure 6. Contrast curve for (a) formulation D and (b) formulation E.

the number of pendant epoxy rings. The organization of the 4-EP pendant groups leads to high UV absorbance, not found in 2-EP and 3-EP. Formulation D and E were prepared (with 2-EP and 3-EP compounds, respectively) so as to contain the exact number of equivalents of epoxy as formulation A, Table 1. To evaluate the impact of 2-EP and 3-EP on the polymer photosensitivity at 365 nm, a series of UV absorption experiments were conducted. The absorbance of dilute solutions of 2-EP and 3-EP were measured in PGMEA, which was transparent in the wavelength range of interest.[10] 2-EP had very low absorbance at wavelengths from 300 to 400 nm while 3-EP had higher molar absorptivity in the UV, Figure 5. However, the absorptivity of 3-EP in PGMEA was low as compared to the absorptivity of a dilute solution of 4-EP and CPTX in PGMEA. The molar absorbance of 3-EP, 4-EP, and CPTX are 113 (L/mol m), 172,287 (L/mol m), and 395,779 (L/mol m), respectively. The high UV absorptivity of 4-EP from 300 to 400 nm is due to the ethyl

linkage in the chemical structure of the 4-EP molecule. 2-EP and 3-EP showed lower sensitivity compared to 4-EP because of the methyl group in the center of their structure.

Contrast experiments were performed to compare the sensitivity and the contrast of the formulations. As shown in Figure 6, contrast values of 11.4 and 11.5 were obtained for formulation D and E, respectively. The contrast values for formulations D and E were higher than that for BF ($\gamma = 7.4$), because of the added epoxy; however, it is lower than that of formulation A ($\gamma = 24.2$). The developing time also increased from 3.00 to 3.40 min for formulations B and C, respectively, due to the higher epoxy content of these formulations. This shows that additional epoxy crosslinker affected the solubility of the unexposed polymer and somewhat improved the polymer-to-substrate adhesion. The D_{100} value of these formulations was similar to that of BF, Table 2, showing that 2-EP and 3-EP did not affect the polymer sensitivity. This result is congruent with the previous observation that 2-EP and 3-EP have very low UV absorptivity at the wavelength of interest.

The ability to fabricate high-aspect-ratio structures is one of the most desirable attributes of a photosensitive polymer. The effect of the 2-EP and 3-EP crosslinkers on the patternability of high-aspect-ratio features was evaluated. Hollow-core features with 3 μm diameter opening were fabricated in 39-μm thick films using formulation D and E. Both formulations resulted in 5 : 1 aspect-ratio structures, and the development of higher-aspect-ratio structures resulted in film delamination. Previously, an aspect-ratio of 5 : 1 and 13 : 1 were obtained for BF and formulation A, respectively.[10] This shows that only 4-EP improved the polymer ability to pattern high-aspect-ratio structures because of the improved sensitivity, contrast and adhesion.

Nanoindentation was used to evaluate the reduced modulus and hardness of formulation A, D, and E, compared to BF. The reduced modulus of formulations A, D, and E (160°C cure for 1 h) was 2.84, 2.85, and 2.84 GPa, respectively. All formulations resulted in a hardness value of 0.14 GPa. The results show that there was no significant difference between the mechanical properties of the various formulations with additional epoxy crosslinker, which implies a similar crosslink density. The lower modulus value for BF is simply due to the lower epoxy content, resulting in a lower number of crosslinks.

Swelling experiments were performed to investigate the relative degree of crosslinking. The mass of each sample was measured

Table 2. Properties of PNB Formulations

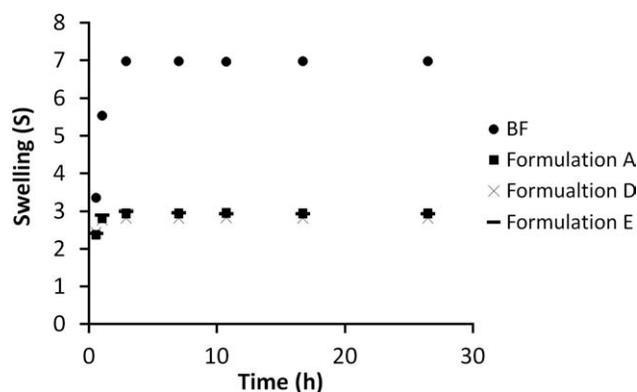| Formulation	Contrast (γ)	Sensitivity (D_{100}, mJ/cm^2)	Developing time (min)	Aspect-ratio (height : width)	Modulus (GPa)	Hardness (GPa)
BF	7.37	66	3	5 : 1	2.80	2.13
A	24.2	18	4 : 30	13 : 1	2.84	2.14
B	26.5	16	4 : 15	13 : 1	2.84	2.14
C	33.4	14	4 : 50	14 : 1	2.86	2.14
D	11.4	65	3 : 40	5 : 1	2.85	2.14
E	11.5	65	3 : 40	5 : 1	2.84	2.14

Figure 7. Influence of 2-EP, 3-EP, and 4-EP crosslinker on swelling of crosslinked cured polymer.

at six different times during a 26 h swelling period. Each data point is the average of four measurements and the average of standard deviation for each point was less than 0.0003. Figure 7 shows an increase in weight with the swelling time. No significant difference was found between formulation A, D, and E when the epoxy content was identical. This shows that the addition of a crosslinker to the polymer increases the degree of crosslinking between the epoxy and the polymer reaction sites, regardless of the functionality of the crosslinker. This agrees with the nanoindentation results, showing that each epoxy compound resulted in a similar degree of crosslinking. The degree of swelling was greater for BF because it has a lower molar epoxy content than the other formulations.

CONCLUSIONS

The tetra-functional epoxy-based crosslinker with high UV absorptivity at 365 nm, 4-EP, was used as the photosensitizer in the polymer. 4-EP was used to replace the noncrosslinking UV sensitizer in the polymer resulting in improved photolithographic characteristics and sensitivity. 4-EP resulted in a more effective acid-catalyzed route to epoxy crosslinking within the polymer compared to the noncrosslinking photosensitizer. The addition of a small quantity of 4-EP (3 wt % of solution) resulted in improved UV sensitivity of the polymer at 365 nm. The di- and tri-functional crosslinkers (with similar chemical structures) showed no significant effect on the polymer sensitivity. The contrast value of the polymer, 7.4, increased to 33.4 by the addition of 3 wt % of 4-EP. A minor increase in the contrast of the base polymer was observed through the addition of the di- and tri-functional crosslinkers. The polymer with additional 4-EP crosslinker showed excellent polymer-to-substrate adhesion enabling the fabrication of 14 : 1 high-aspect-ratio structures with high-fidelity and straight side-walls. It can be concluded that 4-EP can replace the photosensitizer in the polymer formulation and improve the polymer patternability and photosensitivity. The addition of 4-EP to the polymer resulted in high contrast, high sensitivity, excellent adhesion, and the ability to make high-aspect-ratio structures, making this polymer suitable for MEMS and microelectronics packaging applications.

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