Positive Tone, Polynorbornene Dielectric Crosslinking

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The processing and properties of a positive-tone, aqueous develop, epoxy crosslinked permanent dielectric based on a polynorbornene (PNB) backbone and bis(diazonaphthoquinone) (DNQ) photosensitive compound were investigated. The developing and cure properties of the films were studied as a function of cure temperature, epoxy crosslinker loading and DNQ loading. Reduced modulus measurements showed that crosslinking of the polymer film occurred via reaction of the polymer with DNQ. The final modulus of the DNQ-crosslinked film was 4.0 GPa. Swelling measurements for a UV exposed film showed material leaching from the film. Residual solvent from swelling measurements was analysed by gel permeation chromatography which showed the indene carboxylic acid form of DNQ leached out of the polymer film. The unexposed film did not exhibit material loss through leaching. When developed, films showed a decline in modulus to 2.6 GPa, likely due to the reaction of DNQ with the aqueous base developer forming nonreactive byproducts that did not contribute to crosslinking. An epoxy crosslinker was added to the formulation which helped crosslink the polymer film by inhibiting uptake of the aqueous base during developing. The epoxy inhibition of the base uptake was confirmed by quartz crystal microbalance, where an increase in epoxy loading led to a decrease in base uptake of the film during developing. ^{19}F-NMR results support the DNQ-PNB crosslinking through esterification. Electrical characterization of the cured PNB films showed a relative dielectric constant of 3.65 for a DNQ and epoxy containing film after curing at 220°C.

Microelectronics packaging faces a continuing challenge to accommodate scaling of electronic components to smaller size and higher performance. A higher density of electronic components requires superior dielectrics, such as in the form of photo-definable dielectrics to insulate the components electrically and mechanically support them.[1]

Polynorbornene (PNB) has shown promise for use as a dielectric because of its low dielectric constant and good mechanical properties.[2] The photo-definability can be achieved with a negative tone or positive tone chemistry. Negative tone materials become less soluble in a developer when exposed to UV radiation, whereas positive tone materials become more soluble in a developer when exposed to UV irradiation. Negative tone PNB dielectrics have been well studied.[3–7] A positive tone chemistry is desirable for packaging applications, because the film is less sensitive to mask defects or particulates during exposure.

Positive tone photo-definability has previously been demonstrated with a bis(diazonaphthoquinone) (DNQ) added to a polynorbornene polymer.[8] The DNQ additive in the PNB film inhibits dissolution by formation of a hydrogen bonded complex. Ultraviolet exposure causes the DNQ to undergo the Wolff rearrangement to form an indene carboxylic acid. Unlike DNQ, the indene carboxylic acid does not extensively hydrogen bond to the PNB, leading to the solubility switch of the PNB in aqueous base.[9] DNQ-based photochemistry is compatible with an aqueous developer which is more environmentally friendly than solvent-based developers.

A permanent dielectric can be achieved with an epoxy-based crosslinking and DNQ-based photochemistry, similar to previous PNB films.[3,4] Trimethylolpropane triglycidyl ether (TMPTGE) was used as the crosslinking agent with a random PNB copolymer of a fluoroalcohol norbornene and carboxylic acid norbornene, shown in Figure 1. DNQ was used as the photo active compound. This study provides evidence for DNQ crosslinking in the positive tone PNB dielectric.

Experimental

The PNB polymers were a random copolymer of a norbornene fluoroalcohol (75%) and norbornene carboxylic acid (25%) and a homopolymer of norbornene fluoroalcohol (Promerus LLC, Brecksville, OH). Monofunctional and difunctional DNQs were obtained from Promerus LLC. Propylene glycol monomethyl ether acetate (PGMEA), deuterated chloroform, TMPTGE and 3-aminopropyl triethoxysilane (3-APTES) (Sigma-Aldrich) were used as-received. Microposit Developer MF-319, 0.26 N tetramethylammonium hydroxide, was obtained from Doe and Ingalls (Durham, NC). 100 mm diameter, ⟨100⟩ p-doped silicon wafers were used as the substrate for the experiments. Mixtures of PNB, PGMEA, photoactive compound (PAC) and crosslinker were made and allowed to ball-roll for at least 24 h before use. Table I shows the formulations used in this study with additive concentrations given in parts per hundred parts PNB mass (pphr).

The silicon wafers where pretreated with 3-APTES to improve adhesion. A 2 wt% solution of 3-APTES in acetone was puddled on the silicon wafer for 30 s. The wafer was then sprayed with acetone while spinning at a rotation speed of 2500 rpm for 60 s. The PNB mixtures were spin-cast onto silicon wafers using a CEE 100CB spinner at a rotation speed of 2500 rpm for 60 s. The films were soft baked on a hot plate for 2 min at 100°C. The film thickness was measured using a Veeco Dektak profilometer. Films were developed with MF-319 in an agitated puddle fashion. The films were cured in a nitrogen-purged furnace. The temperature of the furnace was ramped to the cure temperature over a period of 130 min, held at the peak temperature for 2 h, and allowed to cool slowly to ambient temperature.

The reduced modulus of the spin-cast films was determined using a Hysitron Triboindenter in a quasistatic nanoindentation mode. A north star standard head diamond tip was used for a varying load of 150 to 550 μN. A constant load time of 20 s was used. Maximum indentation depth across all samples was less than 8% of the film thickness. To minimize variables from the stress of the film, the formulations were spin-coated onto 6.5 cm^2 area silicon substrates. The reduced modulus was determined using Equation 1.[10]

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{dP/dh}{\sqrt{A}} \qquad [1]$$

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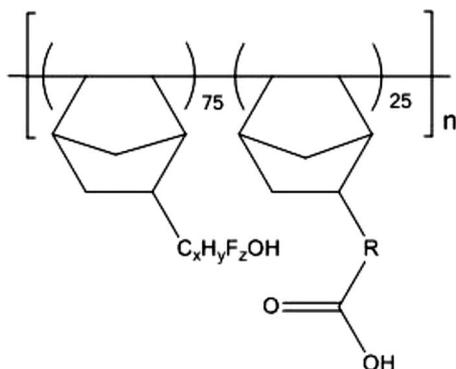zE-mail: kohl@gatech.edu

Figure 1. Random copolymer of polynorbornene with fluoroalcohol and carboxylic acid functionalities.

E_r is the reduced modulus of the material, β is a geometric constant on the order of unity, dP/dh is the slope of the linear portion of the unloading curve, and A is the projected area of the indentation. The projected area of indentation was estimated via Equation 2 by calibration to a polycarbonate standard.

$$A = C_o h^2 + C_1 h + C_2 h^{1/2} + C_3 h^{1/4} + \ldots + C_8 h^{1/128} \qquad [2]$$

Curve-fitting was used by adjustment of the constants C_o to C_8, where C_o is by definition 2.598 for a north star tip. The contact depth from experiment, h_c, was obtained by Equation 3.

$$h_c = h_{max} - \epsilon \frac{P_{max}}{S} \qquad [3]$$

P_{max} is the maximum load, h_{max} is the maximum displacement, ϵ is a geometric constant for the indenter tip, and S is the stiffness. Equations 2 and 3 are the method described by Oliver and Pharr.[11]

Dissolution rates were determined using a Stanford Research Systems (QCM 200) quartz crystal microbalance (QCM). The samples were spin-coated onto a 2.54 cm QCM with 5 MHz unloaded resonant frequency and an active surface area of 0.4 cm^2. The coated QCMs were developed with MF-319 in a 125 μL flow cell connected to a Thermo Scientific 800 μL min^{-1} peristaltic pump. A manual valve positioned 5 cm from the inlet of the flow cell was placed in the flow path to alternate between water and MF-319. The polymer-coated QCM samples were first equilibrated in water before developing to minimize sharp frequency and resistance changes that result from an immersion into a liquid from air. Equation 4 was used to determine the mass changes (Δm).

$$\Delta f = - \frac{2 f_o^2}{A_q \sqrt{\rho_q \mu_q}} \Delta m \qquad [4]$$

Δf is the resonant frequency change, f_o is the resonant frequency of the unloaded quartz crystal, A_q is the active area between the gold electrodes, ρ_q is the density of quartz, and μ_q is the shear modulus of quartz. The thickness was calculated by taking the density of the polymer to be 1.3 g cm^{-3}, as obtained from measuring thickness and mass.

The swelling measurements were performed in PGMEA. Each polymer was submerged in PGMEA and a sample was removed from the PGMEA at 15 minute intervals. Each polymer type was measured

TABLE I. Formulation List. Concentrations are given in parts of chemical per hundred parts PNB mass.

Formulation ID	PAC (concentration)	Additive (concentration)
PNB	None	None
PNB – E	None	TMPTGE (10 pphr)
PNB – D	bis-DNQ (20 pphr)	None
PNB – D & E	bis-DNQ (20 pphr)	TMPTGE (10 pphr)

multiple times and the trends were consistent. Since each individual sample was slightly different (e.g. mass) the values could not be averaged. One data set is shown along with its corresponding gel permeation chromatography (GPC) results. The mass of the polymer was taken after removing excess solvent from the surface. Equation 5 was used to calculate the swelling ratio, or the percent increase in mass of the polymer film.

$$Swelling\ Ratio = \frac{m_i - m_o}{m_o} \qquad [5]$$

In Eq. 5, m_i is the mass of the polymer film at the ith time interval and m_o is the initial mass of the polymer film prior to submersion in PGMEA.

The molecular weight measurements were made by GPC using a Waters 2690 separation module and a 2410 differential refractive index detector. These were connected to Waters Styragel columns (HP 1, HP 3, and HP 4), and THF was used as an eluent and solvent. The molecular weight was compared to polystyrene standards. Fluorine nuclear magnetic resonance (^{19}F NMR) spectroscopy was performed in a Varian Mercury Vx 400 MHz. All samples were dissolved in deuterated chloroform. Heated attenuated total reflectance (HATR) measurements were performed in a Nicolet Magna-IR 560 Spectrometer.

Dielectric measurements were conducted by fabrication of parallel-plate capacitors with a bottom electrode formed from evaporated aluminum metal with a thickness of 300 nm covering the full surface of an oxidized wafer. After spin-coating and curing the film onto the metal substrate, a second layer of metal was deposited through a shadow mask to form the top electrode of the parallel plate capacitor. Contact to the top and bottom metal electrodes of the capacitor was made on a Karl Suss probe station. The capacitance and dielectric loss tangent were measured using a Gwinstek LCR-821 meter. The real part of the relative dielectric constant, ε_r, was determined using Equation 6.

$$\varepsilon_r = C \frac{t}{A \varepsilon_o} \qquad [6]$$

In Eq. 6, C is the capacitance, t is the thickness of the polymer, A is the area of the top electrode pad, and ε_o is the permittivity of free space, 8.854×10^{-12} F/m. ASTM standard D150 – 11 was used to correct the measurements for edge fringing.[12] There were 9 to 15 capacitors tested for each data point (average and standard deviation) presented in the results.

Results and Discussion

Previously, crosslinking in a negative tone polynorbornene material was observed through acid-catalyzed ring-opening of an epoxy.[4] Efficient polymer patterning and crosslinking with a minimal amount of invasive additives is of interest. PNB patterning was achieved via UV exposure and developing of the DNQ additive. Figure 2 shows the UV irradiation induced Wolff rearrangement of DNQ that results in the indene carboxylic acid (III). UV radiation causes the loss of the diazo group and forces a rearrangement of the aromatic ring to form a ketene (II). The ketene is a very reactive species that will react with water to form the indene carboxylic acid (III).

Polymer films with 20 pphr difunctional DNQ and varying loadings of the trifunctional epoxy, TMPTGE, were exposed to a UV dose of 2000 mJ/cm^2 and cured at 200°C for 2 hr. The exposure dose was sufficient to convert the DNQ to the indene carboxylic acid. The cured polymer films were soaked in PGMEA to evaluate the swelling of the polymer which gives an indication of the crosslinking density. Figure 3 shows the swelling ratio for the exposed and cured films expressed as percent mass increase.

The data shows that increasing the epoxy loading leads to higher apparent solvent uptake even though the films were fully cured. The film without epoxy (i.e. zero pphr epoxy) is not shown because the film dissolved in the swelling solvent within the first 15 min. The 2 and 5 pphr epoxy films show a maxima in the solvent uptake after fifteen minutes followed by a decline in mass. The 10 pphr epoxy film
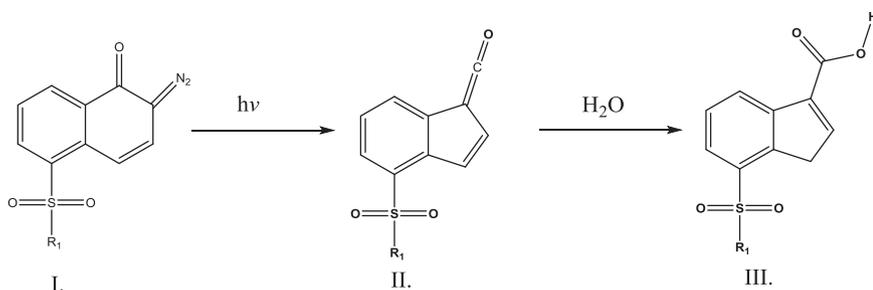
Figure 2. Wolff rearrangement of DNQ moiety (I) to ketene intermediate (II) and with the presence of water to indene carboxylic acid (III).

maintained a constant swelling ratio of approximately 0.18 over all swelling times.

The behavior for the 10 pphr epoxy film was typical for a crosslinked epoxy-based polynorbornene film.[5] After 15 minutes in the swelling solvent, the film was saturated with solvent and the mass uptake of the polymer film did not increase with additional time in the solvent. The maximum uptake in solvent seen in the 2 and 5 pphr epoxy films (followed by a decline in mass with additional time) is uncommon and is the result of swelling and leaching of material from the film. The mass increase at the longest times in the solvent was lower with smaller epoxy loadings supporting the concept that the decrease is due to mass loss from leaching. Higher epoxy loading leads to a greater crosslink density and less material being leached from the film. Compounds that can be leached during swelling studies have the potential to act as mobile charge carriers in a dielectric, increasing the permittivity.

The solvent used in the swelling experiments was analysed by GPC to investigate the leaching of additives from the film. Each solvent was analysed after 90 min of exposure to the samples. A lower retention time corresponds to a higher molecular weight solute in the solvent.

There were two peaks of note in the GPC at retention times of 16 and 25 minutes. The 16 minute retention time corresponds to a material with a molecular weight of approximately 180,000 Da. The 25 minute retention time corresponds to a material with a molecular weight of 880 Da. The polymer film with no TMPTGE, which at least partially dissolved in the solvent, had a broad peak at 16 min retention. This broad peak is consistent with the polymer prior to processing. At 25 min retention, the indene carboxylic acid form of the difunctional DNQ molecule is most apparent in samples containing 0 to 5 pphr TMPTGE. The indene carboxylic acid does not readily react with TMPTGE possibly due to the limited mobility and proximity of the indene carboxylic acid and epoxy.

A set of unexposed films with the same TMPTGE loadings were created to further understand the role of the epoxy. A typical swelling result for the unexposed PNB films is shown in Figure 4. Multiple samples were tested and all gave consistent results. GPC data was collected for the sample used to obtain the data displayed in Fig. 4.
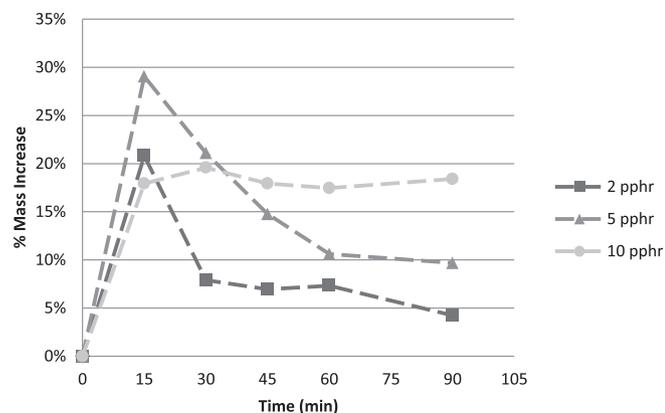
All films remained after 90 min exposure to PGMEA. No significant difference was seen between films containing 2, 5, and 10 pphr TMPTGE loading. The 0 pphr TMPTGE film did not dissolve in the swelling solvent, as occurred with the UV exposed film. A comparison of the exposed and unexposed films of the same composition (TMPTGE loading) can be made. The fact that an unexposed film with no TMPTGE does not dissolve in the swelling solvent and the exposed film does, indicates that additional crosslinking occurred in the unexposed films compared to the exposed films. This additional crosslinking likely occurred via the DNQ, becasue its presence is the only difference between the formulations which dissolved (i.e. UV exposed) and did not dissolve (i.e. unexposed). The swelling behavior of the films containing different amounts of TMPTGE support this conclusion. Unexposed films do not drastically lose mass in the same manner as exposed films, suggesting that the ICA is not an effective crosslinker in the final polymer structure.

The products of the thermolysis of DNQ are likely similar to those formed from UV irradiation, however, when the films were not exposed to UV radiation, the DNQ reaction occurred at a high temperature in the absence of water. The diazo bonds are the least stable ones in the DNQ compound and are the most thermally labile. Without water, the reactive ketene intermediate of the Wolff rearrangement does not convert to a carboxylic acid but is instead available for crosslinking in the unexposed case.

Determining the thermal stability of the DNQ additive was found to be important to understanding the mechanism that likely occurs for DNQ crosslinking. HATR was performed on a thin film of formulation PNB–D to investigate the disappearance of the DNQ diazo FTIR peak. A thin film of PNB-D was doctor bladed onto the ATR crystal. The thin film was heated to 130°C at a ramp rate of 3°C/min and the film was maintained at 130°C for 2 hr. Figure 5 shows the HATR curves at the cure temperature of 130°C as a function of time. The 2050-2175 cm^{-1} region corresponds to the diazo peaks.[13] As time increases, moving down the chart, the diazo peaks area decreased.

The HATR results show a thermal degradation of the diazo group of the DNQ. A thermal degradation of the diazo group leads to a ketene via the Wolff rearrangement. The 130°C cure for 2 hr was sufficient
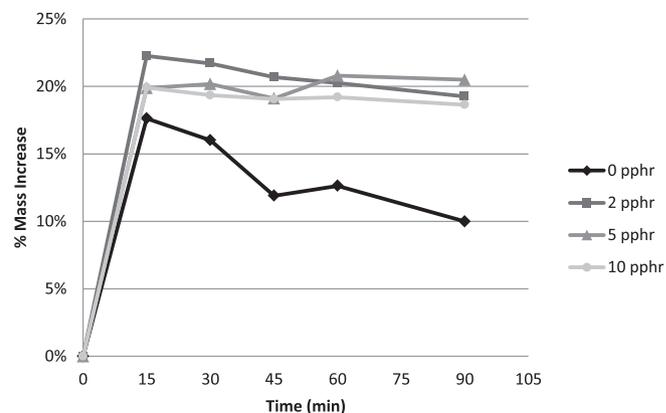

Figure 3. Swelling ratio versus soak time in PGMEA for various TMPTGE loadings (given in pphr) in an exposed, cured film.
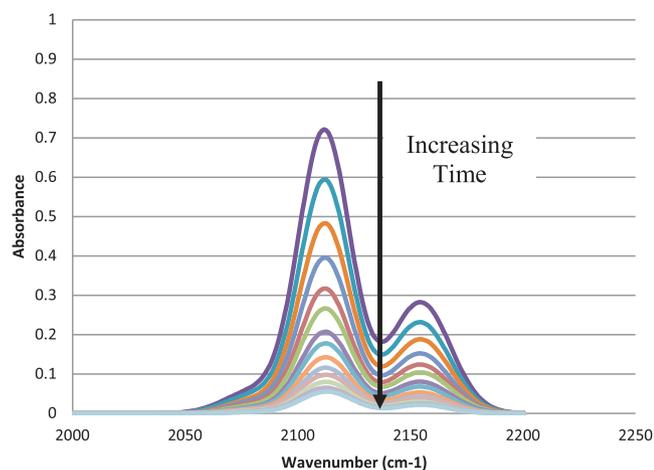

Figure 4. Swelling ratio versus soak time in PGMEA for various TMPTGE loadings (given in pphr) in an unexposed, cured film.

Figure 5. Attenuated total reflectance at 130°C for 2 hours of characteristic diazo peaks (2050-2175 cm^{-1}); absorbance units are arbitrary.

Figure 7. Reduced modulus versus cure temperature of developed PNB–D and PNB–D & E.

energy to remove 98% of the diazo group. Thus, the majority of the DNQ moieties have sufficient thermal energy to form the ketene at the cure temperatures used in this study.

A chemical reaction between the epoxy and the reacted DNQ can occur during curing which likely affects the physical properties of the polymer film. To investigate the consequences of the DNQ crosslinking on the mechanical properties of the material, films were created with the four formulations in Table I, PNB, PNB–D, PNB–E, and PNB–D & E. The reduced modulus was used to compare the mechanical properties of the films. Figure 6 shows the reduced modulus for the four formulations at different cure temperatures. The cure temperature range shown should be high enough to thermally activate the DNQ.

The PNB modulus maintains a consistent value of 2.2 GPa across all temperatures, as expected. During the cure step, a polymer film without a crosslinker did not decrease in modulus as no reaction should be occurring. There was a decrease in modulus when the samples were cured at the highest temperatures, 220°C. It is known that the properties of epoxy-type materials are sensitive to exposure to temperatures above 200°C for long periods of time, such as the two hour cure performed here. Degradation of the crosslinking moieties and/or densification of the films is possible.[3,4] This data shows that curing and long-term exposure to temperatures at or above 220°C should be avoided if changes in modulus are to be avoided. Indentation
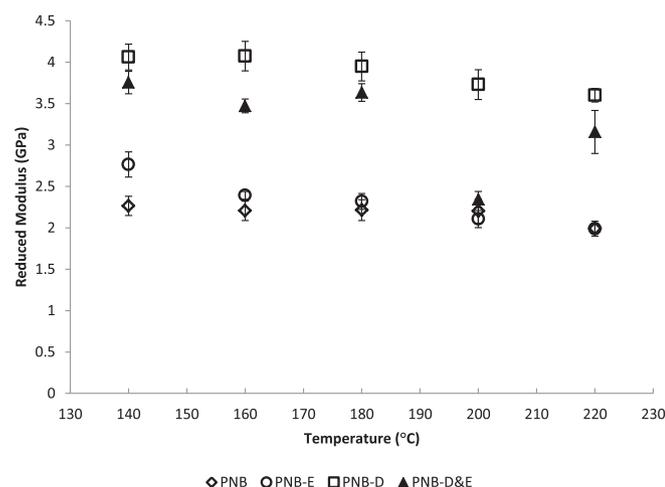
prior to the cure step also showed a modulus of 2.2 GPa. Upon adding TMPTGE to the polymer, or PNB-E, the modulus increased slightly, but the modulus declined with increasing temperature.

Upon adding DNQ to the film, PNB-D, the modulus nearly doubled to 4 GPa. This result shows that DNQ participates in crosslinking. The rigid ballast molecule of DNQ contributes to the polymer structure, as reflected in the higher reduced modulus.

The effect of added, small molecule epoxy functionalities on the curing properties was also investigated. Adding TMPTGE to the formulation, PNB-D & E, causes the modulus to decrease slightly to 3.6 GPa. This decrease compared to the DNQ-only sample is likely a consequence of plasticization of the film by TMPTGE. The structure of TMPTGE would allow for more movement after crosslinking compared to the rigid DNQ structure.

Although the reduced modulus of the undeveloped films provides valuable information, a developing step would normally be used prior to curing the films. PNB–D and PNB–D & E were developed prior to curing. Figure 7 shows the reduced modulus of the developed films versus the cure temperature.

Although the modulus of PNB was 4 GPa after adding DNQ to the undeveloped film, a drop in modulus was observed when the DNQ-loaded film, PNB–D, was developed in aqueous base, MF-319, before curing. The modulus dropped to 2.7 GPa (standard deviation of 0.4 GPa) when cured after exposure to base. Adding TMPTGE to a developed film increased the modulus to the undeveloped value PNB–D, 4.0 GPa. TMPTGE either reduces base uptake in the film during developing or benefits the crosslinking in a similar manner to DNQ, which as previously shown is not likely. This is significant, because when creating features with a DNQ-based, photo-definable PNB dielectric, base will penetrate into the film.

Exposure of DNQ to base has also been shown to lead to side-products.[14] Figure 8 shows two possible products of the base-catalyzed DNQ reaction. This reaction renders the DNQ unable to crosslink the polymer. DNQ crosslinking can also be inhibited by water-uptake during the base develop step through formation of the indene carboxylic acid. Since the intended use of the PNB dielectric material is a photo-definable, permanent dielectric, the aqueous develop step is unavoidable. Base uptake can inhibit the DNQ crosslinking significantly affecting the reduced modulus of the film.

Without an additive to reduce or prevent the aqueous base from swelling into the film, a significant drop in the modulus may occur as the DNQ crosslinking reaction is inhibited. Base uptake was likely minimized by the TMPTGE. The modulus of the TMPTGE-loaded polymer, PNB–E (shown in Figure 6), does not exhibit a modulus that is much different than the base polymer. The epoxy likely does not contribute significantly to the modulus and more likely inhibits DNQ by-product creation to allow this increase in reduced modulus.

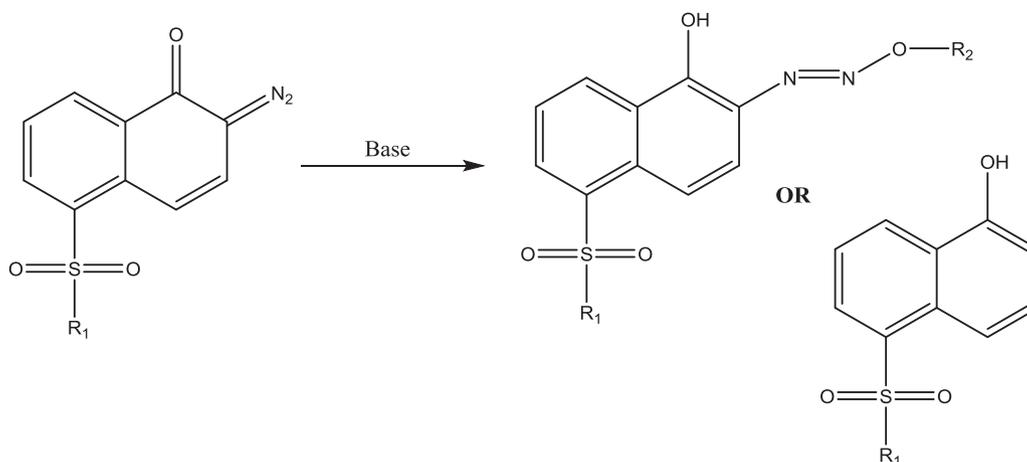**Figure 6.** Reduced modulus vs. cure temperature for undeveloped PNB, PNB-E, PNB-D, and PNB-D & E.

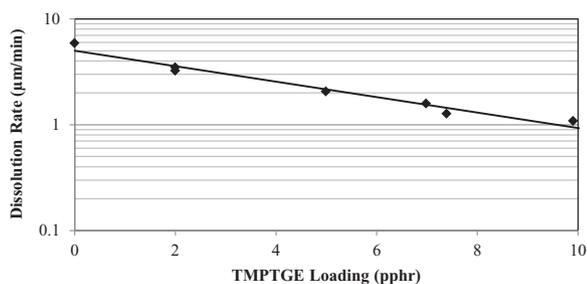**Figure 8.** Base catalyzed products of DNQ as described by Koshiba et al.[13]

Figure 9. Dissolution rate of PNB film containing varied loadings of TMPTGE.

QCM was used to investigate the amount of base uptake during the develop step for the DNQ inhibited films. A dissolution experiment was performed on seven polymer formulations of fluoroalcohol homopolymer with varying loadings of TMPTGE. The fluoroalcohol homopolymer was used because the 75/25 random copolymer of the fluoroalcohol and carboxylic acid decouples from the quartz crystal oscillation, and the measured response is the rate of decoupling rather than the dissolution rate. While the fluoroalcohol homopolymer films had no DNQ added to inhibit base dissolution, the dissolution rate of an uninhibited film is indicative of base uptake in an inhibited film. A similar trend would occur for base uptake in an inhibited film as

observed for an uninhibited film, but on a smaller, possibly unmeasurable scale. Figure 9 shows the log of the dissolution rate at varying loadings of TMPTGE. With increasing TMPTGE concentration, there is a decrease in dissolution rate.

Including TMPTGE in the film will reduce the amount of aqueous base that could potentially react with DNQ. Any water that remains in the film during cure can react with the ketene intermediate and form the carboxylic acid, preventing any reaction of DNQ with the polymer. In additional, the base catalyzed DNQ degradation results in a product that cannot undergo the Wolff rearrangement to form the reactive ketene.[14] The TMPTGE loading in the polymer films used in this study, 10 pphr, greatly reduces the dissolution rate, thereby allowing a developed DNQ loaded sample to form the potential crosslinking.

The modulus results show that DNQ contributes to the thermal crosslinking of the polymer dielectric during cure. To further understand the role of DNQ, a model reaction of norbornane fluoroalcohol with a monofunctional DNQ was used to examine the possible crosslinking mechanism between DNQ and the PNB copolymer. The monofunctional DNQ was dissolved in the norbornane fluoroalcohol at the same molar ratio as the previous formulations used in this study. The solution was continuously stirred and heated to 140°C for 40 min in an argon-filled glove box. ^{19}F-NMR was used to look for a change in structure of the fluoroalcohol pendent group as a result of the reaction. Figure 10 shows the ^{19}F-NMR spectra for the reactants (top) and products (bottom). The insets highlight the difference between
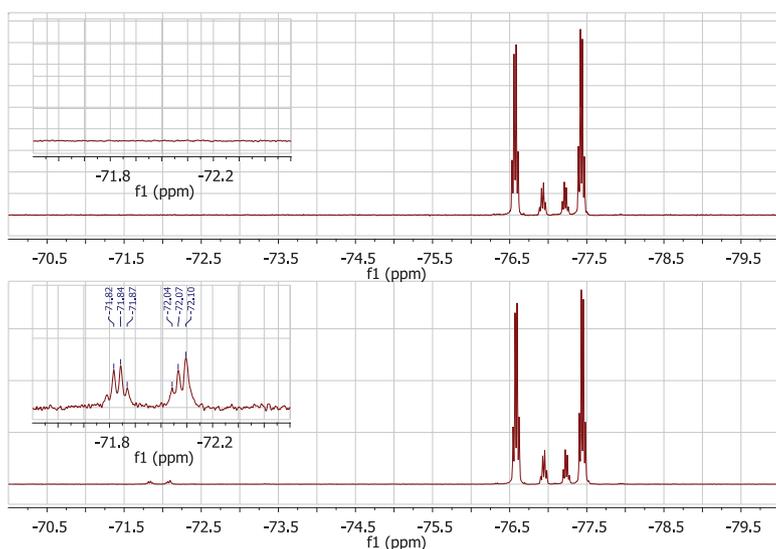

Figure 10. ^{19}F-NMR of model reaction reactants (top) and products (bottom) with insets at -71 to -73 ppm.
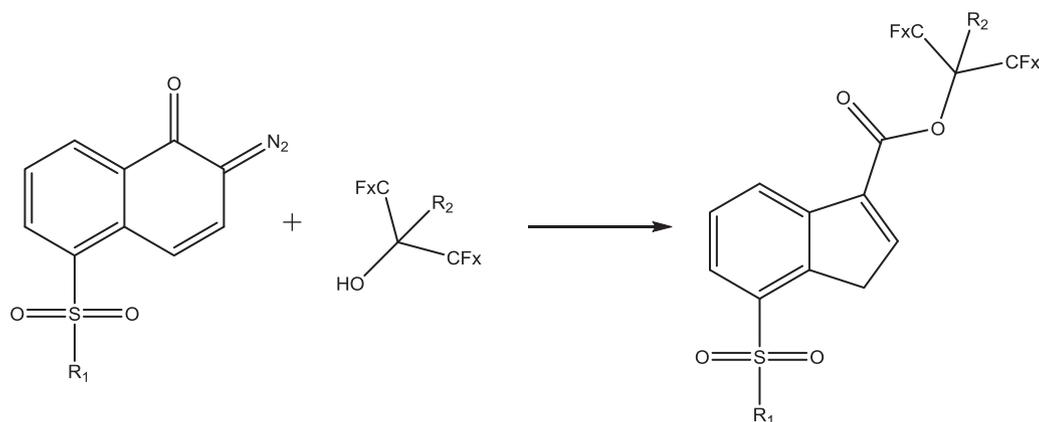
Figure 11. Proposed reaction of DNQ moiety with fluoroalcohol to form ester.

the spectra. The multiplets at -76.4, -76.8, -77.25, and -77.4 ppm are typical of the norbornane fluoroalcohol.

While the bulk of the fluoroalcohol remained unchanged, a new downfield peak was observed. Koshiba, et al. described a reaction of a DNQ moiety with an alcohol, likely reacting with a thermally-derived ketene and forming an ester. Figure 11 shows the proposed DNQ and alcohol reaction for the model reaction in this study. The shift in the ^{19}F-NMR corresponds to an ester linkage formed at the alcohol oxygen in the fluoroalcohol, consistent with the reaction described by Koshiba, et al.[14] In the polymer films described throughout this study, a similar reaction likely occurred, contributing to an increase in crosslinking.

The dielectric constant of the films was measured using a parallel plate capacitor configuration, as described in the Experimental Section. Capacitors were made from PNB–D and PNB–D & E formulations. The relative dielectric constant (i.e. real part of the permittivity) and loss tangent for samples made with PNB–D at different cure temperatures are shown in Figure 12. An increase in cure temperature causes a decrease in the dielectric constant and loss. Developing the PNB-D film prior to cure caused an increase in the dielectric constant compared to the undeveloped film likely due to inclusion of a small amount of aqueous developer.

The loss tangent for the PNB-D samples exhibited a similar dependency on cure temperature to the dielectric constant. A decrease in loss tangent was observed with an increase in cure temperature. Developing the PNB-D samples raised the loss tangent compared to the undeveloped samples due to exposure to aqueous base.
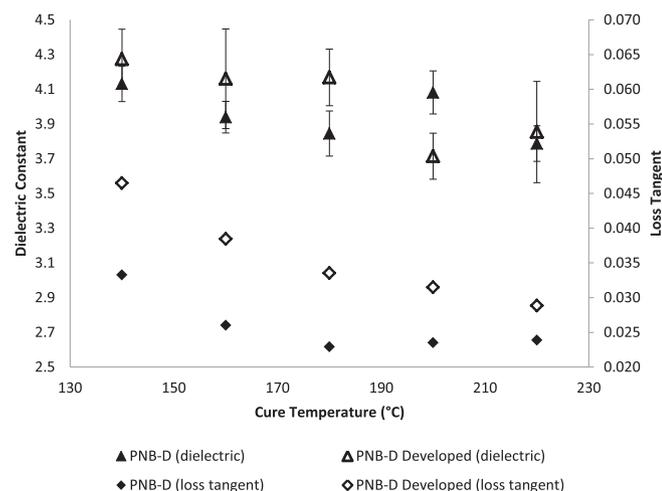

Figure 12. Relative dielectric constant and loss tangent versus cure temperature of positive tone films.
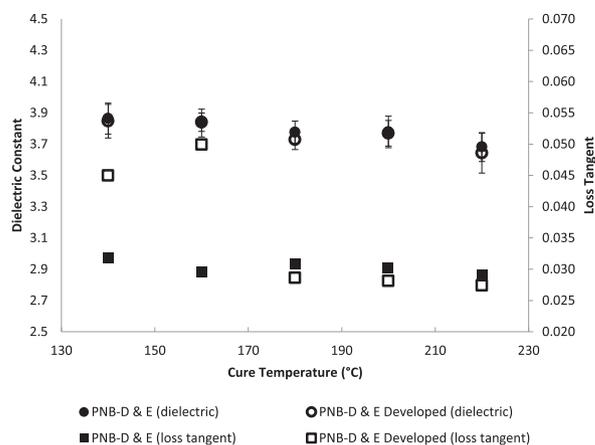

Figure 13. Relative dielectric constant and loss tangent versus cure temperature for positive tone films with TMPTGE.

The addition of the epoxy crosslinker lowered the relative dielectric constant compared to the DNQ-only PNB film. As seen in Figure 13, the PNB–D & E samples have a significantly lower dielectric constant compared to PNB–D at all cure temperatures. The dielectric constant declined with increasing cure temperature for all developed and undeveloped samples. Also of note is the lowest dielectric constant, 3.65, across all sample processing conditions that occurred with a 220ºC cure of the developed epoxy and DNQ-loaded film. The addition of the epoxy crosslinker also changed the cure temperature dependency for the loss tangent compared to the DNQ-only PNB film. The PNB-D & E samples have a nearly constant loss tangent at all cure temperatures.

The lower relative dielectric constant at each cure temperature indicates that the TMPTGE epoxy likely lowered the total polarizability of the film through crosslinking. This can be attributed to reducing the polarizability of present groups and possibly reducing the density of the film. Both developed and undeveloped films showed a steady decline in dielectric constant with cure temperature. At the higher cure temperatures, the polymer would have higher mobility and rate of reaction, thereby increasing the likelihood of an epoxy or DNQ reaction and increasing the crosslink density and decreasing the number of polarizable groups. The difference in the loss tangent between films with and without epoxy can also be attributed to the epoxy lowering the total polarizability of the film.

Conclusions

The mechanical and electrical properties of a positive tone epoxy-based polymer dielectric were examined. The reduced modulus shows

a dependency on the chemical crosslinking structure. Positive tone films with DNQ-based photochemistry are affected by the pH of the film due to aqueous base inhibiting DNQ crosslinking. Evidence for DNQ contributing to the crosslinking of a permanent dielectric film was shown for the first time. The addition of an epoxy crosslinker to the positive tone film inhibited base uptake, thereby allowing DNQ crosslinking to occur. This study provided a fundamental understanding of the effects of additives on the mechanical and electrical properties of the PNB film. Optimizing processing conditions and chemical additives can produce a dielectric material with tunable mechanical and electrical properties.

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