Photosensitive Polynorbornene Based Dielectric. I. Structure–Property Relationships

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ABSTRACT: In the microelectronics industry, the drive for increasing device speed, level of functionality and shrinking size has placed significant demands on the performance characteristics of polymer dielectrics. In this study, a negative acting, photodefinable dielectric formulation based on a copolymer of decylnorborne (decylNB) and epoxynorbornene (AGENB) was investigated for use in electronics packaging. The structure–property relations of this copolymer were investigated. Copolymer composition and processing conditions were shown to significantly affect the properties of the final polymer films. A lower content of AGENB results in lower moisture absorption, dielectric constant, modulus and residual stress, but it compromises multilayer capability. High crosslink density lowers the dielectric constant but increases the modulus and residual stress. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3023–3030, 2004

Key words: crosslinking; dielectric properties; structure–property relations

INTRODUCTION

In the microelectronics industry, the drive for increasing device speed, level of functionality and shrinking size have placed significant demands on the performance characteristics of polymer dielectrics, which existing materials cannot accommodate. The need for novel, low dielectric constant (low-*k*) materials compatible with emerging manufacturing processes and electronic materials has never been greater. Driven by continuous downscaling of feature sizes, microelectronic devices are rapidly becoming smaller in size, while being required to perform critical functions at higher speeds and incorporate higher integration of functionality. Increasing device complexity in turn creates a greater demand for low-*k* polymeric materials because signal propagation speed is related to both the resistance, R, of the metal line carrying the current and the capacitance, C, of the surrounding insulator.[1] Reducing the capacitance of the insulator increases the signal propagation speed. In addition, the crosstalk between adjacent metal lines decreases.

Today, inorganic materials, such as SiO_2, are the most commonly used materials for insulators and passivation layers. The inorganic dielectric materials possess good thermal, mechanical and dimensional stability properties. However, they have relatively high dielectric constants, in the range of 3.5 to 5.0, which are not suitable for next generation of packaging applications.

Organic materials have been attracting attention because of their relatively low dielectric constants and the ease in processing. Epoxy, polyimide, and benzocyclobutene (BCB) are the most commonly used organic dielectrics, especially for electronic packaging. However, the microelectronics industry continues to demand improvements in the electrical, mechanical, chemical and thermal properties of these polymeric dielectrics.

Polynorbornene Copolymer

Polynorbornene (Avatrel™ 2000P) is a cyclic olefin based dielectric material produced through the addition copolymerization of cyclic olefin monomers with a variety of Group VIII transition metal catalysts. The catalyst controls polymerization of the polycyclic monomers, resulting in the formation of high molecular weight copolymers without unsaturation in the polymer backbone. The copolymer composition is controlled by the feed ratio of monomers in the polymerization reaction.

The electronic packaging application requires that the dielectric polymer demonstrate the following characteristics: (1) improved electrical properties compared to existing polymer materials, (2) photodefinability, (3) low stress (low modulus) and (4) compatibility with existing microelectronic processing techniques.

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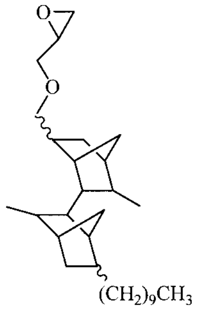
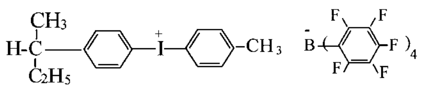
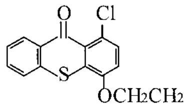


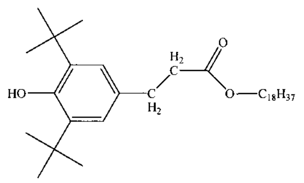
Polymer matrix: copolymer of decyl norbornene and allyl glycidyl ether normbornene



Photoinitiator: 4(methylphenyl)-4′-(1-methylethylphenyl) iodonium tetrakis (pentafluorophenyl) borate



Photosensitizer: 1-chloro-4-propoxy-9H-thioxanthen-9-one (CPTX)



Antioxidant: octadecyl 3,5 di-tert-buty-4-hydroxycinnamate (Irganox™ 1076)

Figure 1 Chemical structures of norbornene copolymer, photoinitiator, photosensitizer and antioxidant.

Based on these requirements, two monomers, allyl glycidyl ether norbornene (AGENB) and decyl norbornene (decylNB) were selected. The copolymers evaluated in this study were synthesized by varying the ratio of the two monomers. The general structure of the copolymer is shown in Figure 1.

In this copolymer, the decyl side groups increase the intrachain mobility, resulting in improved mechanical properties. Epoxy side groups were introduced to provide crosslinkable sites, resulting in improvement in chemical, thermal and electrical properties. DecylNB and epoxy norbornene were randomly polymerized to form poly(decylNB-*co*-AGENB) copolymer. In this article, the designation of each copolymer represents the molar fraction of decylNB and AGENB. For example, 40/60 refers the copolymer containing 40 mol % decylNB and 60 mol % AGENB.

In this study, the structure–property relations of thin films prepared from various copolymers of decylNB-*co*-AGENB were investigated. Specifically, the properties of moisture absorption, multilayer capability, dielectric constant, modulus and residual stress were examined. The effects of copolymer composition and processing conditions on these properties were explored.

EXPERIMENTAL

Polynorbornene copolymer (Promerus LLC) was received as a pure polymer dissolved in mesitylene at 45 wt % concentration. The polymer solution was formulated with photoactive compounds before use. The concentration of photoactive compounds is represented as the weight percent of dry polymer in the solution. Unless described otherwise, all polymer solutions were formulated with 3 wt % photoacid generator (PAG), 1.5 wt % sensitizer, and 1.5 wt % antioxidant. The chemical structures of the PAG, the sensitizer and the antioxidant are shown in Figure 1. Copolymers of decylNB and AGENB (decylNB/AGENB) with monomer compositions of 40/60, 50/50, 60/40 and 70/30 were used in order to explore the effects of copolymer composition on film properties. The weight average molecular weight (M_w) and the polydispersity (n) of each formulation were as follows: 40/60 (M_w = 129,000; n = 2.63); 50/50 (M_w = 126,000; n = 2.25); 60/40 (M_w = 124,000; n = 2.25); 70/30 (M_w = 120,000; n = 2.11).

Unless described specially, all polymer films were processed as follows. A solution of decylNB/AGENB polymer and mesitylene solvent was spin coated onto an oxidized silicon wafer at 500 rpm for 10 s followed by 1000 rpm for 60 s. The polymer film was soft baked at 100°C for 10 min and was then exposed to 0 to 500 mJ/cm^2 UV radiation (measured at 365 nm). A post-exposure bake at 120°C for 20 min was performed and followed by a 200°C bake for 1 h with nitrogen purging.

Moisture absorption of the polymer film was measured using a quartz crystal nanobalance (QCN). The characteristic oscillation frequency change in a quartz crystal resonator is related to a mass change that occurs in the material coated directly onto a quartz crystal. A 1 μm layer of polymer was coated onto a quartz crystal and thermally cured after a 500 mJ/cm^2 UV light exposure. The coated quartz crystals were then exposed to a 60% relative humidity (RH) environment and allowed to equilibrate for 48 h. The moisture absorbed by the sample was calculated based on the change in the oscillation frequency of the crystal substrate.

Relative permittivity and loss of the polymer film were measured using a HP 4236 LCR meter on a Karl Suss MODEL Probe station. The measurements were taken at a frequency of 10 kHz in a 50% RH environment. Parallel plate capacitors were made using the polymer films as the dielectric media between two parallel plates. The relative permittivity and loss tangent were calculated based on the readings of capacitance and conductance. In-plane and through-plane refractive indices of the films were evaluated using a Metricon prism coupler. A Helium-Neon laser emitting at 632.8 nm was used as the light source.

The modulus and glass transition temperatures of the polymer films were measured using a TA 2980 dynamic mechanical analyzer (DMA). Free films were obtained by lifting off the polymer from the silicon substrate through exposure to 48% hydrofluoric (HF) acid for 1-2 min. The HF etched the native oxide on the silicon wafer and lifted off the polymer film. Measurements were performed at frequency of 1Hz with an amplitude of 15 μm. The glass transition temperatures were determined using a heating rate of 5°C/min and were based on the peak position of tan δ.

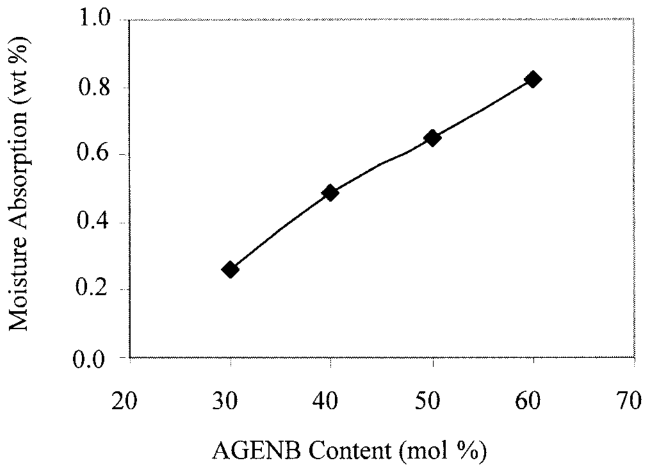


Figure 2 Moisture absorption of cured polymer films as function of AGENB content.

The residual stress values of the thin films were determined using a Flexus Model F2320 Stress Analyzer. This instrument measures the curvature of a substrate produced by the stress in the film.[2] The stress was calculated using Stoney's equation.[3] All of the measurements were made on single mode 4 inch diameter silicon wafers using a He-Ne laser.

The conversion of epoxide groups in the decylNB/AGENB copolymer was measured using a Nicolet Magna FTIR 560 spectrometer. FTIR scans of samples were collected in transmission mode on KBr crystals. The peak at 844 cm^{-1}, associated with C—O—C stretching, was used to monitor the conversion.

RESULTS AND DISCUSSION

Low moisture absorption is a crucial requirement for any polymer that is to be used as a dielectric material in electronics packaging. Moisture can have several deleterious effects, including raising the dielectric constant, corroding nearby metal and causing outgassing during subsequent processing, resulting in blistering and delamination of the films. The moisture absorption values of cured polymer films with various copolymer compositions were obtained at a RH of 60%. The results are shown in Figure 2. The polynorbornene copolymer has low moisture absorption because the molecule consists primarily of a saturated hydrocarbon molecular architecture. The moisture uptake of the copolymers increased from 0.2 wt % to 0.8 wt % at 60% RH when the molar amount of AGENB monomer in the copolymer increased from 30 to 60 mol %. The moisture absorption of the polymer films increased with increasing AGENB content due to the polar nature of the epoxy functional groups.

Of prime importance in many microelectronic applications is the need to apply multiple layers of a

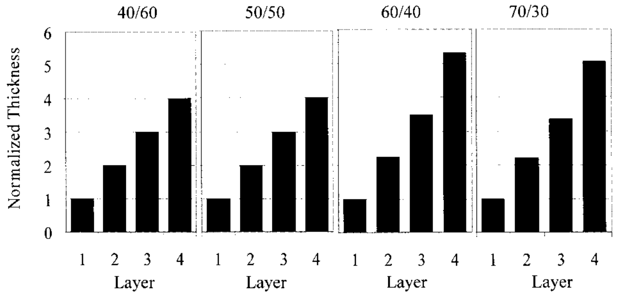


Figure 3 Normalized film thickness as a function of deposited layers.

dielectric material in successive processing steps in order to fabricate a complete device. Such multilayered structures require that previously deposited polymer films not be altered in any way by the sequential deposition of other polymer layers. For negative acting or crosslinking materials, it is critical that sufficient crosslink density be generated in a fully cured polymer film to prevent swelling by the carrier solvent of the polymer solution used to deposit subsequent layers.

The solvent resistance of fully cured polymer films was tested as follows. A polymer film was spin coated onto a silicon wafer, exposed to UV radiation and thermally cured. The thickness of the film was measured, and a normalized value of 1 was assigned to this structure. The normalized film thickness is the ratio of the total thickness of the polymer film to the thickness of the first layer. Up to three subsequent layers of polymer film were deposited on top of the original layer, using identical process conditions for each successive layer. After each additional layer was added and cured, the total film thickness was measured and a normalized film thickness was calculated. The normalized total thickness of the polymer film versus the number of layers deposited is shown in Figure 3.

The multilayering capability of the copolymers with high AGENB content, the 40/60 and the 50/50 decylNB/AGENB copolymers, is excellent. The data clearly indicate that the copolymer must contain a minimum of 50 mol % of AGENB monomer in order to produce sufficient solvent resistance to permit effective multilayer film structures. For the copolymers containing either 50 or 60 mol % of AGENB monomer, each additional layer of the polymer had the same thickness as the previous layers. However, for the copolymers containing either 30 or 40 mol % of the AGENB, the each additional layer of polymer resulted in a structure with a total thickness more than twice that of the original layer.

The good solvent resistance associated with high AGENB content is due to high crosslink density in the fully cured polymer films. A significant amount of the solvent cannot diffuse into the crosslinked polymer layer when another aliquot of polymer solution is deposited on top of it. As a result, the thickness of each layer is similar. In the films with low crosslink density, the polymer chains are not tightly crosslinked. Therefore, when the top layer of polymer solution is deposited on top of the bottom layer, the solvent in the top layer diffuses into the bottom layer, resulting in the swelling of the bottom layer. In addition, the top layer of polymer solution becomes more viscous; it is more difficult to spin out, resulting in a thicker top layer. The thickness of the polymer film therefore increases.

The role of a dielectric material is first and foremost electrical isolation. The dielectric constant is a measure of the charge storage and loss of the material. Decreasing the dielectric constant of the polymer can result in an increase in speed and density of a device by allowing closer placement of metal conduction lines with control of current leakage and crosstalk.

The relative permittivity and loss tangent values for the cured polymer films were obtained for various copolymer compositions exposed to 365 nm UV radiation. The results are shown in Figure 4. The relative permittivity increased with AGENB content in the

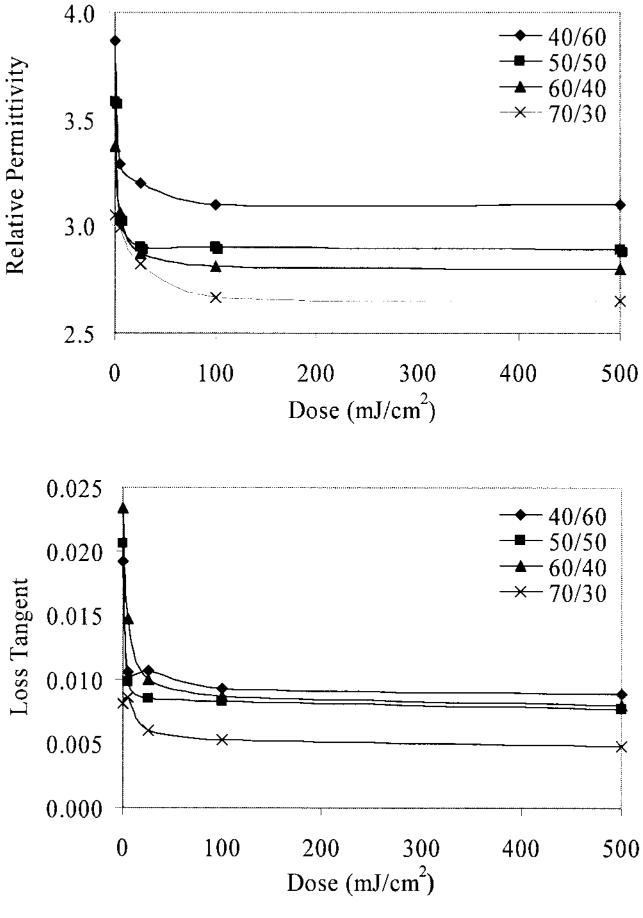


Figure 4 Relative permittivity and loss tangent of cured polymer film as functions of exposure dose.

film. For the fully cured polymer, which was exposed to a dose of 500 mJ/cm^2 of 365 nm UV radiation and then cured for 1 h at 200°C under nitrogen, the relative permittivity increased from 2.65 to 3.10 as the AGENB content increased from 30 to 60 mol %. For a given copolymer composition, the relative permittivity decreased with exposure dose. The relative permittivity of the polymers containing 60 mol % and 30 mol % AGENB decreased, respectively, from 3.87 to 3.10 and 3.05 to 2.65 as the dose increased from 0 to 500 mJ/cm^2.

The loss tangent showed a similar trend; it increased with AGENB content and decreased with exposure dose. The values of loss tangent for the polymers containing 60 and 30 mol % AGENB varied, respectively, from 0.0192 to 0.0089 and 0.0081 to 0.0048 as the dose increased from 0 to 500 mJ/cm^2.

Dielectric permittivity is related to the capacitance of a material or its energy storing ability and measures the polarization of the medium per unit of applied electric field. It consists of three parts: electron polarization, dipole polarization, and ionic polarization.[4] The electron polarization arises from the electron cloud displacement under the electric field. The dipole polarization arises from the unbalanced polar linkages in the molecules. The ionic polarization arises from the motion of mobile ions within the sample under an electric field.[5]

The increasing of relative permittivity with AGENB content is due to the higher electron and dipole polarizations. The electron and dipole polarizations are related to the chemical structure of the polymer molecules. The oxygen atom in the epoxy ring results in higher electron polarization than carbon and hydrogen atoms. Eucken and Meyer[5] give the following dipole moments for these bonds: C—C, 0.0; C—H, 0.4; C—O, 0.7.

The dipole moment of C—O bonds is higher than that of C—C and C—H bonds. As a result, increasing the concentration of AGENB in the copolymer results in higher electron and induced dipole polarization. The ionic polarization in the copolymer mainly comes from the movement of small ions (H$^+$) produced by the decomposition of photoactive compounds and impurities. It is independent of the copolymer composition.

In copolymers with the same AGENB content, the relative permittivity decreases with increasing dose. One explanation for the lower relative permittivity is the lower dipole and ionic polarizations at a higher conversion of the epoxy groups and a higher crosslink density. In order to test this hypothesis, the contributions from electron, dipole and ionic polarizations to the relative permittivity were decoupled. The contribution to the relative permittivity by electron polarization was calculated as the square of the refractive index of the polymer film.[5] The contributions from dipole and ionic polarizations were combined, since it is difficult to separate these two effects. Figure 5 shows the contributions by the electron, dipole and ionic polarizations.

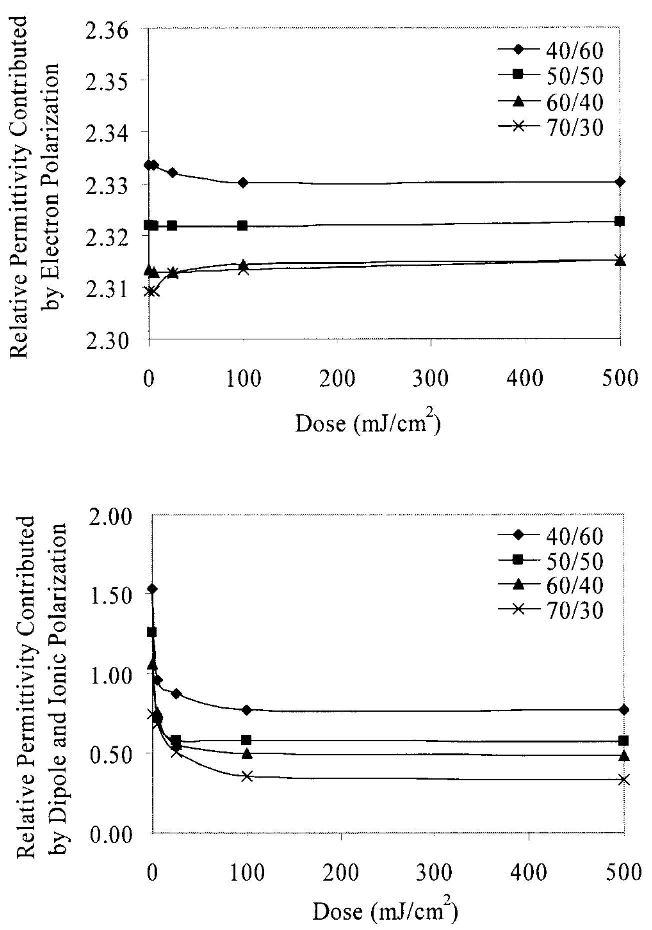


Figure 5 Relative permittivity contributed by (a) electron polarization and (b) dipole and ionic polarization.

The contribution from electron polarization showed little variation at different doses. The values were between 2.31 and 2.33 as the dose varied from 0 to 500 mJ/cm^2. The contribution by the electron polarization cannot explain the lower relative permittivity at a high exposure doses. In contrast, the contribution by dipole and ionic polarizations decreased with increasing dose. It decreased from 1.5364 to 0.7658 as the dose increased from 0 to 500 mJ/cm^2 for the polymer containing 60 mol % AGENB. The corresponding decrease was from 0.7405 to 0.3350 for the polymer containing 30 mol % AGENB.

The decrease in dipole and ionic polarization with exposure dose is due to several factors. First, the dipoles are strongly affected by the changes at the molecular level resulting from the chemical reaction and by the physical modification of their macromolecular environment.[6] The dipole decreases when the cyclic epoxy rings open during the crosslinking reaction,

TABLE I
Glass Transition Temperatures of Pure Polymer and Cured Formulated Polymer

Formulation	40/60	50/50	60/40	70/30
T_g (pure polymer)	173°C	147°C	138°C	126°C
T_g (cured polymer)	> 230°C	—	—	> 192°C

forming linear C—O—C linkages. Secondly, the conversion of epoxy groups in the polymers exposed to various dosages is different. FTIR results showed that the conversion of epoxy groups increased from 30% to 90% as the dose increased from 0 to 500 mJ/cm^2. The higher concentration of unreacted epoxy groups increases the dipole polarization, resulting in a higher relative permittivity. Thirdly, the highly crosslinked molecular chains minimize the chain segment mobility and lead to less orientation of the polar groups under the applied field. Therefore the lower relative permittivity in the polymer films exposed to higher doses is mainly attributed to the lower dipole polarization.

The decrease of ionic polarization with exposure dose is due to the lower concentration of charged ions and lower mobility. During the reaction, charged ions produced from photoactive compounds, H$^+$, react with the monomer to initiate polymerization. Some photoactive compounds diffuse out of the polymer film during the soft bake and post bake processes.[7,8] The concentration of photoactive compounds therefore decreases. The high crosslink density also inhibits the mobility of charged carriers through the matrix,[9] resulting in lower ionic polarization.

The loss tangent of the polymer film, which is the ratio of loss factor to relative permittivity, decreases with increasing dose. This decrease of loss tangent occurs when the loss factor decreases faster than the relative permittivity with increasing dose. The energy loss results from viscous drag as the chain segments rotate through the surrounding medium.[5] In the films with low crosslink density, there are many short chain segments that can move and rotate. The energy loss associated with viscous drag contributes to a high loss factor. As the crosslink density increases, the molecular chains tangle together, limiting the mobility of the chains and decreasing the energy loss.

Dielectric materials must be thermally stable at all temperatures the electronic package may encounter. This includes temperature changes that occur during deposition and etching of various metal layers as well as those that occur during the solder reflow process. One measure of thermal stability is glass transition temperature (T_g). Ideally, the electronic package should not be exposed to temperatures substantially above its glass transition for extended periods because its mechanical properties can dramatically change after this transition.

The glass transition temperatures of pure polymer and cured formulated polymer were evaluated using the DMA. The glass transition temperature was determined based on the peak position in the curve of tan δ versus temperature. A summary of the glass transition temperatures is listed in Table I.

The glass transition temperatures of both the unformulated and the fully cured, formulated copolymer films increased with decreasing decylNB content. When the decylNB content decreased from 70 to 40 mol %, the glass transition temperature increased from 128 to 173°C for the unformulated copolymer. The cured copolymer showed a corresponding temperature increase from 190 to 230°C. As the amount of flexible decyl side groups decreased, a lower level of plasticization of the copolymer occurred, and the glass transition temperature increased. An increase in glass transition temperature also occurs due to an increase in crosslink density for films with higher contents of epoxy groups.

In addition to providing electrical isolation, an interlevel dielectric must provide mechanical stability. A dielectric layer provides a framework by which metal lines are supported. The modulus and residual stress are critical properties that will determine the long-term structural stability of the final packaged device.

The moduli of the soft baked, post-exposure baked and cured samples were measured using the DMA. The conversion of the epoxy groups of these samples was measured using Fourier transform infrared spectroscopy (FTIR). The modulus of each polymer film as a function of conversion of epoxy groups was obtained. The results are shown in Figure 6.

The moduli of soft baked (100°C for 10 min), post baked (500 mJ/cm^2, 120°C for 20 min) and cured (160°C for 1 h) 40/60 polymer films were 620 MPa,

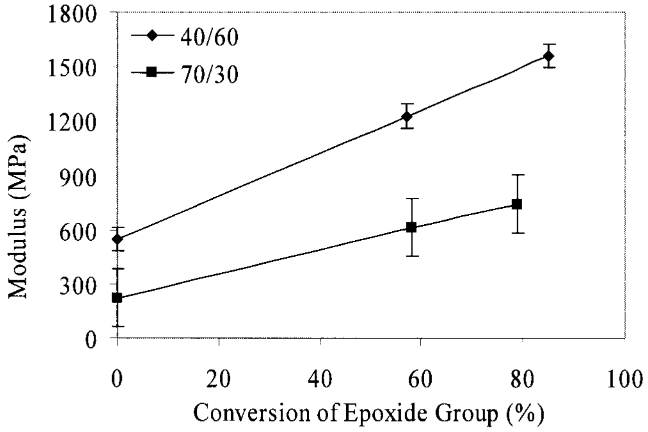


Figure 6 Modulus versus conversion of epoxy groups for 40/60 and 70/30 polymer films.

1220 MPa, and 1560 MPa, respectively. The moduli of 70/30 polymer films with similar conversion of epoxy groups were lower, at 220 MPa, 615 MPa, and 740 MPa, respectively. The increase in modulus with increasing AGENB content and conversion of epoxy groups is a result of the increasing crosslink density in the copolymer.

Residual stress in a substrate coated with a copolymer film is generated as a result of solvent evaporation, crosslinking of the polymer film at temperatures higher than ambient, and the thermal expansion coefficient mismatch between the copolymer film and the substrate. The magnitude of the stress generated is related to the coefficient of thermal expansion (CTE), the modulus, and the Poisson's ratio of the films.[10,11]

Residual stress was evaluated for soft baked, post-exposure baked and cured polymer films with various copolymer compositions. The degree of conversion of the epoxy groups in these films was measured using FTIR. Figure 7 gives the residual stress as a function of conversion of AGENB groups for all 40/60, 50/50, 60/40, and 70/30 copolymers.

The residual stress increased with AGENB content and conversion of epoxy groups. The stress values of soft baked 70/30 and 40/60 polymer films were 1.66 MPa and 6.66 MPa, respectively, while the stress increased to 6.00 MPa and 22 MPa for the polymer films with 80% conversion of epoxy groups, respectively.

During soft bake, the polymer films were heated to 100°C for 10 min and then cooled to ambient temperature. The initial stress in the soft baked films comes from the evaporation of solvent and the subsequent shrinkage of the copolymer film. The CTE mismatch during the thermal process also contributes to the stress buildup in the soft baked film. During the post bake process, the copolymer films were baked at 120°C for 20 min. Some residual solvent evaporated, resulting in further shrinkage of the polymer film. The higher bake temperature caused a higher CTE mismatch between polymer film and substrate. In addition, the modulus of the polymer film increased due to the crosslinking reaction during post bake. All of these factors contribute to the increasing stress in post-exposure baked polymer films. During the final cure, the copolymer film was maintained at 200°C for 1 h. This higher temperature cure process further increases the CTE mismatch and the modulus of the polymer film, resulting in higher stress in cured polymer films.

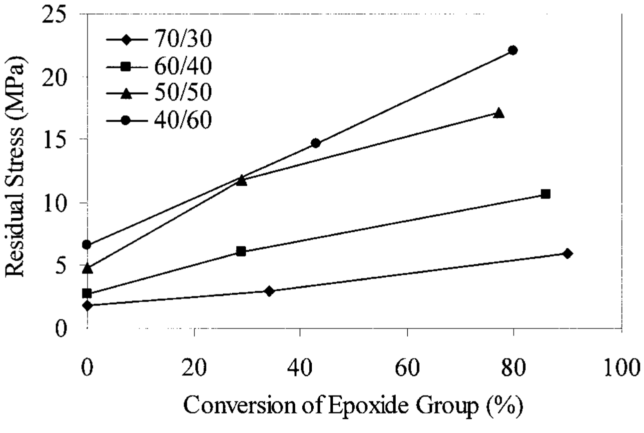


Figure 7 Residual stress as a function of conversion of epoxy groups at 25°C.

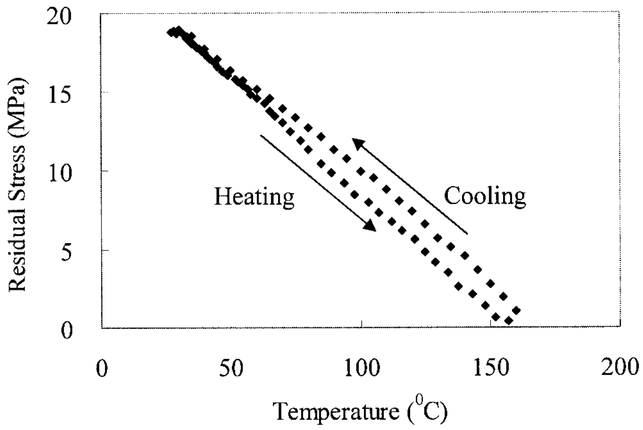


Figure 8 Stress as a function of temperature during thermal cycle for cured 40/60 polymer film.

The dynamic stress measurement of the cured polymer film was repeated for several thermal cycles (heat to 160°C at 5°C/min, then cool to 25°C at −5°C/min). The stress as a function of temperature during thermal cycle was obtained for cured polymer films (Fig. 8).

It was found that the stress change during the thermal cycle was repeatable. The stress first decreased with increasing temperature due to the higher mobility of chain segments and higher free volume at higher temperatures. The residual stress increased during cooling because of the CTE mismatch and lower mobility of chain segments at lower temperatures.

CONCLUSIONS

Poly(decylNB-*co*-AGENB) has low moisture absorption in the range of 0.2≈0.8 wt % at 60% RH, low dielectric constant in the range of 2.5≈3, low modulus between 700≈1600 MPa, and low residual stress between 0≈25 MPa. Both the copolymer composition and the processing conditions affect the properties of the final polymer. A lower content of AGENB results in lower moisture absorption, dielectric constant, modulus and residual stress but leads to poor multilayer capability. Higher crosslink density of the polymer film lowers the dielectric constant but increases the modulus and residual stress.

References

1. International Technology Roadmap for Semiconductor, 2001; http://public.itrs.net.
2. Grove, N. R.; Zhao, Q.; Kohl, P. A.; Bidstrup-Allen, S. A.; Shick, R. A.; Goodall, B. L.; McIntosh, L. H.; Jayaraman, S. Adv Microelectronics 1996, Jul/Aug, 16–18.
3. Bravman, J. C.; Nix, W. D.; Barnett, D. M.; Smith, D. A. Mater Res Soc Symp Proc 1988, 130, 41.
4. Stoney, G. G. Pro Royal Soc 1909, A82, 172.
5. Brydson, J. A. In Plastics Materials; Reed International Books, Oxford Press: Boston, MA, 1989; Vol. 130, Chapter 6, pp 105–117.
6. Eucken, A.; Meyer, L. Physics 1929, 30, 397.
7. Casalini, R.; Corezzi, S.; Livi, A.; Levia, G.; Rolla, P. A. In Conference Record on the IEEE International Symposium on Electrical Insulation, 1998; p 161.
8. Bai, Y. Ph.D. Dissertation, Georgia Institute of Technology, 2001.
9. Chinwalla, P. Ph.D. Dissertation, Georgia Institute of Technology, 2001.
10. Crivello, J. V.; Lee, J. L. J Polym Sci 1983, 1097, 953.
11. Han, H.; Gryte, C.; Tong, H.; Feger, C. ANTEC 1988, 28(4), 599.