Crosslinking and Decomposition Reactions of Epoxide-Functionalized Polynorbornene. II. Impact of Reactions on Mechanical Properties

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ABSTRACT: Low dielectric constant materials are critical to meeting the demand for continual reduction in feature sizes and increase in interconnect density required for future high-speed microelectronic devices. Polymers based on functionalized norbornenes are inherently attractive for these applications as they exhibit good electrical properties such as a low dielectric constant and appealing mechanical properties. Although polynorbornenes inherently possess properties that are attractive for microelectronics packaging, films of these polymers are not solvent-resistant. Solvent-resistant crosslinked films can be attained by generation of acid species to promote cationic crosslinking of epoxide side groups. This article is the second part of a two-part study investigating the crosslinking of a copolymer of decyl norbornene and epoxide norbornene. In the first part of this study, it was proposed that epoxide decomposition reactions are also possible at cure temperatures greater than 160°C. This decomposition mechanism results in the complete loss of crosslinkable epoxide groups while leaving the norbornene backbone intact. Although crosslinking and decomposition reactions have independent mechanisms, both reactions directly affect the level of crosslinking. In this part of the study, the solvent swelling behavior, tensile modulus, elongation to break, and residual stress were investigated for polymer films cured under various conditions to validate the proposed mechanisms. The trends observed with these properties are consistent with the counteracting nature of epoxide crosslinking and decomposition reactions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1020–1029, 2004

Key words: epoxy; dielectives; crosslinking

INTRODUCTION

The current trends in the semiconductor industry lead to a continually decreasing component size and increasing processor speeds as seen in the appearance of multigigahertz processors and high-performance portable palmtop computers. There is a considerable amount of research and development focused on the application of low-dielectric constant polymers as insulators to reduce the spacing between metal lines for various microelectronics applications.[1–3] Dielectrics based on a polynorbornene backbone are attractive for microelectronics packaging applications because they possess a low dielectric constant (ε_r ~2.2–3.0) and low moisture uptake (0.1–1.0 % by weight).[4–6] The first part of this study investigated the reactions occurring during the cure of polynorbornene functionalized with decyl and epoxy side groups intended to produce crosslinks. Two independent reactions were identified: epoxide crosslinking and epoxide decomposition.

The proposed mechanism for production of a crosslinked film follows a cationic propagation initiated by acid generators. This reaction has been well studied for other epoxide systems.[7–10] Infrared studies in the first part of this study provided evidence supporting the proposed mechanism. On exposure to light or elevated temperatures, an onium salt ($Ph_2I^+X^-$) additive decomposes to form a protic acid (HX).[11] The resultant protic acid can attack the oxygen of an epoxide ring to open the ring and form a hydroxyl group and a carbocation. Crosslinks are formed when the carbocation attacks the strained oxygen of a neighboring epoxide group. Termination is possible in the presence of a nucleophilic impurity (*Z*). The proposed crosslinking reaction is shown in Figure 1.

There is substantial evidence from the results of the first part of this study that decomposition reactions associated with an epoxide side group can occur at cure temperatures greater that 160°C.[6] The ether moiety in the epoxide structure may be catalyzed by the presence of acid to cleave. Subsequent isomerization at the oxygen anion produced will result in a carbonyl group. This mechanism results in the loss of the complete epoxide structure. The epoxide group can exist in unreacted, ring-opened or crosslinked forms; however, it is unlikely there will be any unreacted epoxide rings at the decomposition temperature. The proposed decomposition reaction is shown in Figure 2. The number of crosslinks in the system will be reduced if these epoxide groups are decomposing and volatiliz-

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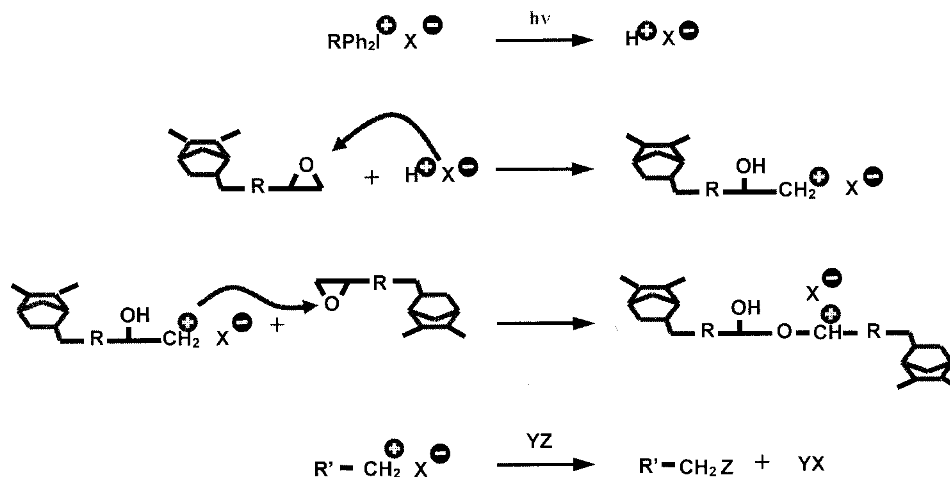


Figure 1 Proposed crosslinking mechanism.

ing. Similar decomposition mechanisms have been proposed for bisphenol A diglycidyl ether (BADGE)-type epoxies.[12–14]

The level of crosslinking is therefore directly influenced by the extent of both of these reaction mechanisms. Many film properties are determined by the level of crosslinking in the polymer film.[15] The work presented in this article tracked solvent swelling, the residual stress, the modulus, and the elongation to break in films that are cured under conditions that promote crosslinking and decomposition reactions to different extents to validate the proposed reaction mechanisms.

EXPERIMENTAL

Materials

The general structure of a copolymer of decyl norbornene and epoxide norbornene is shown in Figure 3. The polymer is a random copolymer in which each of the seven-member norbornene rings on the backbone is functionalized with either decyl or epoxide side groups. For convenience, the mol ratio of decyl-to-epoxide side groups is to describe the specific copolymer used. For example, a 40/60 DecNB/EpNB corresponds to a polymer where 40 mol % of the norbornene backbone units possess decyl side groups, whereas the remaining 60 mol % of backbone units have epoxide side groups. The polymer is prepared as a 20 wt % solution in mesitylene. A sensitized (365 nm) iodonium salt is used as the photoacid generator.

Techniques

Fourier transform infrared spectroscopy (FTIR) is used to track the chemical changes that occur in the film. FTIR scans are collected in transmission on potassium bromide (KBr) substrates using a Nicolet Magna IR 560. Samples are prepared by coating each KBr substrate with a polymer solution and heating to 100°C to drive off the solvent. Sixty-four scans at a resolution of 4 cm^{-1} are averaged for each measurement.

The swelling of the crosslinked polymer film on silicon on exposure to a solvent was measured using a noncontact variable wavelength interferometric thickness monitoring tool. This tool is typically used to measure the dissolution rates of photoresist systems. The thickness change is measured *in situ* as a film of the polymer is swollen with the solvent. Swelling is measured as the percent thickness change that occurs on solvent incorporation into the film. Two good solvents of polynorbornene systems were chosen: amyl acetate and mesitylene.

The residual stress is measured for polymer films coated on 4-in. (100) silicon wafers at room temperature using a He—Ne laser-based Flexus stress analyzer (Model F2320).[16] The residual stress in a film is calculated by monitoring the difference in the wafer curvature between an uncoated silicon wafer and one coated with the polymer.

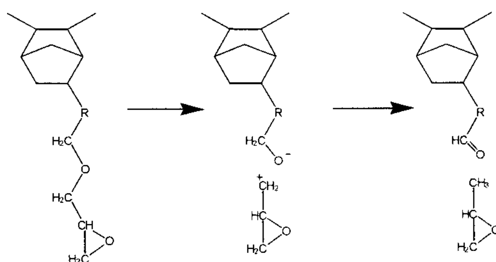
The tensile (Young's) modulus and elongation-to-break values are estimated by Instron tensile testing of free-standing polymer films.[5] The modulus is determined from the slope of the stress–strain curve in the low-strain elastic region. The elongation at break is estimated to be greater than the maximum strain measured before brittle failure.

RESULTS AND DISCUSSION

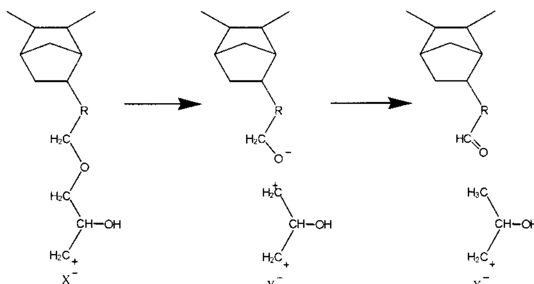
Swelling

Polymer films of a thickness of approximately 5 μm are spun on silicon wafers. These films are soft-baked,

Unreacted Epoxide Group:



Opened Epoxide Group:



Crosslinked Epoxide Groups:

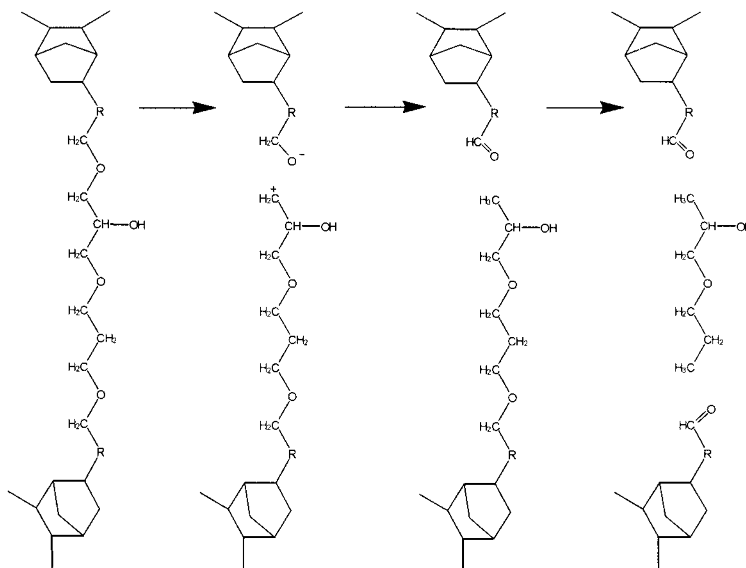


Figure 2 Proposed decomposition mechanism for the formation of carbonyl groups and loss of hydroxyl groups.

exposed to 500 mJ/cm^2, and cured in a nitrogen-purged furnace. The cure temperature and time are varied to drive the crosslinking and decomposition reactions to different extents. The cure time is controlled to be either "short" or "long." A short cure time is one that is as short as possible at that cure temperature. For temperatures less than or equal to 120°C, the sample is loaded into a tube furnace at the designated temperature under a nitrogen purge. For cure temperatures greater than 160°C, the sample is ramped at 5°C per minute to the temperature in a nitrogen purge tube furnace and cooled naturally without a hold time at the designated temperature. A sample cured using a long cure time was cured long enough to assume that all changes that can occur have occurred in the polymer film. Long cures are performed by ramping a sample at 5°C per minute and holding at that temperature for at least 10 h in a nitrogen-purged tube furnace.

Table I lists the percent swelling measured in both solvents for each cure condition. The percent swell is noted at 100% for samples that dissolve completely in

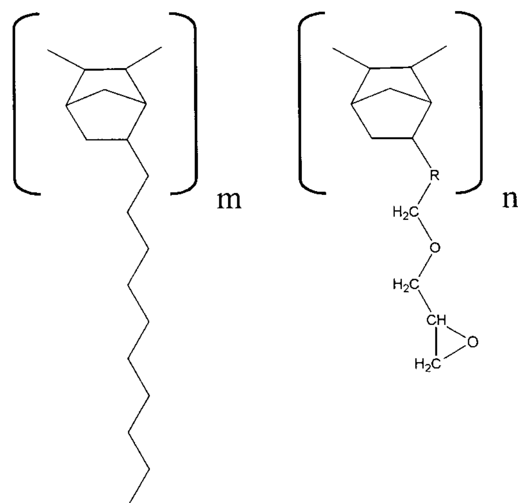


Figure 3 General structure for a copolymer of decyl norbornene and epoxide norbornene (decyl:expoxide, *m*:*n*).

the solvent. A polymer-coated KBr crystal is paired with each film cured to monitor chemical changes by FTIR as a result of the cure condition. The relevant infrared peak information for each cure condition is also listed in Table I. In this table, the loss of epoxide peaks can be quantified as the percent of epoxy groups remaining, whereas changes in the carbonyl and hydroxyl content can only be quantified in absorbance values relative to the unchanging internal reference at 1460 cm^{-1}.

Figure 4 displays the percent swelling versus cure temperature for short cure times. Films that are tested immediately after UV exposure (at 30°C) dissolve easily on testing for both 40/60 and 70/30 DecNB/EpNB. Infrared analysis in the first part of this study indicated approximately 25% of the epoxide rings are opened for samples cured under these conditions. This suggests that, although some epoxide groups are opened, an insignificant portion of these groups actually participated in the crosslinking reactions. Solvent resistance with low swelling can be achieved by increasing the cure temperature to 95 and 120°C for short cure times. Samples cured at 180 and 220°C swell to a slightly higher degree, suggesting that a loss of crosslinks due to decomposition mechanisms is possible even for short cure times. This is especially

TABLE I
Percent Swelling and Infrared Peak Information Data for Samples of 40/60 and 70/30 DecNB/EpNB Cured at Different Conditions

			Swelling percent		FTIR peak information (normalized to internal reference)		
DecNB/EpNB	Cure temperature (°C)	Cure time	In mesitylene	In amyl acetate	Epoxide remaining (% 844 cm^{-1}, height)	C=O (1737 cm^{-1}, area)	OH (3300–3600 cm^{-1}, area)
Short cures							
40/60	30	6 h	100.0[a]	100.0[a]	75.0	0.57	6.46
40/60	95	5 min	10.4	13.8	62.4	1.04	10.11
40/60	120	5 min	12.6	11.1	51.5	1.33	13.00
40/60	180	0 hold, ramp only	8.9	11.5	10.3	3.43	13.34
40/60	220	0 hold, ramp only	22.1	21.2	0.0	n/a	n/a
70/30	30	6 h	100.0[a]	100.0[a]	76.2	0.82	3.63
70/30	95	5 min	25.3	18.3	58.3	0.73	3.18
70/30	120	5 min	26.8	22.5	23.7	1.06	8.73
70/30	180	0 hold, ramp only	35.7	16.8	0.0	4.84	3.21
70/30	220	0 hold, ramp only	52.1	36.1	0.0	n/a	n/a
Long cures							
40/60	30	168 h	21.4	12.5	64.9	0.58	7.48
40/60	95	10 h	6.8	6.4	28.3	1.65	19.26
40/60	120	10 h	5.4	9.3	9.8	1.94	25.11
40/60	160	10 h	14.7	15.1	0.0	7.33	9.86
40/60	180	10 h	28.1	14.8	0.0	n/a	n/a
40/60	220	10 h	34.7	30.8	0.0	10.67	8.07
70/30	30	168 h	63.3	30.9	68.7	0.90	3.65
70/30	95	10 h	n/a	13.1	53.8	0.78	3.83
70/30	120	10 h	14.1	5.9	51.1	n/a	5.35
70/30	160	10 h	42.8	31.6	23.2	0.36	8.69
70/30	180	10 h	42.1	n/a	n/a	n/a	n/a
70/30	220	10 h	80.0	70.5	0.0	4.71	1.83

[a] Dissolved in test, noted as 100% swell.

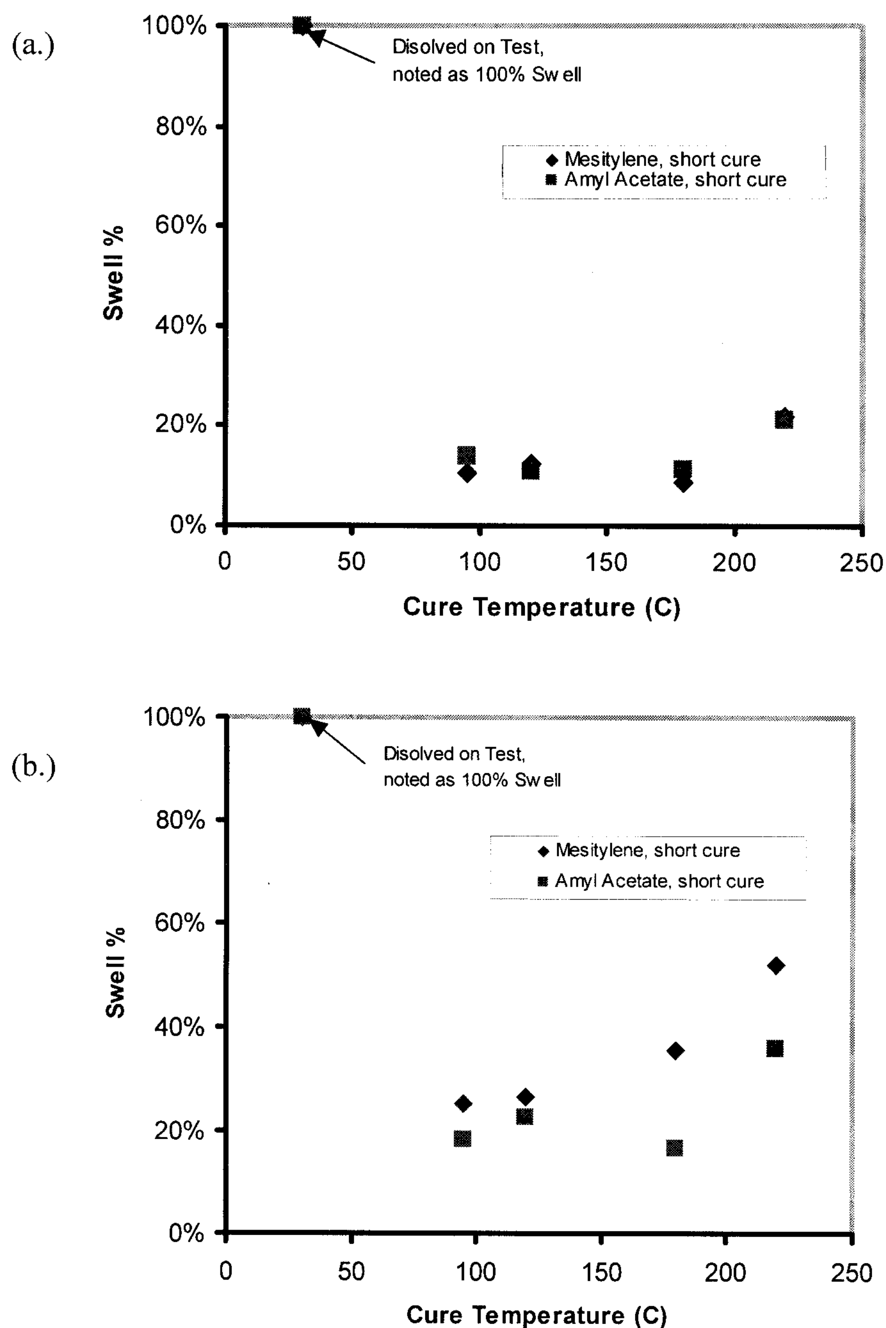


Figure 4 Percent swell versus cure temperature for samples of (a) 40/60 and (b) 70/30 DecNB/EpNB cured for short times.

seen for samples of 70/30 DecNB/EpNB, which shows an increase in swelling from ~20 to ~50% by changing the cure temperature from 120 to 220°C.

Figure 5 displays the percent swelling versus cure temperature for long cure times. A sample exposed and allowed to cure at room temperature for 168 h is solvent-resistant. This indicates that appreciable crosslink formation is possible at room temperatures after exposure, but requires long cure times. The percent swelling measured decreases to a minimum at a cure temperature of 120°C, but increases as the cure temperature is increased to greater than 160°C. This phenomenon can be attributed to the competing effects between crosslinking and decomposition reactions. Crosslinking reactions appear to dominate the swelling behavior for temperatures to 120°C. At temperatures above 160°C, the swelling increases sharply, suggesting that the decomposition of crosslinks is occurring. A sample of 40/60 DecNB/EpNB cured at 120°C has a swelling of ~10% for samples. Samples cured at 220°C, however, have swelling extents of ~40%. The decomposition effects of crosslinking on

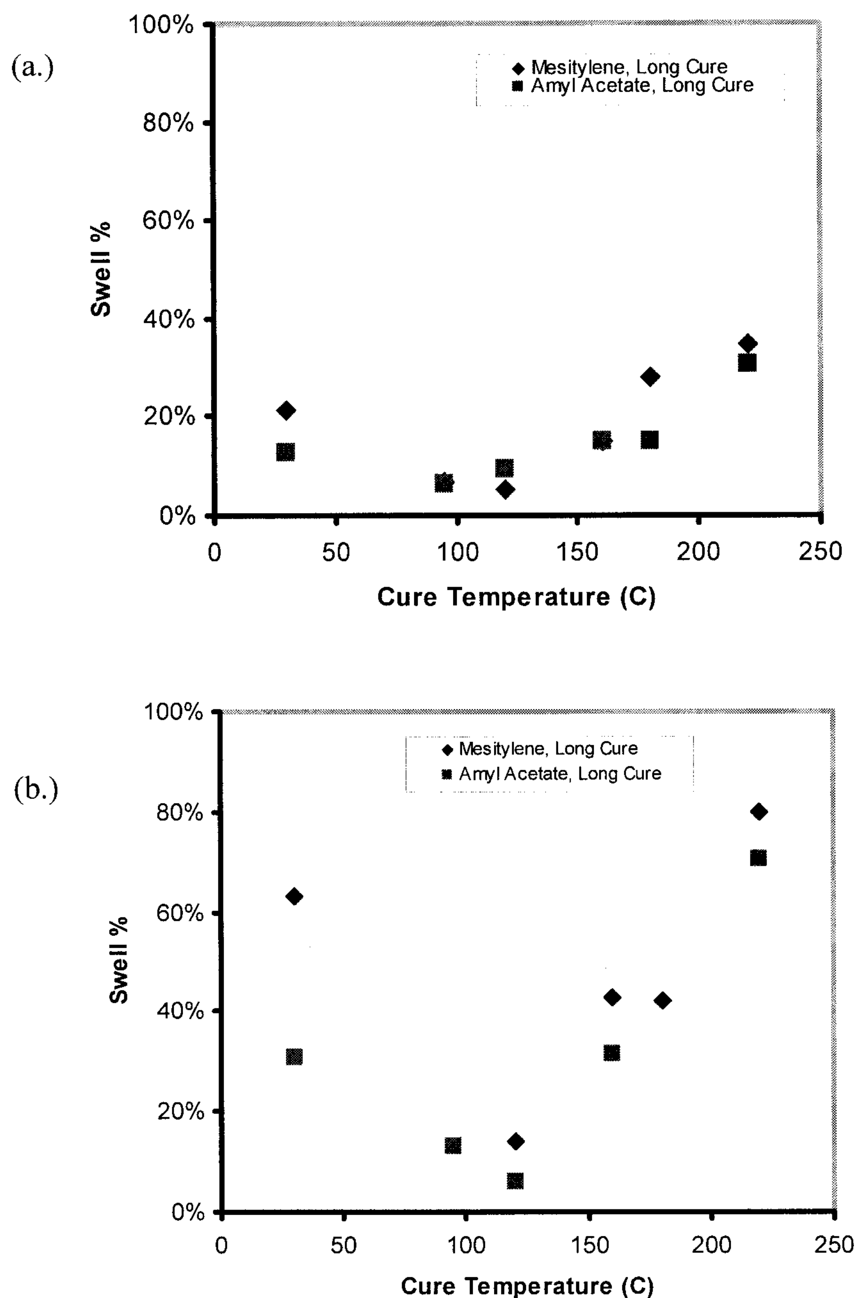


Figure 5 Percent swell versus cure temperatures for samples of 40/60 and 70/30 DecNB/EpNB cured for long times.

the swelling are more dramatic for samples of 70/30 DecNB/EpNB. This implies that fewer epoxide rings are involved in the crosslinking of 70/30 than 40/60 DecNB/EpNB, and, therefore, this system is more sensitive to a decomposition reaction that results in the loss of epoxide. The swelling of 70/30 DecNB/EpNB increases from ~10% for a sample cured at 120°C to ~80% for a sample cured at 220°C.

Infrared analysis is performed in parallel to these swelling measurements. Figure 6 shows the carbonyl peak (1737 cm^{-1}) area versus the percent swelling for samples of 40/60 DecNB/EpNB cured for long cure times. It is important to recall that the proposed decomposition mechanism predicts isomerization of cleaved ether moieties after decomposition results in the formation of carbonyl groups. Carbonyl formation should therefore be exclusively related to the decomposition reactions and independent of the crosslinking reactions. As the crosslinking reaction proceeds, the swelling decreases and the carbonyl content remains low (shown by the arrow labeled $T < 160$°C). At cure temperatures above 160°C, the decomposition reaction proceeds, resulting in a pronounced increase in both swelling and carbonyl content. Figure 7 shows the hydroxyl peak area (3600–3300 cm^{-1}) versus the percent swelling for samples of 40/60 DecNB/EpNB

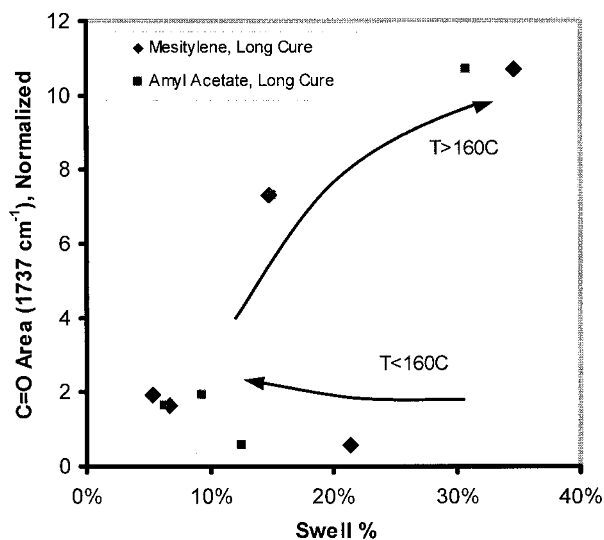


Figure 6 Carbonyl peak (1737 cm^{-}) area versus percent swell for samples of 40/60 DecNB/EpNB cured for long times.

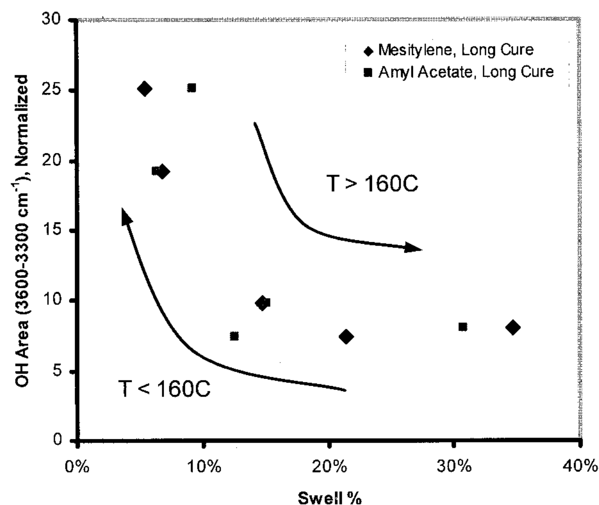


Figure 7 Hydroxyl peak (3600–3300 cm^{-}) area versus percent swell for samples of 40/60 DecNB/EpNB cured for long times.

cured for long cure times. Lower percent swelling values were observed for samples with a higher hydroxyl content. Hydroxyl groups are formed when a protic acid opens an epoxide ring. Although this ring opening cannot be directly related to crosslinking, it is assumed that a greater level of crosslinks follows a higher level of acid-promoted ring opening. For films cured at temperatures less than 160°C, the hydroxyl content increases as a direct result of acid-catalyzed ring opening. At temperatures greater than 160°C, decomposition of crosslinks results in a net decrease in the hydroxyl content as these groups leave the system as part of the volatilized epoxide group.

Tensile modulus and elongation at break

Fully formulated polymer films of 40/60 and 70/30 DecNB/EpNB are spun on silicon wafers at a thickness of approximately 15 μm. These films are soft-baked, exposed to 500 mJ/cm^2, and cured in a nitrogen-purged furnace. The samples are cured at 160 and 220°C for two cure times. The samples are ramped at 5°C per minute to the temperature and either immediately cooled or held at the temperature for 10 h. A summary of the tensile modulus and elongation-at-break results for free-standing films are shown in Table II.

The tensile modulus is approximately 1000 MPa for 40/60 and 70/30 DecNB/EpNB samples that are simply ramped to the designated temperature and cooled without a hold temperature. Curing for long cure times (10 h) at 160 and 220°C results in a decrease in tensile modulus by approximately one-third, possibly due to loss of linkages by decomposition. By increasing the cure time from no hold to 10 h at the designated temperature, the elongation at break increases by approximately a factor of two. A decrease in crosslinking due to decomposition will produce a less constrained film that is able to extend more. It is important to recall that the elongation-at-break values are a strong function of the sample preparation and, in

TABLE II
Young's Modulus and Elongation-to-Break Data for Samples of 40/60 and 70/30 DecNB/EpNB Cured at Different Conditions

DecNB/EpNB ratio	Cure temperature (°C)	Cure time (h)	Tensile modulus (MPa)		Elongation to break
			Average	Standard deviation	
40/60	160	0 hold, ramp only	1161.9	17.5	1.98%
40/60	160	10	332.2	12.5	3.95%
40/60	220	0 hold, ramp only	1072.4	3.7	2.64%
40/60	220	10	349.3	12.9	6.32%
70/30	160	0 hold, ramp only	1081.4	76.2	1.71%
70/30	160	10	466.5	44.5	2.40%
70/30	220	0 hold, ramp only	1181.8	124.1	4.27%
70/30	220	10	358.6	63.3	6.92%

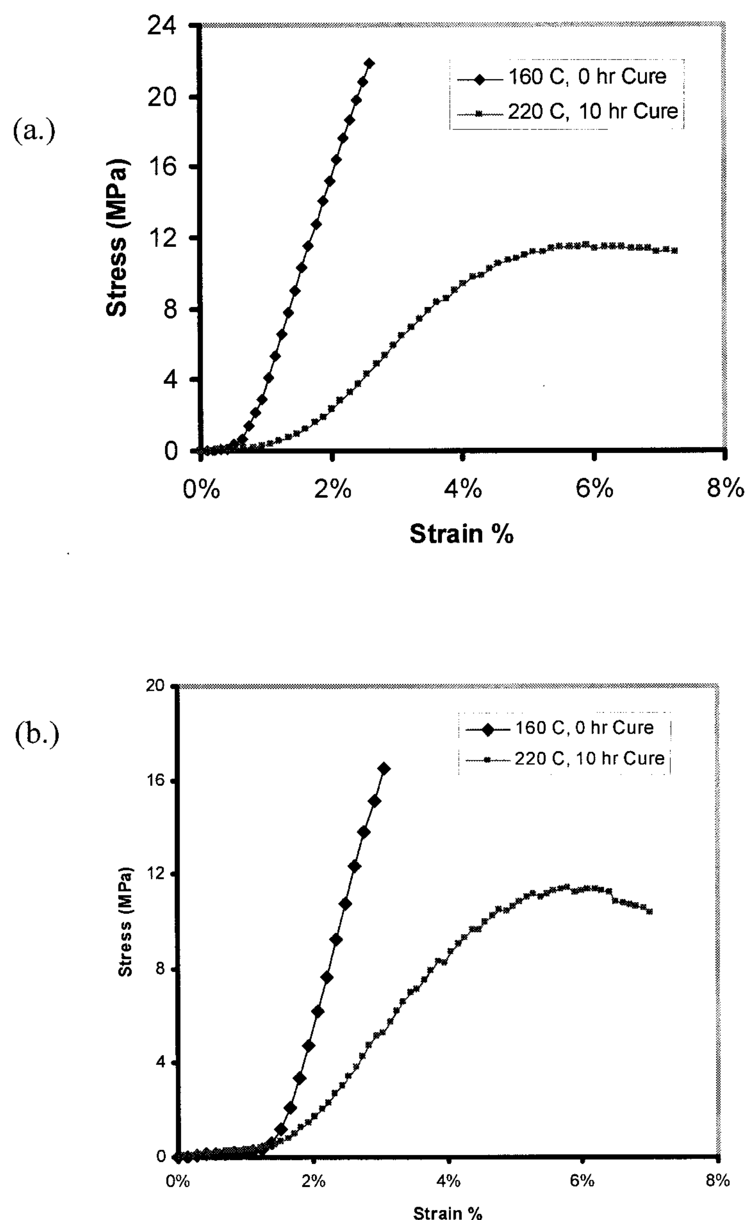


Figure 8 Stress-versus-strain curves for samples of (a) 40/60 and (b) 70/30 DecNB/EpNB cured at 160°C for no hold and 220°C for 10 h.

general, are underestimates of the true values. Defects during production of the free-standing strips may result in premature failure by modes other than brittle tensile fracture.

The mechanical properties of a polymer film are closely related to the crosslinking. This is especially true for temperatures greater than the T_g, but also true for temperatures less that than the T_g. Samples with a greater level of crosslinking are expected to have a higher tensile modulus and lower elongation at break.[15] The presence of crosslinks inhibits the ability of a polymer chain to elastically stretch. A less crosslinked film may also be able to plastically deform if the polymer chains can slide irreversibly past one another.

Figure 8 shows the stress-versus-strain data for 40/60 and 70/30 DecNB/EpNB at extreme cure conditions. A cure at 160°C with no temperature hold should produce a high level of crosslinking by the reaction. A cure at 220°C for 10 h should result in a substantial decrease in the number of crosslinks due to epoxide decomposition. It is clear that samples cured at 160°C with no hold extend into the purely elastic region before brittle failure. Samples cured at 220°C for 10 h, however, undergo plastic deformation. For 70/30 DecNB/EpNB, the film actually extends past the yield point of the polymer, suggesting that the film is able to strain further without any further increases in stress (cold drawing) before brittle failure. The increase in elongation at break observed for these cure

TABLE III
Residual Stress Data for Samples of 40/60 and 70/30 DecNB/EpNB Cured at Different Conditions

Polymer	Cure temperature (°C)	Cure time	Stress (MPa)
Shorter cures			
40/60	Soft-bake Only	—	6.3
40/60	160	No hold	13.7
40/60	180	No hold	18.6
40/60	220	No hold	13.1
70/30	Soft-bake Only	—	3.9
70/30	160	No hold	3.9
70/30	180	No hold	5.4
70/30	220	No hold	1.3
Long cures			
40/60	120	10 h	21.5
40/60	160	10 h	14.8
40/60	180	10 h	15.7
40/60	220	10 h	10.6
70/30	120	10 h	3.5
70/30	160	10 h	4.9
70/30	180	10 h	2.4
70/30	220	10 h	−0.2

conditions is due to plastic deformation and not due to a higher tensile strength.

Residual stress

Samples of 40/60 and 70/30 DecNB/EpNB are spun, soft-baked, exposed to 500 mJ/cm^2, and cured on silicon wafers. Table III summarizes the residual stress measurements performed for samples cured under different conditions. The stress increases with cure temperature for longer cure times. This is especially evident for samples of 40/60 DecNB/EpNB, in which the level of crosslinking is greater. Similar results were observed with the swelling measurements shown earlier. As can be seen in Figure 9, the residual stress decreases with the cure temperature for longer cure times. For a sample of a 70/30 DecNB/EpNB cure at 220°C for 10 h, the residual stress is approximately zero. This decrease in stress may be due to a decreasing modulus or due to stress relief due to plastic deformation.

Infrared analysis is performed on a KBr-coated sample processed in parallel to the stress samples. Higher levels of hydroxyl content indicate a greater level of ring opening by acid attack. As before, it is assumed that a higher level of crosslinking will follow ring opening. The greatest residual stress is measured for a sample of 40/60 DecNB/EpNB cured at 120°C for 10 h. This cure condition has been shown to produce the highest level of crosslinking (lowest swelling).

The percent swelling is measured for the samples cured under similar cure conditions. Figure 10 displays the percent swelling versus residual stress for samples of 40/60 DecNB/EpNB. Films with a greater

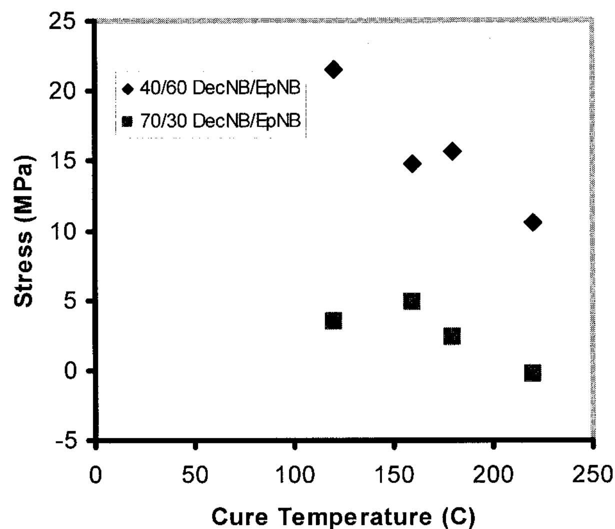


Figure 9 Residual stress versus cure temperature for samples of 40/60 and 70/30 DecNB/EpNB for 10 h.

amount of crosslinking (lower swelling) have a higher residual stress. The residual stress is therefore directly controlled by the level of crosslinking. These data support the hypothesis that the formation of crosslinks produces higher-stress films, whereas breaking of crosslinks by decomposition produces lower stress films.

CONCLUSIONS

It is clear from the results presented in this article and a previous study[6] that decomposition reactions are possible during the cure of a copolymer of decyl norbornene and epoxide norbornene at temperatures

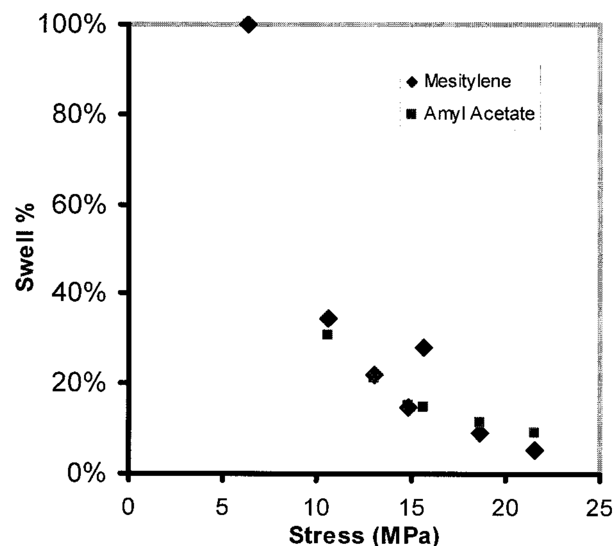


Figure 10 Swelling percent versus residual stress for samples of 40/60 DecNB/EpNB for all cure temperatures tested.

greater than 160°C. This mechanism has been proposed to be independent of ring opening or the crosslinking reaction. Epoxide decomposition and crosslinking reactions can occur simultaneously at temperatures above 160°C; however, the decomposition reaction is slow compared to the kinetics of epoxide ring opening.

Acid-catalyzed scission at the ether moiety of the epoxide side group will result in the complete epoxide group. If this epoxide group has participated in the formation of crosslinks, this mechanism will result in the complete loss of the linkage. Polymer films cured at conditions favoring this decomposition mechanism ($T > 160°C$) have markedly different properties than those of films cured in nondecomposing conditions ($T < 160°C$). The percent swelling and elongation at break increases significantly, whereas the modulus and residual stress decrease significantly. Additionally, a polymer film cured under decomposing conditions was shown to plastically deform, whereas polymer film cured under nondecomposing conditions deforms only elastically.

Two independent reactions were identified during the cure of a copolymer of decyl norbornene and epoxide norbornene initiated by a photoacid generator. The photo or thermal generation of acid will promote epoxide ring-opening reactions and subsequent formation of crosslinks. This reaction is likely to be limited by the diffusive mobility of reactive groups (generated acid and opened epoxide rings) to unopened epoxide rings. At temperatures greater than 160°C, a decomposition mechanism occurs by which the cleavage occurs at the ether linkage, resulting in complete loss of the epoxide group. Both of these mechanisms are supported by infrared and mechanical property studies.

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