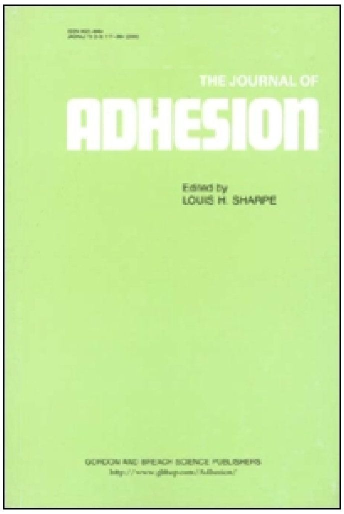

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Mechanical and Dynamic Mechanical Properties of Photocrosslinked Norbornene-Thiol Copolymer Films

M. A. Rakas[a]; A. F. Jacobine[a]
[a] Chemical and Materials Science, Loctite Corporation, Newington, CT, U.S.A.

To cite this Article Rakas, M. A. and Jacobine, A. F.(1992) 'Mechanical and Dynamic Mechanical Properties of Photocrosslinked Norbornene-Thiol Copolymer Films', The Journal of Adhesion, 36: 4, 247 — 263
To link to this Article: DOI: 10.1080/00218469208026529
URL: http://dx.doi.org/10.1080/00218469208026529

J. Adhesion, 1992, Vol. 36, pp. 247–263
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Mechanical and Dynamic Mechanical Properties of Photocrosslinked Norbornene-Thiol Copolymer Films*

M. A. RAKAS** and A. F. JACOBINE

Chemical and Materials Science, Loctite Corporation, 705 North Mountain Road, Newington, CT 06111, U.S.A.

(Received May 4, 1991; in final form December 10, 1991)

A number of novel organic norbornene and norbornene siloxane polymer precursors have been synthesized as part of an on-going research project to produce a non-acrylate, UV-curable adhesive system. These precursors (monomers or oligomers) are di-, tri- and tetra-functional. The crosslinking agent is a multifunctional thiol.

The organic norbornene systems, formulated to stoichiometry, have been characterized using thermal, static and dynamic mechanical analysis. We have found that norbornene ester systems have a range of physical properties, with tensile moduli ranging from 820–2300 MPa (118–350 kpsi), tensile strengths of 17–61 MPa (2.5–8.8 kpsi) and elongations of 4–100%. Glass transition temperatures range from 30–71°C for samples cured at room temperature with a dose of 620 mJ/cm^2.

Norbornene siloxanes crosslinked with thiol siloxanes have been formulated with increasing levels of a high surface area reinforcing agent. Tensile properties of filled films show that filler loading to 30 wt% significantly increases peak stress and elongation to break above that of 25 wt% filler. The addition of filler did not appear to increase the T_g of the films in this series monotonically. Increased levels of filler were found to produce films with a broadened cold crystallization range and an increased melting temperature.

KEY WORDS Low-intensity UV-curable adhesives; norbornene-thiol copolymer; norbornene siloxane-thiol siloxane copolymer; non-acrylate photocrosslinkable adhesive; thiol-ene copolymerization.

INTRODUCTION

The photoinitiated reaction of a multifunctional thiol and a multifunctional norbornene resin has been shown to be a step growth kinetic process, although polymerization propagates *via* a radical mechanism.[1] This laboratory has synthesized a family of norbornene esters[2] and a telechelic norbornene-functionalized polydimethylsiloxane[3] which can be crosslinked with compatible thiols under ultraviolet (UV) conditions. The synthetic methodology used in preparing these norbornene-functionalized resins has already been reported.[4] These materials are particularly

---

*Presented at the 14th Annual Meeting of The Adhesion Society, Inc., Clearwater, Florida, U.S.A., February 17-20, 1991.

**Corresponding author.

interesting from the standpoint of network studies: under the polymerization conditions used, neither the norbornene functionality nor the thiol functionality will homopolymerize, but will instead react to form an **A-B** type copolymer. This results in a very well-defined network, although some ring formation is expected to occur. In addition, the resulting products would be expected to show good adhesion to metal; organosulfur derivatives coordinate strongly to metal and metal sulfide surfaces,[5] strongly enough such that self-assembly of thiol monolayers adsorbed onto gold surfaces has been shown to occur.[5-7] This strong coordination has been exploited on a macroscopic level as well, with the synthesis and testing of several mercaptoester compounds. When these compounds are used as coupling agents, the bond strength of a joint is increased, even after the assembly is exposed to water.[8]

These resins and the resulting polymers generated are of interest because of their performance properties as well as the ease of synthesis of a wide range of monomers and oligomers with the norbornene functionality, thus allowing the ability to design in mechanical properties as well as curing characteristics.[9,10] The cured polymers have been found to be useful as coating and adhesive materials; they are fast curing and possess excellent adhesion to a variety of substrates, as shown in Tables I and II. On the basis of these adhesive properties, it was decided to synthesize a variety of norbornene-based resins.

TABLE I
Adhesive properties of thiol crosslinked norbornene resins

Resin	Substrate (to glass)	Tensile strength, MPa	Aged strength 50°C, 100 Hrs	60°C, 95% RH 10 days
EBPA-DN	Steel Pin	6.34	8.62	15.9
TMP-TN	Steel Pin	4.17	4.67	10.7
HDDN	Steel Pin	5.22	7.89	0
Loctite 350	Steel Pin	6.93	9.27	14.9
EBPA-DN	Glass Lap	4.02	na	na
EBPA-DN	Epoxy Glass	4.29	"	"
EBPA-DN	Phenolic	5.52	"	"
EBPA-DN	Steel	6.60		
Loctite 370	Steel	4.11		
Dymax 181	Steel	3.60		

TABLE II
Cure profile determination: low intensity cure (30 mW/cm^2), polycarbonate/polycarbonate bond, with 20 mil gap and 5 second cure time

Formula	Lap strength, psi
Loctite 352	93
Norland 60™	0
EBPA-DN	500
TMP-TN	415
HDDN	1485

This work is concerned with the mechanical and dynamic mechanical behavior of these materials after having been photocrosslinked as films. In order to study the effects of functionality only one compatible crosslinking thiol was used for all of the organic-based norbornene resins; all films contained stoichiometric amounts of reactants. The functionality of the norbornene esters ranged from two to four, and formulations of blends of two norbornene ester resins with the thiol crosslinker were prepared to study the ability of the various resins to modify and extend the range of properties available. The thiol-crosslinked norbornene siloxane was used as a vehicle to study the optimization of filler loading and the effect of increasing amounts of filler on the bulk tensile properties as well as its relationship to thermal properties including T_g and melting temperature. Again, this was done by using only one siloxane-based thiol crosslinking agent and by reacting stoichiometric amounts of the reagents.

EXPERIMENTAL

All organic-based formulations studied were based on 1:1 norbornene/thiol stoichiometric equivalents, and contained Darocur 1173 photoinitiator (E. M. Industries, 2% w/w). The norbornene ester monomers shown in Figure 1a were reacted

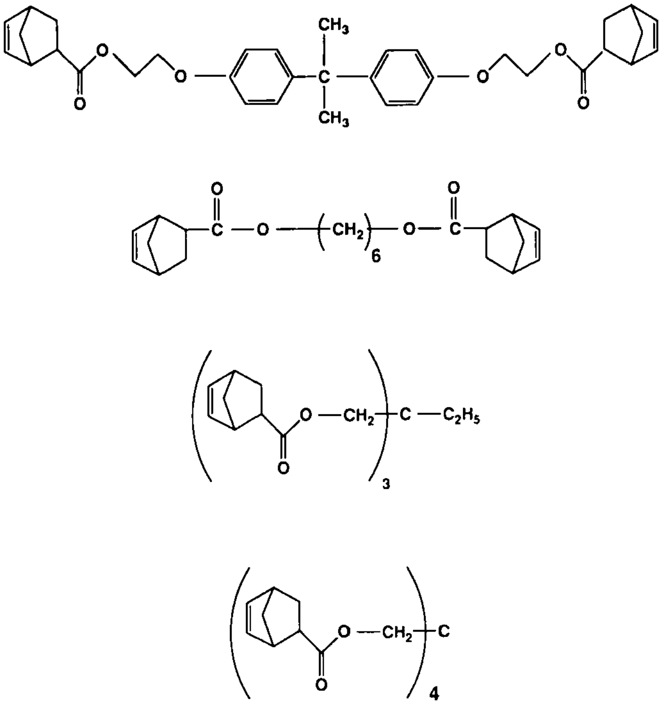

FIGURE 1a Norbornene ester monomers. *Top to Bottom:* Ethoxylated bis-phenol A dinorbornene [EBPA-DN]; Hexanediol dinorbornene [HDDN]; Trimethylolpropane trinorbornene [TMP-TN]; Pentaerythritol tetranorbornene carboxylate [PETN].

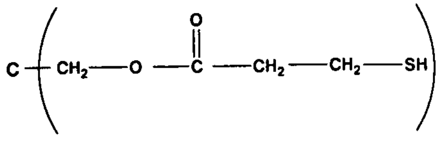

FIGURE 1b Pentaerythritol tetra-(3-mercaptopropionate) [PETMP].

with the tetra-functional organic thiol crosslinking agent, pentaerythritol tetra-(3-mercaptopropionate) [PETMP] (Evans Chemicals), shown in Figure 1b. Mixtures of norbornene esters were 1:1 based on weight, and were crosslinked with a stoichiometric equivalent of PETMP. For less cumbersome documentation, films will be referred to only by their norbornene component(s). All samples were cured in the UV Fusion System™; films were passed through the system twice, one pass per side for a total dose of 620 mJ/cm^2. Film thicknesses ranged from 11–16 mils (0.011–0.016 inches or 0.028–0.041 cm), except for trimethylolpropane trinorbornene films (TMP-TN) which were between 15 and 27 mils (0.038–0.068 cm). Dimensions of samples were measured to ±0.0001 inch and an average was taken of four measurements. Samples were discarded if widths or thicknesses differed by more than 2%.

The norbornene siloxane oligomer used in these studies was a difunctional telechelic with M_n~28,000 (referred to as 28N), shown in Figure 2a. This was reacted stoichiometrically with the pentafunctional thiol siloxane oligomer [3K5M], (M_n~3,000, shown in Figure 2b), whose pendant thiol groups are randomly distributed along the chain backbone. A high surface area reinforcing fumed silica, Wacker

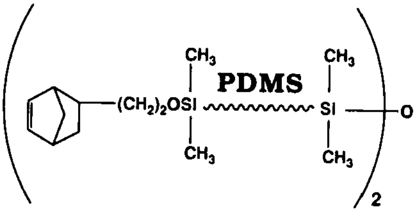

FIGURE 2a The norbornene siloxane oligomer (referred to as 28N).

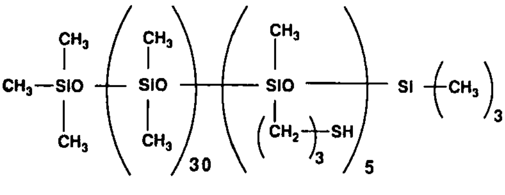

FIGURE 2b The penta-functional thiol siloxane oligomer used as the crosslinking agent [3K5M].

HDK-H2000, was added at loadings of 0–41% (w/w); 1.52 wt% DEAP photoinitiator was added to all formulations. A 3-roll mill, which provides high shear mixing, was utilized to "wet in" the filler after it had been mixed in by hand or by an air motor. Formulations were cured at a dose of 4200 mJ/cm^2 per side, also using the UV Fusion System™. Film thickness was 70 mils (0.07 inches or 0.178 cm).

Dynamic mechanical analysis was carried out on the Rheometrics Dynamic Mechanical Analyzer II in oscillatory shear strain, using the torsion rectangular tool. For the organic norbornene esters, the linear elastic region [LER] was found to be between 0.1% and 0.4% strain. All sweeps of these materials were run at a frequency of 10 radians per second (rad/sec). For the norbornene siloxane/thiol siloxane films [28N films], the LER was found to be between 0.1–0.6% strain for most films, although this did vary somewhat as a function of filler loading. During a temperature sweep, the lower strain was employed initially, and the autostrain adjustment was used to increase the strain as the material softened after T_g. Strain and temperature sweeps for all 28N films were run at a frequency of 1 rad/sec; this rate was chosen after reviewing some recent DMA work on filled silicones.[11] The T_g values reported in this paper are the average of the values obtained from two temperature sweeps; there was no difference of more than 4°C between two runs for any sample, and the two values for most samples differed by less than 3°C.

To determine tensile properties, an Instron 4505 Universal Tester was equipped with a 50-lb tensile load cell or, in the case of the norbornene siloxane/thiol films, a 100 N (22.48 lb.) dual tension/compression cell. Tensile properties of the organic norbornene films were determined using a modified ASTM D882-83 test, where guidelines for width:thickness ratio and minimum/maximum sample width were followed. Gage lengths of all samples tested were 1.97 inches. The ASTM test requires that crosshead speed be 0.2 in/min for these samples, unless ultimate elongation is greater than 20%. For samples which showed high elongation to break, three samples were run at 0.2 in/min (for accurate Young's modulus determination), and three samples were run at 0.2 in/min initially, then at 2 in/min after 20% elongation had been reached. Samples were milled from 0.5 inch width to 0.25 inches, in order to minimize failures from edge effects. ASTM D 412-83 was used to determine tensile properties for the norbornene siloxane/thiol siloxane films.

RESULTS AND DISCUSSION

Films of Norbornene Ester/Thiol Copolymers

By synthesizing a number of norbornene monomers and resins and studying their structure/property relationships, it was expected that properties could then be designed into formulations by proper backbone selection and functionality level. Data from tensile tests of films containing a single norbornene component are presented in Table III and show that a wide range of tensile properties is spanned by the thiol/norbornene copolymers.

Figure 3 shows representative stress-strain curves for two hexanediol dinorbornene [HDDN] samples which were subjected to different testing speeds. The first curve shows the results of testing at the crosshead speed initially calculated to be

TABLE III
The tensile properties of norbornene-thiol films containing a single norbornene resin

	HDDN	TMP-TN	EBPA-DN	PETN
Tensile Modulus, MPa	830±200	2275±50	1930±300	1550±180
Tensile Strength, MPa	15.5±0.4 @ 0.2"/min 18.1±0.8 @ 2"/min	61±3.3	40±5.1	47.2±6.0
% Elongation	105±12	4.1±0.6	2.9±0.5	4.9±0.5

required by the ASTM method, 0.2 in/min throughout the test. At very low levels of strain, a high stress response is immediately generated. An intrinsic yield point is reached almost immediately, and strain softening follows. At around 60–80% strain, strain hardening sets in and continues until failure.

Due to the conditions of the ASTM test and the high elongation to break, three HDDN film samples were tested using a crosshead speed of 2 in/min above 20% elongation. A representative stress-strain curve for these samples is also shown in Figure 3. The peak in stress response which occurs between 20% and 40% strain is an artifact due the sudden increase in the crosshead speed. At 2 in/min, stress did not continue to increase with strain, but instead decreased and then maintained a constant level of stress with increasing strain. This appears to indicate that a second

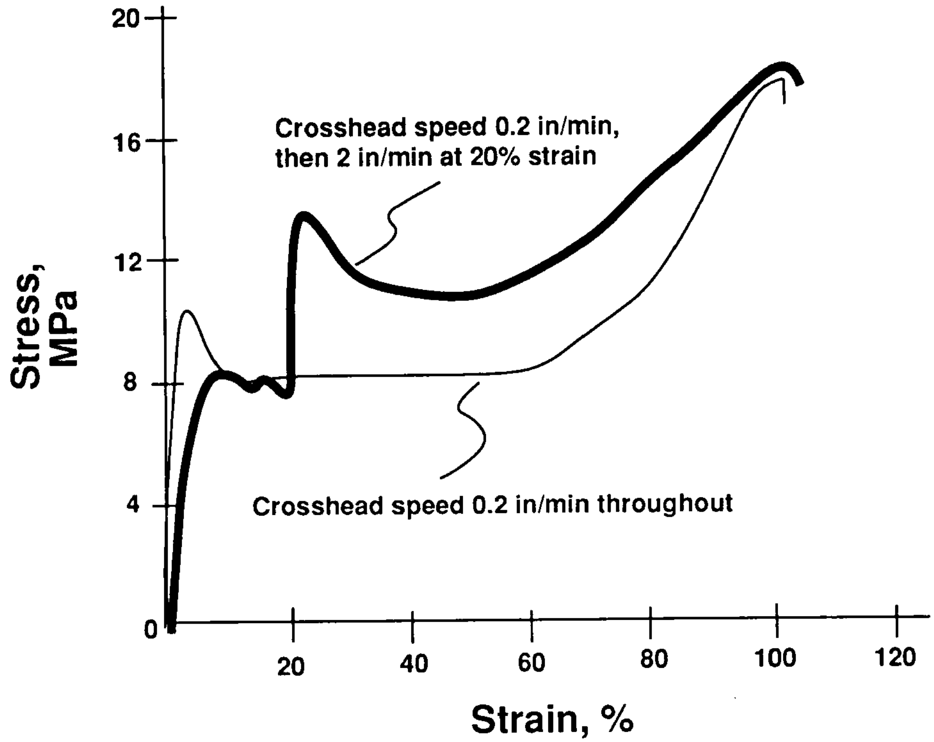

FIGURE 3 Representative stress-strain curves of crosslinked hexanediol dinorbornene [HDDN] films at two different crosshead speeds: 0.2 in/min throughout the test *vs.* an increase from 0.2 in/min to 2.0 in/min after 20% elongation.

yield point in the polymer had been initiated by increasing crosshead speed. After approximately 50% elongation, strain hardening occurs at a higher level of stress than for samples tested at the slower rate. The average tensile strength for these three samples was 18.1 MPa as compared with 15.5 MPa for the samples tested at 0.2 in/min throughout. The tensile strength of the samples tested at the higher speed is approximately 17% greater, which is statistically significant since the coefficient of variance for both sets of samples was less than 5%. The tensile strength of HDDN copolymer films increased when polymer chains were given less, not more, time to rearrange. (The values listed for modulus and elongation to break in Table III for HDDN films are the average values from the two sets of samples).

The HDDN film appears to show more ductile failure than found in the other norbornene-thiol copolymers studied. Generally it has been observed that in crosslinked systems, brittle fracture occurs through localized shear yielding, rather than a crazing mechanism.[12] This indicates that a relatively high amount of viscoelastic and plastic energy dissipation is occurring in the HDDN system. It is important to bear in mind that this material was tested at room temperature, less than 10°C below its T_g. The chains, particularly the hexamethylene units, might have had enough thermal energy for configurational rearrangement in order to accommodate the increasing stress.[13] A theory developed by Bowden and co-workers[14] views the critical step in the yield process as the thermal nucleation under stress of small disc-shaped sheared regions in the polymer. It has been shown for a crosslinked epoxy network that this theory fits the experimental data at temperatures very near T_g.[15] The uniaxial compression tests as a function of temperature which would test the validity of this model for the norbornene/thiol system are being scheduled.

A representative stress-strain curve for the crosslinked film of ethoxylated bisphenol A dinorbornene ester [EBPA-DN] is shown in Figure 4, and is similar to that of the TMP-TN film. This curve shows an initial linear elastic region which ends before 0.5% strain and is followed by a nonlinear region where stress is continually increasing; no yielding occurs prior to failure. The middle range of tensile properties that can be formulated is slightly increased by blending together two of the three norbornene esters (see Table IV). Stress-strain curves show that the unusual features found in HDDN films are apparently masked by the addition of EBPA-DN or TMP-TN to HDDN to prepare the corresponding blended film, as shown by the stress-strain curve of an EBPA-DN/HDDN film, also shown in Figure 4. Due to the high strain to break in HDDN, one would expect some increase in elongation to break in films where HDDN is a component; however, when added to EBPA-DN or TMP-TN, the elongation to break of these materials is not significantly increased.

Dynamic mechanical analysis [DMA] of these films was performed to determine the T_g values as well as the storage and loss shear moduli (G' and G'', respectively) in order to obtain information about the crosslink densities of these materials, using the relationship between the shear modulus (G) and the molecular weight between crosslinks (M_c) predicted by the statistical theory of an ideal rubber:[16]

$$G = \frac{\rho RT}{M_c} \qquad (1)$$

TABLE IV
The tensile properties of norbornene-thiol films containing a 50/50 (w/w) blend of two norbornene resins

	EBPA-DN/TMP-TN	EBPA-DN/HDDN	TMP-TN/HDDN
Tensile Modulus, MPa	2600 ± 300	2000 ± 50	1700 ± 40
Tensile Strength, MPa	44 ± 16	39 ± 4.1	44 ± 2.3
% Elongation	2.2 ± 0.9	2.8 ± 0.4	3.4 ± 0.4

T_g values for the films discussed here are shown in Table V. As opposed to its lack of influence on tensile properties, when the more flexible HDDN was blended with TMP-TN or EBPA-DN, the T_g of the blend was lowered roughly by an arithmetic average. The values of G′ in the rubbery plateau region were always above 10^8 dyne/cm^2. According to several sources,[17,18] crosslinked networks having values of the shear modulus G (or G′, if G′ >>G″, as it is in the rubbery plateau region) in excess of 10^8 dyne/cm^2 follow non-Gaussian statistics. This means that the method by which the molecular weight between crosslinks, M_c, is determined is decidedly more involved; one method[18a] has used a series of films composed of off-stoichiometric reactants and compared results generated through dynamic mechanical analysis, swelling experiments and the application of equations developed by Langley[18b] and also by Scanlan.[18c] This method has not yet been applied to determine M_c for the organic norbornene-thiol copolymers, but it is possible to say that, due to the high value of G′, a highly crosslinked network is present and thus M_c is probably very low. There are two other experimental techniques used to obtain M_c. One of

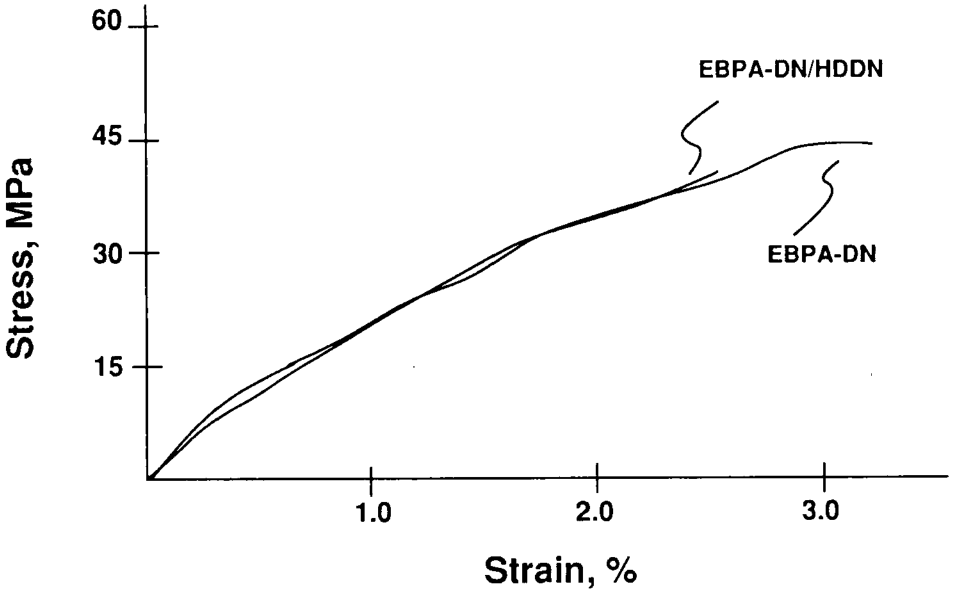

FIGURE 4 Representative stress-strain curves for the crosslinked films of ethoxylated bis-phenol A dinorbornene ester [EBPA-DN] and EBPA-DN/HDDN.

TABLE V
Glass transition values for the organic norbornene-thiol films discussed in this paper

Norbornene Component(s)	Temperature at which a maxima in tan δ occurs (°C)	Value of G′ at 15°C past T_g
EBPA-DN	36.4	9.1×10^8
TMP-TN	67.8	3.1×10^8
HDDN	30.1	7.2×10^8
TMP-TN/EBPA-DN	52.7	2.7×10^8
HDDN/EBPA-DN	35.9	3.6×10^8
TMP-TN/HDDN	46.9	6.9×10^8
PETN	71.5	2.7×10^8

these, swelling, was tried for these materials with poor results. When a piece of film was immersed in a "good" solvent, tetrahydrofuran (THF), the sample rapidly began to flake apart in fairly large "chunks", before uniform swelling could take place. It was attempted to produce a theta solvent by mixing THF with nonsolvents, such as isopropanol, but the ideal proportions which would result in swelling rather than flaking were not found. The second method analyzes elongational data in order to calculate the reduced stress[19] (f*) from the construction of a Mooney-Rivlin plot. If the assumptions of the phantom network are met, then

$$f^*_{ph} = (1 - 2/\phi)\frac{\rho RT}{M_c} \qquad (2)$$

where ρ is the density of the bulk polymer and φ is the functionality of the crosslinks. Since M_c of these materials cannot be obtained through swelling experiments or the application of the straightforward relation between shear modulus and M_c, the more involved methods used by Yeo *et al.*[18] and the construction of Mooney-Rivlin plots and the application of Equation 2 will be used in the future to obtain and compare these data.

It is important to realize that the T_g of many UV "room temperature" curing systems is highly dependent on the radiation cure dose;[20] the light sources themselves generate substantial heat apart from the heat of reaction. Recent work has shown that T_g is not primarily a function of curing temperature, but of the percent conversion of the monomeric/oligomeric reactive species.[21] If the external temperature is near or above the ultimate T_g of the (to be cured) material, mobility of the reacting species is prolonged and thus greater conversion is achieved. This in turn will act to increase the T_g; Kloosterboer and Lijten have shown for an acrylate system that as conversion approaches 100%, a few percent increase in conversion can substantially raise T_g.[20] To illustrate this effect in the norbornene-thiol system, Figures 5 and 6 compare DMA temperature sweeps for a sample cured at a total dose of 620 mJ/cm^2, *versus* a sample cured at a total dose of 1800 mJ/cm^2. The T_g has increased by approximately 8°C; however, both samples appeared to be equally cured and in fact we found that the tensile modulus for the higher dose sample remained essentially unchanged, at 1870 MPa.

In terms of broad-based results, the data obtained for the films composed of two norbornene resins indicates that the resins do mix on a molecular level; there is no indication of phase separation of the individual components. This is claimed by

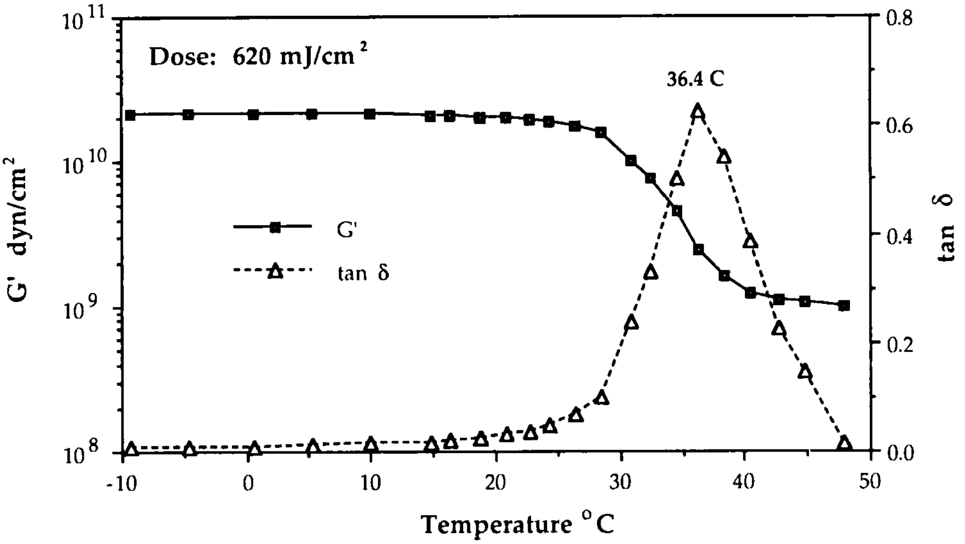

FIGURE 5 Results of a DMA temperature sweep for an EBPA-DN film cured at a total dose of 620 mJ/cm^2.

using the widely-accepted criteria that the presence of a single T_g indicates mixing on a molecular level, while immiscible blends (whose homopolymers have different T_g values) are characterized by more than one glass transition.[22] For each of the three-component systems studied, we observe only one glass transition.

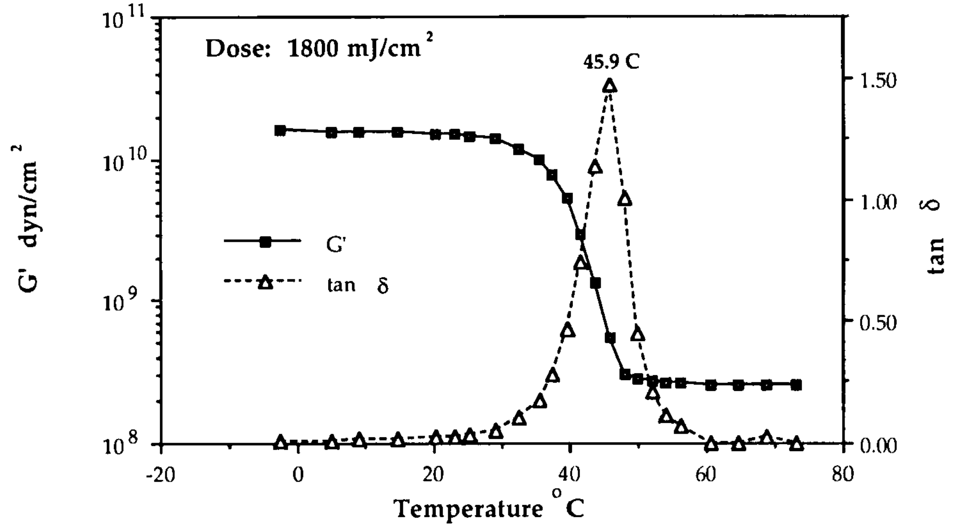

FIGURE 6 Results of a DMA temperature sweep for an EBPA-DN film cured at a total dose of 1800 mJ/cm^2.

Norbornene Siloxane-Thiol Siloxane Films

These films will be referred to as 28N/X, where X denotes the weight percent of filler present; for example, 28N/35 is a film of norbornene siloxane crosslinked with the thiol siloxane, containing 35 wt% filler. Originally, only two filler loadings were tested, 28N/25 and 28N/35. As shown in Table VI, peak stress, elongation to break and tear properties of the 28N/35 film are significantly above those of the 28N/25 film; peak stress and elongation to break effectively double, although the weight percent of filler has not. These unusual, apparently synergistic effects were interesting enough to compel a more thorough investigation of the effect of filler loading on mechanical and dynamic mechanical performance over a wider range of loadings, as well as to determine if these data were reproducible.

The peak tensile stress and elongation to break of films having from 5–41 wt% HDK-H2000 filler are shown in Figure 7. The sharp jump in properties is reproducible, and occurs between 25- and 30-wt% loading. These data also show that in terms of mechanical properties, increases in maximum tensile stress and elongation above 30 wt% filler loading are relatively small, especially when compared with the extra effort needed to "wet in" the filler.

TABLE VI
Tensile properties for norbornene siloxane-thiol siloxane films with 0%, 25- and 35-wt% HDK-H2000 reinforcing fumed silica

	PFS 28N/ Unfilled	PFS 28N/3K5M/ 25% HDK-H2000	PFS 28N/3K5M/ 35% HDK-H2000
Peak Stress, MPa	0.38	3.4	6.5
Peak Strain, %	320	365	518
Tear, pli	—	64	140
Durometer, Shore A	—	30	36

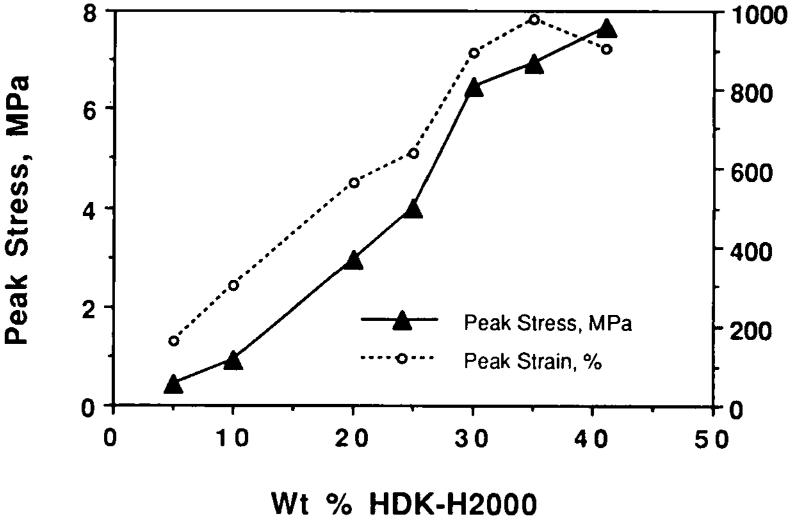

FIGURE 7 Peak stress and peak strain for films having from 5–41 wt% HDK-H2000 reinforcing silica.

The thermal, rheological and microstructural properties of poly(dimethylsiloxane) [PDMS], unfilled and as a silica-reinforced composite, have been the subject of numerous investigations.[23-26] Early volume *versus* temperature plots showed that high molecular weight PDMS had a T_g of approximately −123°C and crystallized at *ca.* −60°C.[27] More recent work[26] has found that T_g is −127°C and T_m is −60°C for a completely crystalline sample, although a value of *ca.* −40°C appears to be a more representative value.[19] (Some silicone suppliers refer to this transition as the "softening point".) When 15 volume % of a fumed silica is added, the T_g increases by about 8°C.[28] Except for the crosslinking norbornene endgroups, 28N is structurally quite similar to PDMS.

The object of the DMA analysis was to observe what effect filler and filler concentration had on T_g, cold crystallization and the melting point of these cured filled composites. The tan δ trace of any of these materials shows three maxima with that at the lowest temperature assigned as the T_g and that at the highest temperature, the melting point; it is reasonable to assign the diffuse local peak in tan δ between these two as being due to cold crystallization. Figure 8 shows the tan δ traces for the 28N/0, 28N/25 and 28N/35 composites. First, it appears that HDK-H2000 has little or no effect on the T_g of the 28N/HDK-H2000/siloxane thiol composite. While the T_g is not constant throughout this series (it varies between −115 and −122°C),

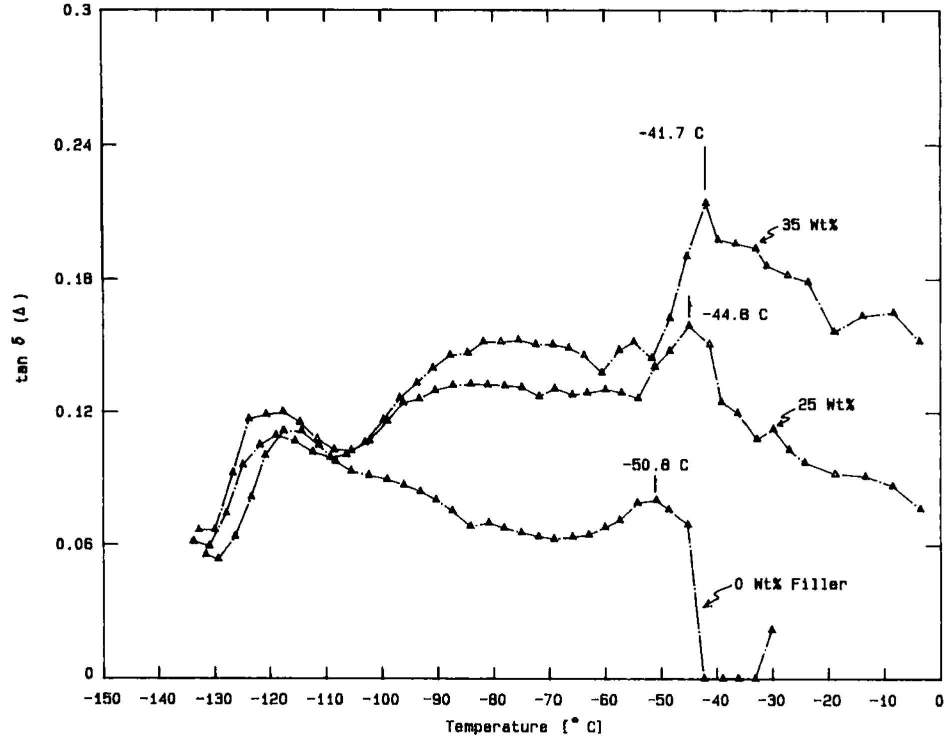

FIGURE 8 The tan δ traces for norbornene siloxane-thiol siloxane composites with 0 wt%, 25 wt% and 35 wt% HDK-H2000.

there is no pattern of monotonic or correlatable change. Figure 9 shows that the location of what is believed to be cold crystallization appears to broaden and shift to significantly higher temperatures (from *ca.* −95°C to a broadened transition between −80°C and −70°C) as filler loading is increased from 0 wt% to 35 wt%.

Lastly, whether the melting point is shifted with increasing filler content depends on which data are viewed. Although the distribution of chain lengths means that a transition such as melting of crystallites occurs over a range of temperatures, the temperature of the midpoint of that transition (T_M) can be defined as the maximum in tan δ.[29] For the purposes of comparison between these filled norbornene siloxanes, the melting point (T_m) can be taken as the midpoint temperature,[30] although that is not strictly correct. One interpretation of the data is that the presence of filler increases T_m, and that to some extent, increasing levels of filler do increase T_m. Also, the tan δ peak sharpens as filler level increases, dramatically so for the highest filled sample, 28N/35. Another explanation, based on the narrowing of the tan δ peak, comes from researchers who found *via* DSC or other thermodynamic measurements, that the melting zone contains two peaks, between −65°C and −40°C.[11,31–33] It has been proposed[34] that the two peaks correspond to different types of crystal structures: aciform crystals, which melt at the lower temperature, and those produced *via* spherulitic growth, which melt at the higher temperature.

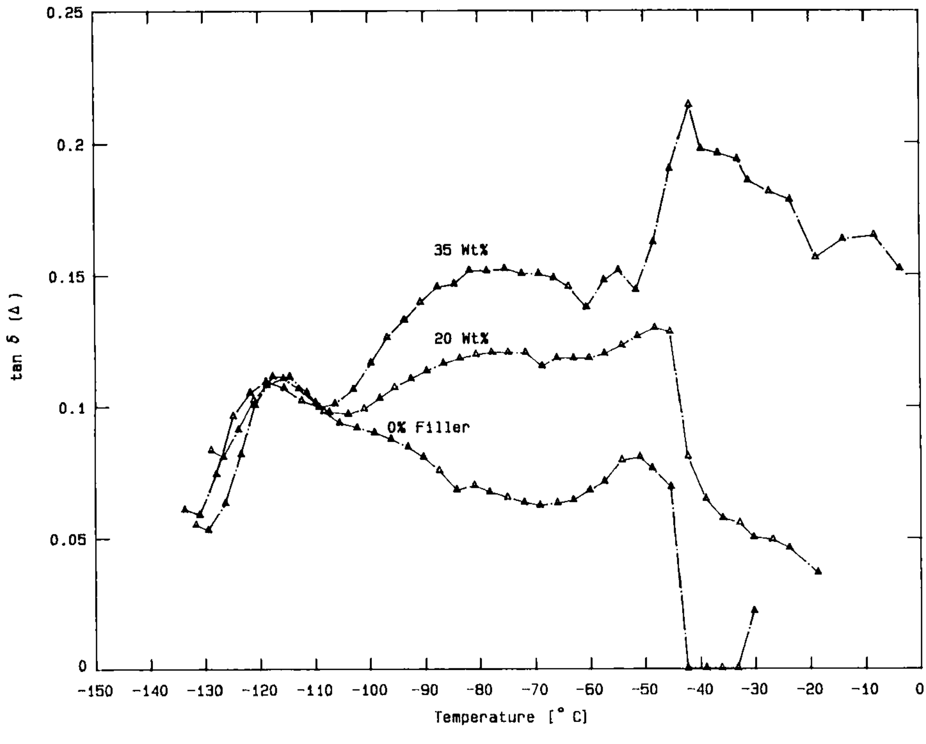

FIGURE 9 The apparent influence of filler loading from 0% to 35 wt% HDK-H2000 on cold crystallization as shown by the broadening and shifting of the tan δ peak.

It is possible that the single broad peak seen for 0 wt% loading is poorly-resolved and is possibly two peaks which overlap. High filler loadings encourage spherulitic growth which produces crystals that melt at higher temperatures; when one structure vastly predominates over the other (as is suspected at high filler loadings), the peak representing the melting transition would become much sharper.

However, the elastic shear modulus (G′) trace must also be examined. Since this is a semicrystalline polymer, G′ does not fall off rapidly after T_g, as it does for an amorphous polymer. The crystallites act as a combination of filler and additional crosslink points,[35] reinforcing the material—until they are melted, and G′ drops rapidly. When the G′ traces for the same samples shown in Figure 8 are overlaid as shown in Figure 10, there are no meaningful differences between the drop in G′ and filler levels.

Dynamic mechanical analysis does monitor thermodynamic transitions, but does so by measuring changes in molecular mobility rather than by obtaining thermodynamic quantities such as H, ΔC_p, ΔV, *etc.* These transitions should next be studied using low temperature dynamic scanning calorimetry, which this laboratory will have acquired in 1992. This technique should be particularly useful in observing T_m and the cold crystallization transition. The thermodynamic data (starting slightly below the onset of cold crystallization and following through melting) will be compared with the dynamic mechanical data, thus aiding interpretation of future dynamic mechanical results of other silicone/silica systems.

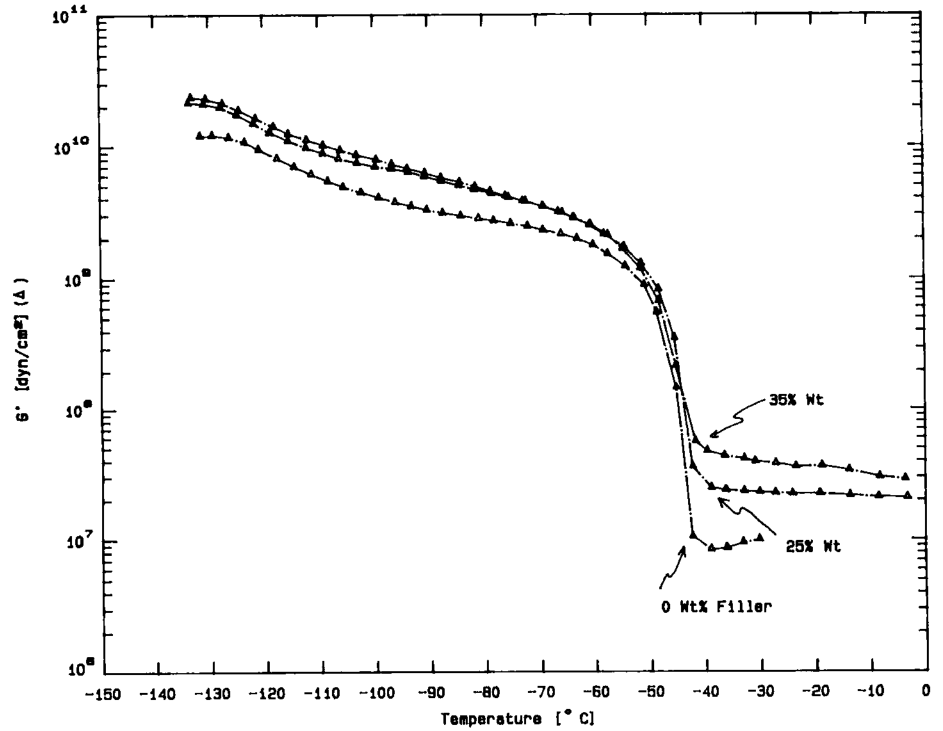

FIGURE 10 The traces of the shear storage modulus (G′) for the same samples shown in Figure 8.

CONCLUSIONS

The results obtained for the organic norbornene ester-thiol films indicate that T_g correlates well with functionality; tensile moduli correspond sporadically. The highest T_g was obtained for a film of PETMP and PETN, a tetrafunctional norbornene ester. However, this material was not as stiff as films prepared from some di- and tri-functional resins. For example, a crosslinked film of PETMP and TMP-TN, which is trifunctional, had the highest tensile moduli and the second-highest T_g. As expected, a more flexible material is formed by the crosslinked HDDN resin due to its six methylene units in the backbone. The resulting cured film, though soft, has a high elongation to break and would be an appropriate choice as a coating for a stiff substrate exposed to changing thermal conditions. Tensile properties of the films consisting of a blend of two norbornene resins crosslinked with thiol show that tensile properties were not considerably modified by blending two norbornene esters, although T_g was modified as predicted by the Flory-Fox equation.[4]

In order to understand the effect of the norbornene endgroups and the thiol crosslinker on structure/property relationships, films were also made of two resins which are the acrylate analogs of EBPA-DN and HDDN: ethoxylated bis-phenol A diacrylate [EBPA-DA] and hexanediol diacrylate [HDDA]. Photoinitiator (Darocur 1173, 2 wt%) was added, but no thiol (difunctional acrylates will crosslink without an additional crosslinking agent). The same curing schedule was followed as for the norbornene-thiol films. An immediate difference could be seen while HDDA was being polymerized: due to the high degree of shrinkage and internal stress caused by polymerization and solidification, cracks emanated in all directions through the film, to the extent that it was not possible to obtain pieces for DMA or tensile samples. It is not uncommon to see high rates of shrinkage and large internal stresses generated with acrylate resins; due to gelation of the system at very low degrees of conversion, the majority of material has not reacted when vitrification sets in. The material is thus a very unforgiving glass as the majority of monomer continues to react. However, difunctional norbornene materials which follow step-growth kinetics are approximately 57% converted before gelation.[4] Much less stress is generated while the material is polymerizing, since it is still in a semi-liquid/non-vitreous state and stresses can easily be dissipated.

EBPA-DA formed a very clear film, and tensile tests identical to those of EBPA-DN were run. The tensile results obtained for EBPA-DA show that end-group functionality and the presence of a tetrafunctional thiol does not have a major effect on tensile properties, which remain quite close to those of EBPA-DN. Tensile modulus was 1840 MPa, tensile strength 55 MPa and elongation to break was found to be 7.7% (all values are averages). However, the T_g of EBPA-DA is higher than that of the corresponding norbornene-thiol film (74°C *vs.* 36°C); this is attributed to the larger free volume caused by the less efficient packing of the bicyclic norbornane rings, which in turn will act to reduce the T_g.

The norbornene siloxanes appear to have two sub-melting and one melting transition. The first sub-melting transition, located between −122°C and −115°C, is believed to be the T_g of the PDMS segment. The presence of filler increases and broadens the higher sub-T_m transition from *ca.* −90°C to between −80°C and

−70°C. This transition is present in pure PDMS at roughly the same temperature[33,36] as our unfilled system and it too shifts with the addition of filler;[36] it has been attributed to cold crystallization.[11,31] The effect of increasing the temperature of cold crystallization on bulk properties is unknown. The addition of filler increases peak tensile stress and strain properties of the material at room temperature, with 30-wt% loading being optimal in terms of peak stress, peak strain and processability. Evidence from dynamic mechanical analysis shows that the molecular-level thermal properties (such as the increase in the melting point) are dependent on the presence and level of filler. However, this change in molecular thermal properties does not influence the location of the *ca.* 3-decade drop in G′, indicating no significant change in the dependence of the mechanical properties of the bulk films on temperature, regardless of filler level.

Acknowledgements

The authors would like to thank S. T. Nakos for his synthetic expertise and R. Jones for performing the tensile tests for the organic norbornene-thiol films. D. Mancini was instrumental in carrying out the dynamic mechanical characterization of the filled norbornene siloxane materials; P. Salamon coordinated the testing of the lap shear data presented in Table II.

References

1. C. R. Morgan, F. Magnotta and A. D. Ketley, *J. Polym. Sci., Polym. Chem. Ed,* **15**(3) 627 (1977).
2. W. J. Steinkraus, J. Woods, J. M. Rooney, A. F. Jacobine and D. M. Glaser, U. S. Patent 4,808,638 "Thiolene Compositions Based On Bicyclic 'Ene Compounds," February 28, 1989, assigned to Loctite Corporation.
3. A. F. Jacobine, D. M. Glaser and S. T. Nakos, European Patent Application 0388028, published September 19, 1990.
4. D. M. Glaser, P. J. Grabek, A. F. Jacobine, D. Mancini, M. Masterson, S. T. Nakos, M. A. Rakas and J. G. Woods, *J. Appl. Polym. Sci.,* 1991, in press.
5. C. D. Bain, E. B. Troughton, Y-T. Tao, J. Evall, G. M. Whitesides and R. G. Nuzzo, *J. Am. Chem. Soc.,* **111,** 213 (1989).
6. E. B. Troughton, C. D. Bain, G. M. Whitesides, R. G. Nuzzo, D. L. Allara and M. D. Porter, *Langmuir,* **4,** 365 (1988).
7. R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.,* **105,** 4481 (1983).
8. R. G. Schmidt and J. P. Bell, *J. Adhesion,* **25,** 85 (1988); R. G. Schmidt and J. P. Bell, *J. Adhesion,* **27,** 135 (1989).
9. A. F. Jacobine, D. M. Glaser and S. T. Nakos, in *Radiation Curing of Polymeric Materials,* **ACS Symposium Series 417,** C. E. Hoyle and J. F. Kinstle, Eds. (American Chemical Society, Washington, D.C., 1990).
10. A. F. Jacobine, D. M. Glaser, S. T. Nakos, M. Masterson, P. J. Grabek, M. A. Rakas, D. Mancini and J. G. Woods in *Radiation Curing of Polymers,* (Royal Society of Chemistry, London, 1991), pp. 342–357.
11. M. I. Aranguren, Ph.D. Thesis, U. Minnesota, 1990.
12. A. J. Kinloch and R. J. Young, *Fracture Behavior of Polymers* (Applied Science Publishers, Essex, U.K., 1983), Chapts. 4 and 8.
13. D. W. van Krevelen, *Properties of Polymers: Correlations with Chemical Structure* (Elsevier, New York, 1972), Chapt. 10.
14. P. B. Bowden and S. Raha, *Phil. Mag.,* **29,** 149 (1974).
15. S. Yamini, R. J. Young, *J. Mat. Sci.,* **15,** 1814 (1980).
16. L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon Press, Oxford, 1975), Chapts 6 and 8).
17. L. W. Hill and K. Kozlowski, *J. Coat. Tech.,* **59**(751), 63–71 (1987).

18a. J. K. Yeo, L. H. Sperling, and D. A. Thomas, *J. Appl. Polym. Sci.,* **26,** 3977 (1981).

18b. N. R. Langley, *Macromolecules,* **1**(4), 348 (1968).
18c. J. Scanlan, *J. Polym. Sci.,* **43,** 501 (1960).
19. J. E. Mark and B. Erman, *Rubberlike Elasticity A Molecular Primer* (Wiley, New York, 1988).
20. J. G. Kloosterboer and G. F. C. M. Lijten, in *Cross-Linked Polymers,* R. A. Dickie, S. S. Labana and R. S. Bauer, Eds **ACS Symposium Series 367** (American Chemical Society, Washington, D.C., 1988).
21. A. Hale, C. W. Macosko, and H. E. Bair, *Macromolecules,* **24**(9), 2610 (1991).
22. F. E. Karasz and W. J. MacKnight, in *Polymer Blends,* Vol. 1, D. R. Paul and S. Newman, Eds. (Academic Press, New York, 1978), pp. 186–243.
23. M. I. Aranguren, E. Mori and C. W. Macosko, submitted to *J. Coll. & Interface Sci.,* (1991).
24. M. I. Aranguren, C. W. Macosko, B. Thakkar and M. Tirrell, *Mater. Res. Soc. Symp. Proc.,* **170,** 303 (1990).
25. D. C. Edwards, *J. Mat. Sci.,* **25,** 4175 (1990).
26. M. Varma-Nair, J. P. Wesson and B. Wunderlich, *J. Therm. Anal.,* **35,** 1913 (1989).
27. C. E. Weir, W. H. Laser and L. A. Wood, *J. Res. Nat. Bur. Stand.,* **44,** 367, (1950).
28. F. O. Stark, J. R. Falender and A. P. Wright,"Silicones," in *Comprehensive Organometallic Chemistry,* G. Wilkinson and F. Stone, Eds, (Pergamon Press, New York, 1982).
29. J. D. Ferry, *Viscoelastic Properties of Polymers, 3rd edition* (Wiley, New York, 1980), Chapts. 12 and 16.
30. L. Hill, private communication, 1991.
31. E. L. Warrick, O. R. Pierce, K. E. Polmanteer and J. C. Saam, "Silicone Elastomer Developments 1967–1977," in *Rubber Chemistry and Technology,* **52,** 476 (1979).
32. C. M. Huggins, L. E. St. Pierre, and A. M. Bueche, *J. Phys. Chem.,* **64,** 1304 (1960).
33. S. J. Clarson, K. Dodgson and J. A. Semlyen, *Polymer,* **26,** 931 (1985).
34. J. D. Helmer and K. E. Polmanteer, *J. Polym. Sci.,* **13,** 2113 (1969).
35. J. J. Aklonis and W. J. MacKnight, *Introduction to Polymer Viscoelasticity, 2nd edition,* (Wiley, New York, 1983), Chapt. 3.
36. A. Yim and L. E. St. Pierre, *Polym. Letts.* **8,** 241 (1970).