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Surface characterization of cross-linked elastomers by shear modulation force microscopy

Y. Zhang[a], S. Ge[a], M.H. Rafailovich[a,*], J.C. Sokolov[a], R.H. Colby[b]

[a]*Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, NY 11794, USA*
[b]*Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA*

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Abstract

Brominated poly(isobutylene-*co*-4-methylstyrene) (BIMS) is a synthetic terpolymer which can be stoichiometrically cross-linked by *N*,*N*′-dicinnamylidene-1,6-hexanediamine (DIAK). The degree of cross-links on bulk samples was determined by measuring the low frequency shear modulus with parallel plate method. The surface modulus of the same samples was measured using a new method, shear modulation force microscopy (SMFM). The moduli of the bulk sample and the surface were found to have the same scaling with the cross-link density, and good agreement with rubber elasticity theory was obtained in both cases. The SMFM was then used to monitor the cross-linking process, as a function of DIAK concentration and curing time, in thin films where standard rheological methods cannot be applied. The results show that in all cases the cross-linking reaction at the surface reaches saturation in less than 10 min as compared to at least 1 h in the bulk samples.

Keywords: Shear modulation force microscopy; Mechanical properties; Cross-linked elastomer

1. Introduction

Elastomeric materials are often cross-linked in order to control their mechanical properties. The degree of cross-links as well as the reaction dynamics is crucial to the performance of the final product. Traditional methods such as dynamic mechanical analysis, tensile testing, or spectroscopic methods measure only bulk properties. Hence these techniques do not work well when the cross-linked product is only a coating or the relevant region is at the surface of the material. Investigation of the cross-link density and kinetics at surfaces and in ultra-thin polymer films requires a microscopic approach. Here we describe a new scanning force technique, shear modulation force microscopy (SMFM), which was recently shown to be very effective in measuring surface viscoelastic properties and glass transition temperatures of polymer thin films [1]. In this paper we show that this technique, which essentially probes the surface modulus, can also be used to investigate the surface cross-link density.

The system we chose to study is brominated poly(isobutylene-*co*-paramethylstyrene) (BIMS, Fig. 1), a synthetic terpolymer of isobutylene (IB), paramethylstyrene (PMS), and parabromomethylstyrene (BrPMS). The distribution of IB, PMS and BrPMS of the terpolymer is random due to the polymerization and bromination procedures [2]. The ratio of PMS to IB composition can be continuously varied to control the modulus. BIMS polymers can be stoichiometrically cross-linked by *N*,*N*′-dicinnamylidene-1,6-hexanediamine (DIAK) at 423 K in the presence of small amount of water (Fig. 1). Usually the components are mixed in a Brabender mixer and allowed to react for different times. This procedure is not satisfactory for thin films since the materials can react from the heat. Fortunately, both BIMS and DIAK are soluble in toluene, hence one can also cross-link thin films after spin coating solutions of BIMS and DIAK on silicon substrates. The degree of the cross-links is then simply controlled by the ratio of DIAK to BIMS and the curing time.

In this work, we first calibrate the technique by measuring the low frequency shear modulus of bulk cross-linked samples using standard rheological methods, and then measure their surface mechanical response using SMFM. We also show how SMFM can be used to monitor the cross-linking process in thin films where standard rheological methods cannot be applied.

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* Corresponding author.

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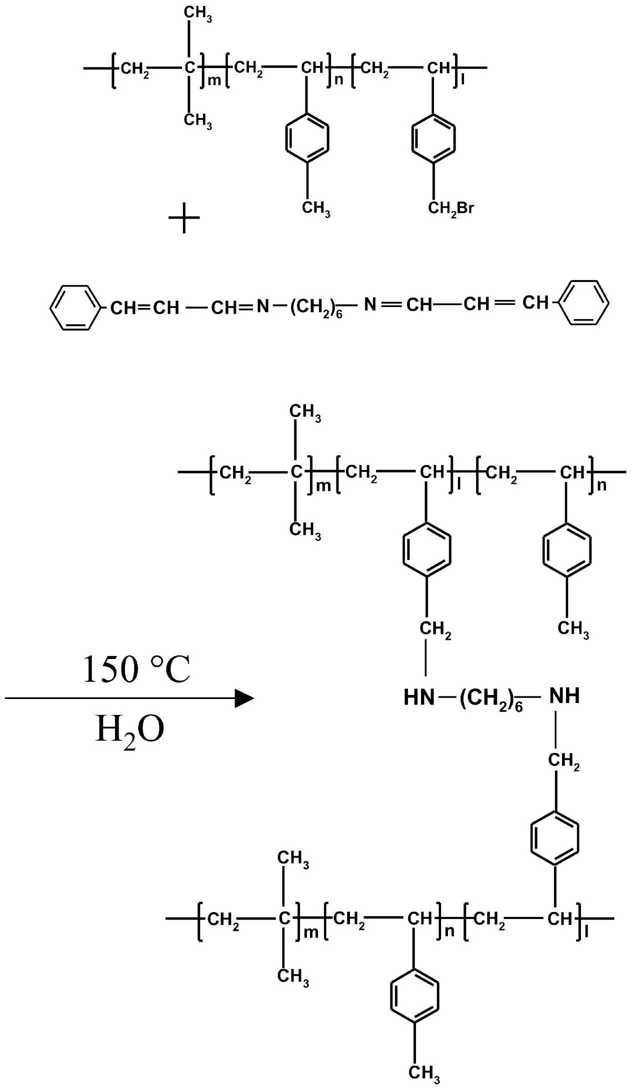

Fig. 1. Molecular structure of BIMS, DIAK, and the scheme of cross-linking reaction.

2. Experimental section

The characteristics of four types of BIMS terpolymers are listed in Table 1. The polymers and DIAK were provided by ExxonMobil Research and Engineering Company, Annandale, NJ. These commercial polymers have M_n of 170–190 kg/mol with polydispersity of $M_w/M_n = 2.5–2.7$. It should be noted that all four types of BIMS have large amounts of isobutylene content (>96 mol%) and similar molecular weight. Although the amount of DIAK crosslinker was measured by weight, for clarity purposes, we convert wt% to mol% using 57.5 g/mol as the average monomer mass for all BIMS terpolymers. Consequently we can directly compare the amount of crosslinker with the bromide mole percentage of each BIMS. The DIAK amount cannot simply be described by a stoichiometric ratio to bromide since the bromide content in each BIMS is different.

Table 1
The characteristics of four types of BIMS terpolymers

Elastomer	Br (mol%)	IB (mol%)	Total PMS (mol%)
BIMS-A	0.75	96.3	3.7
BIMS-B	0.75	97.6	2.4
BIMS-C	1.2	96.3	3.7
BIMS-D	1.8	96.3	3.7

The bulk samples for rheological measurement were prepared by casting 1.5 mm thick samples from toluene solutions with the prescribed amount of DIAK and BIMS-A (Br = 0.75 mol%). The resultant three samples with 0.08, 0.17, and 0.34 mol% of DIAK, were cured in air at 423 K for 2 h. The shear modulus and phase angle were measured with an ARES rheometer (Rheometric Scientific, NJ) using parallel plate method. Subsequently the surfaces of the bulk samples were studied by the SMFM technique.

The polymer thin films were prepared by the following procedure. BIMS polymers were first dissolved in toluene at a concentration of 20–25 mg/ml. DIAK was dissolved in toluene at a concentration of 5 mg/ml. DIAK solution was then mixed with various BIMS solutions of prescribed volume ratios. Silicon wafer pieces of 2 cm by 2 cm size were cleaned and etched in HF to ensure a hydrophobic surface. The mixed solution was then spin coated on a silicon wafer at 2500 rpm. The resultant samples, with coatings of approximately 250 nm thick, were dried in vacuum and placed on a preheated aluminum block in an oven at 423 K and 30% relative humidity. After being cured for prescribed times, the samples were quenched to room temperature by being placed on a cold aluminum block. It should be noted that the BIMS layers slowly cross-link with DIAK in air even at room temperature. Therefore, curing was immediately followed by SMFM analysis.

The experimental setup of the SMFM method is described in an earlier article [1]. A schematic diagram of the electrical connection is given in Fig. 2 The AFM used in this study is a Digital Instruments Dimension 3000 located in a sealed glove box. Samples were measured at 298 K in purged dry nitrogen. We used the same etched silicon cantilever (Digital Instrument) with a spring constant of ~0.1 N/m for all measurements. A sinusoidal drive signal with a frequency of 1400 Hz was applied to the x-piezo controlling the cantilever, inducing a small oscillatory motion of the tip parallel to the sample surface. A drive frequency of 1400 Hz was chosen for the measurements since it lies in the flattest region of the cantilever's response curve. We used a drive signal amplitude of 15 mV which corresponds to an x-piezo displacement of 3 nm. A normal load force of 25 nN was applied to maintain tip contact with the sample. The lateral deflection of the cantilever was detected through a position-sensitive diode and was fed into a dual-phase lock-in amplifier set at the tip modulation frequency.

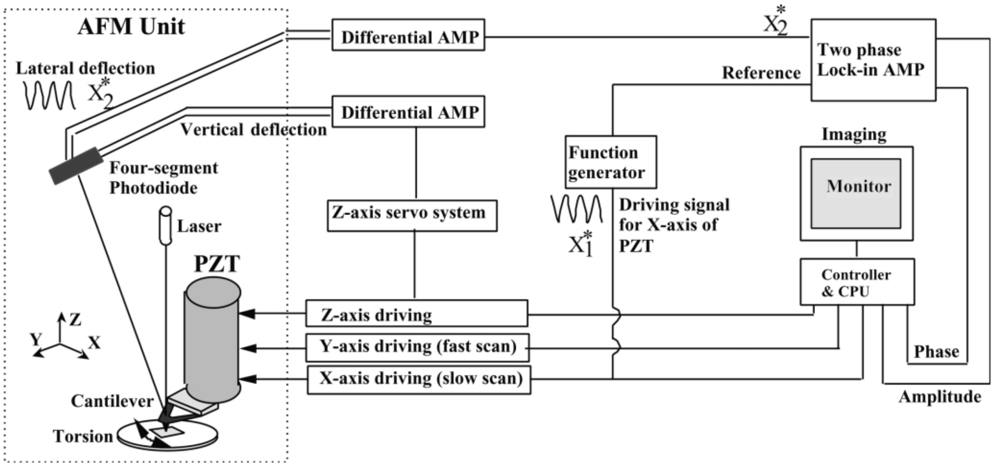

Fig. 2. Diagram of the electrical connection of SMFM.

3. Results and discussion

In our measurement, a small fixed sinusoidal drive signal, ΔX_p is applied to the x-piezo in a direction perpendicular to the fast scan direction inducing a small oscillatory motion of the cantilever tip parallel to the sample surface. At the same time, a normal force is applied to maintain tip contact with the sample. The lateral deflection amplitude of the cantilever, ΔX, which is proportional to the torsion of the cantilever ΔX_{lever} can be measured as a function of temperature using a lock-in amplifier, tuned to the drive frequency.

A full theory of operation would include an account of the elastic behavior of the tip and cantilever, tip–polymer interaction, and polymer viscoelastic response. Such a theory is not currently available and the precise experimental characterization of the tip and tip–polymer interface is difficult and incomplete. The elastic part of the response could be modeled using a Hertz-type analysis [3] involving three coupled springs, cantilever, tip and tip–sample contact, with the lateral displacement of the x-piezo, ΔX_p, being distributed between the compliant elements,

$$\Delta X_p = \Delta X_{\text{lever}} + \Delta X_{\text{tip}} + \Delta X_{\text{contact}} \tag{1}$$

If the tip does not slip relative to the sample then the lateral force acting on the three springs must be equal, i.e.

$$\begin{aligned} k_{\text{lever}}\,\Delta X_{\text{lever}} &= k_{\text{tip}}\,\Delta X_{\text{tip}} = k_{\text{contact}}\,\Delta X_{\text{contact}} \\ &\equiv k_{\text{eff}}(\Delta X_{\text{lever}} + \Delta X_{\text{tip}} + \Delta X_{\text{contact}}) \end{aligned} \tag{2}$$

and $k_{\text{eff}} = (1/k_{\text{lever}} + 1/k_{\text{tip}} + 1/k_{\text{contact}})^{-1}$

The observed decrease of ΔX_{lever} with increase of cross-link density of a cross-linked system indicates k_{eff} decreases despite the hardening of the sample elasticity. In elastic contact theory, the contact stiffness for a spherical tip is given by [3–6]

$$k_{\text{contact}} = 8aG^* \tag{3}$$

where a is the contact radius, $G^* = [(2 - \upsilon_{\text{tip}})/G_{\text{tip}} + (2 - \upsilon_{\text{polymer}})/G_{\text{polymer}}]^{-1}$. Here G_{tip} and G_{polymer} are the tip and polymer shear moduli, υ_{tip} and $\upsilon_{\text{polymer}}$ are the Poisson ratios of tip and polymer, respectively. If G^* were determined primarily by G_{polymer} and a given by the Hertz value for indentation of an elastic substrate by a hard tip: [7] $a = (1/\sim E^*)^{1/3}$ and $E^* = E_{\text{polymer}}/(1 - \upsilon^2_{\text{polymer}})$, then $k_{\text{contact}} \sim G^{2/3}_{\text{polymer}}$. This contribution, if dominant, would cause k_{eff} to increase with cross-link density increase, contrary to observation. Applying the JKR theory to the contact would increase a, tending to increase the Hertz estimate of k_{contact} but not sufficiently to overcome the decrease in k_{eff}. A possible explanation is that the Hertz model approximates the indentation and lateral motion as decoupled and a more realistic theory of the lateral response of the polymer in the case when the tip penetration is large will give a higher k_{contact}. We may also say, from independent experiments on glass transition measurement [1,8] that the result of lower modulus samples giving higher ΔX_{lever} is also observed. We interpret this to mean that we are dealing primarily with elastic effects (viscous creep being secondary). At this point, we can only conclude qualitatively that the increase in tip penetration as the polymer softens leads to a larger lateral deflection.

The lateral deflection, ΔX, plotted as a function of the drive amplitude from the surface of three molded and lightly cross-linked bulk samples, is shown in Fig. 3. From the figure we can see that ΔX is proportional to the drive amplitude for all samples at drive amplitudes less than 30 mV. For amplitudes greater than 30 mV, the ΔX values of the higher cross-linked samples become non-linear, indicating that the tip penetration is smaller and hence the cantilever slips. From the figure we can also see that ΔX

decreases with increasing cross-link density, indicating that the modulus is increasing. In order to compare to our results with bulk measurements we first calculate the predicted modulus based on rubber elasticity theory.

Since the DIAK concentration in all molded samples is less than the stoichiometric amount of bromide, the cross-link density of the three samples can be calculated assuming a complete conversion of DIAK molecules. From the classical rubber elasticity theory [9,10] we find:

$$G = \rho RT/M_x \tag{4}$$

where ρ is the density of the polymer (950 kg/m^3), $R = 8.31$ J/(mol K), T is the temperature (423 K). M_x is the average molecular weight of the chain between the cross-linked sites given by:

$$M_x = 57.5(\times 10^{-3}\ \text{kg/mol})/(2\phi) \tag{5}$$

or

$$G = k\phi \tag{6}$$

Here ϕ is the mol% of the DIAK crosslinker in the three samples, which represents the relative cross-link density, and $k = 2\rho RT/0.0575 = 1.16 \times 10^8$ Pa.

Using Eq. (4), we could calculate the shear modulus at 423 K as a function of crosslinker amount. The values are listed in Table 2 and plotted as a solid line in Fig. 4(a). We can then compare the calculation with the values of the low frequency shear moduli measured on samples of known cross-link density with the standard parallel plate method at 423 K. The results are plotted in Fig. 4(a) as open circles and are tabulated in Table 2. The dashed line is the linear fit to the data. From the figure we can see that the slope of the theoretical line is higher than that of the measured line. This is due to the fact that some of the DIAK molecules are 'wasted' making dangling structures that do not bear stress, causing the measured modulus to be smaller than the predicted value by rubber elasticity theory [10]. To probe the relationship between measured bulk modulus and their surface mechanical response, we plotted ΔX, the slope of the linear part on the surface mechanical response curve in Fig. 3, as a function of measured bulk modulus shown in Fig. 4(b). From the figure we find that the relationship is linear with a fitted slope of -0.7, then for the BIMS/DIAK cross-linked system we have:

$$\Delta X \sim G^{-0.7} \tag{7}$$

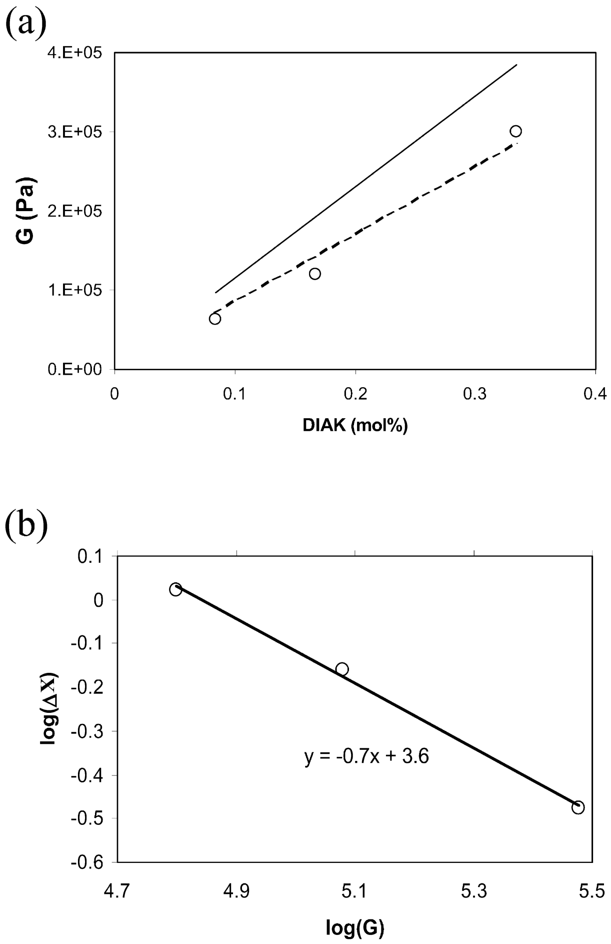

Fig. 4. (a) Shear modulus G estimated from Flory rubber theory (solid line) and measured by a rheometer (circles with dashed linear fit) vs DIAK amount (mol%) for three bulk samples of BIMS-A (Br = 0.75 mol%). (b) log(ΔX) vs. log(G) where G is the shear modulus measured by a rheometer.

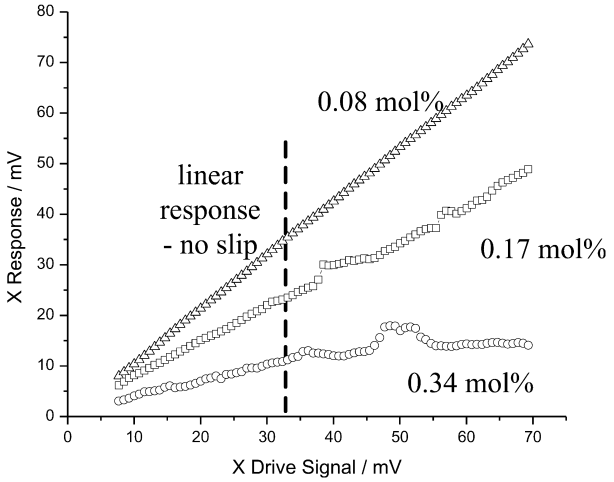

Fig. 3. Lateral response (ΔX) vs drive amplitude for three bulk samples.

We then apply the SMFM method to study the relative

Table 2
The DIAK crosslinker amount, average molecular weight between cross-linked sites, and the shear moduli at 423 K for molded and cured BIMS-A samples obtained from rubber elasticity theory and rheometer

DIAK (mol%)	M_x (kg/mol)	Estimated modulus from rubber theory (Pa)	Measured modulus (Pa)
0.08	34	9.7×10^4	6.3×10^4
0.17	17	1.9×10^5	1.2×10^5
0.34	8.6	3.8×10^5	3.0×10^5

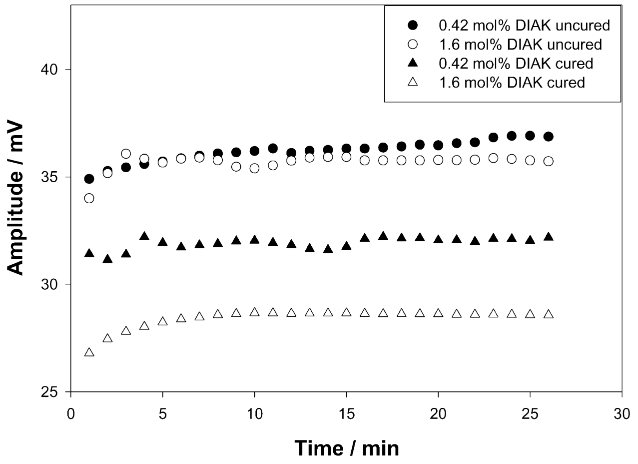

Fig. 5. ΔX vs observation time curves for uncured and cured BIMS-B (Br = 0.75 mol%) layers with 0.42 and 1.6 mol% of DIAK.

surface modulus as a function of cross-link density for spin coated thin films where standard bulk measurements are not possible. In Fig. 5 we plot ΔX as a function of observation time for uncured and cured BIMS-B (Br = 0.75 mol%) samples with 0.42 and 1.6 mol% DIAK. The ΔX values are the same for the two uncured BIMS samples, as expected. On the other hand, the ΔX values for cross-linked samples were reduced by approximately 10 and 20%, for the $\phi =$ 0.42 and 1.6 mol% samples, respectively, indicating that the surface becomes more rigid with increasing cross-link density. One should also notice from the figure that it takes about 5 min for ΔX to reach its equilibrium value on the sample surface. Hence all data discussed in this paper were obtained from the average values of ΔX after 5 min of contact, where we assume that the sample–tip interaction has equilibrated. Only then can we assume that the indentation depth h is constant and the contact area is only a function of the surface modulus of the films.

In the cross-linking reaction, two bromide groups in BIMS are linked by one DIAK molecule through nucleophilic substitution. Since the bromide content of various BIMS is well characterized, the amount of DIAK required to fully substitute the bromide sites can be simply estimated from the stoichiometric molar ratio of DIAK to bromide (1:2), assuming the conversion of bromide is close to complete. We chose BIMS-D, which has the highest bromide content (1.8 mol%), to investigate the amount of DIAK required to fully cross-link the elastomer film. Specifically, 0 (control) to 6.7 mol% of DIAK was mixed with BIMS-D in the solution for spin coating the elastomer layers. Fig. 6 shows the ΔX values of uncured and cured samples, approximately 200 nm thick, as a function of the DIAK concentration (ϕ). From the figure we can see that, as before, no change in ΔX is observed in the uncured samples, despite the large amount of DIAK added. After curing, ΔX drops sharply in the range of $\phi = 0-2$ mol% and then saturates at approximately 3 mol%. This concentration is then presumed to be the minimum required amount to fully saturate the bromide functionalities in the film. This value is much larger than 0.9 mol%, the calculated stoichiometric amount. This may be due to the preferential segregation of diamine to the Si interface where it hydrogen bonds with surface silanol groups and hence not be available for cross-linking. This observation is different from the results of rheological studies on cured bulk samples, which indicated that the shear modulus reaches its maximum value when DIAK is close to the stoichiometric amount [11].

From the scaling relationship in Eq. (7), we relate the measured values of ΔX to the shear modulus, G, which in turn scales with the DIAK concentration (ϕ). The relative G values, normalized to $G = 1$ at $\phi \sim 3$ mol%, are plotted in Fig. 6 and connected with the dashed line to guide the eye. From the figure we can see that the values of G estimated

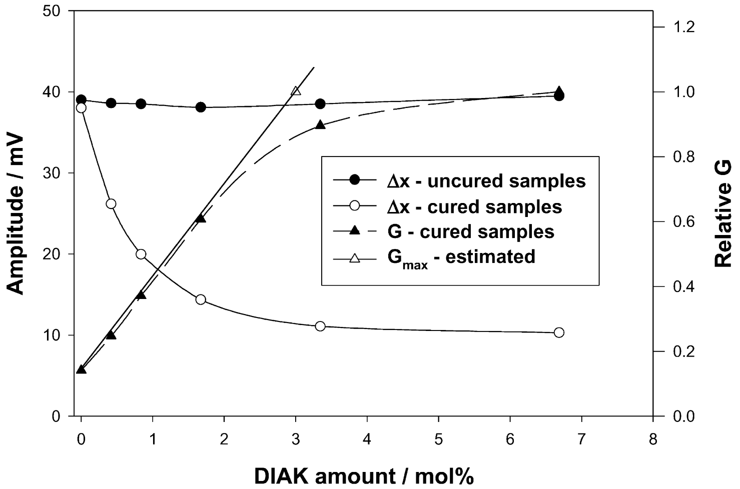

Fig. 6. ΔX (circles) and estimated G (triangles) vs DIAK concentration curves for uncured and cured BIMS-D (Br = 1.8 mol%) layers. The straight line represents the linear regime of G vs DIAK concentration.

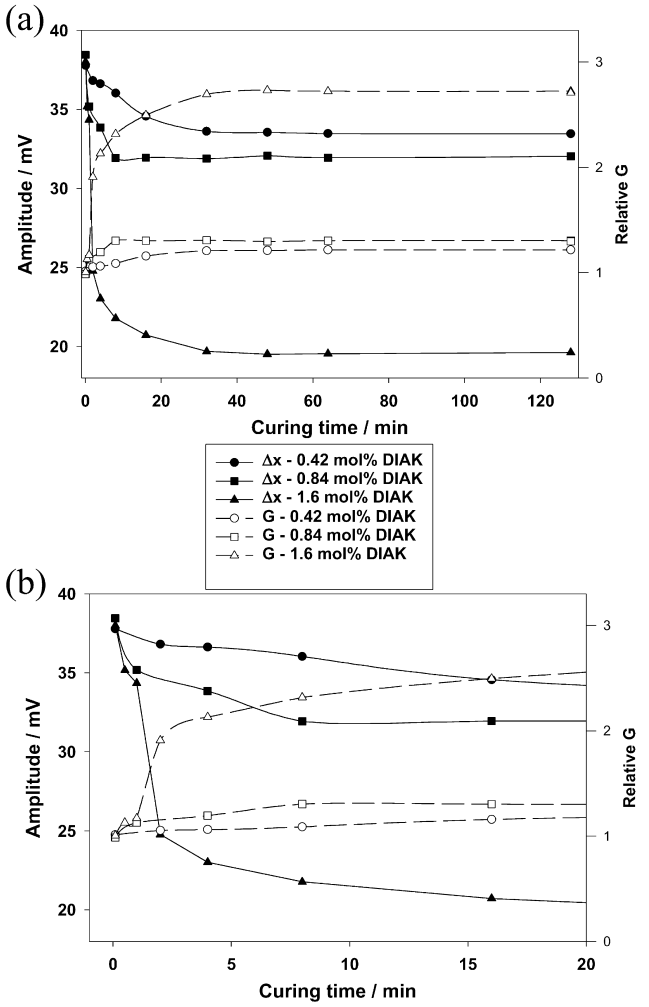

Fig. 7. ΔX and estimated G vs curing time curves for BIMS-C ($Br = 1.2$ mol%) layer with 0.42, 0.84, and 1.6 mol%. (a) and (b) are plotted at different time scales.

from Eq. (7) scale linearly with the cross-link density, as predicted by the rubber elasticity theory in Eq. (4), in the range of $\phi = 0.5-2$ mol% and saturate for $\phi \sim 3$ mol% where further cross-linking does not occur.

We also investigated the kinetics of the cross-linking reaction in order to determine whether any difference exists between the bulk and the thin films. In the bulk, the cross-linking reaction is known to take approximately 60 min at 423 K to reach completion even for DIAK concentrations that are close to or larger than the stoichiometric values.

Here we studied the change in modulus as a function of curing time for thin films of BIMS-C ($Br = 1.2$ mol%) with three different concentrations of DIAK, $\phi = 0.42$, 0.84, and 1.6 mol%. Fig. 7(a) shows the ΔX values of the three sets of samples as a function of curing time, while Fig. 7(b) shows an expanded portion of the data at short times. In all sets, the ΔX values decrease with increasing curing time, to a final plateau value which decreases with increasing DIAK concentration. From the figure we can also see that the curing time required for ΔX to reach the equilibrium value decreases with increasing DIAK concentration. The curve with the lowest DIAK concentration, $\phi = 0.42$ mol%, takes approximately 20 min to reach equilibrium, while ΔX in the 0.84 mol% curve reaches a constant in less than 10 min. The curve with the highest DIAK concentration ($\phi = 1.6$ mol%) decreases sharply and reaches the plateau value within 2 min. In all cases, the times to complete the reaction at for thin films are much faster than in the bulk, where 1 h or longer is needed to complete the cross-linking reaction [8]. In the bulk the reaction rate is limited by the slow diffusion of water into the hydrophobic polymer. In thin films water diffuses more readily and there is always a residual layer adsorbed at the silicon surface [12].

4. Conclusions

The SMFM technique is highly sensitive to the change in the surface modulus of cross-linked elastomer films. We found that the cross-linking reaction at the surface is significantly faster than in the bulk material. This may be a reflection of the fact that moisture penetrates more readily into a thin film than into the bulk of a hydrophobic polymer. In addition, the amount of DIAK required to fully cross-link the film is much higher than the stoichiometric amount. This may be due to the segregation and hydrogen bonding of the crosslinker with the Si substrate. The cross-linking kinetics at the surface is also highly sensitive to the crosslinker amount in the system. Based on the result of bulk samples, we were able to estimate the relative modulus thus the cross-link density in thin films. Therefore, SMFM can be used to monitor the change in surface cross-link density.

Acknowledgements

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