

# Kinetic and Rheological Characterization of New, Very Soft Polyurethane Elastomers for Comfort Applications

EMILIE SMITH-HEBERER, LIFENG WU and RAFAEL E. CAMARGO

*Huntsman Polyurethanes  
2190 Executive Hills Boulevard  
Auburn Hills, MI 48326*

## ABSTRACT

Soft, gel-like polyurethane elastomers have seen an increased use in many applications where comfort is a key performance requirement. Huntsman Polyurethanes has developed a number of products to fulfill the diverse needs of the market. All of the new materials are completely plasticizer free. In order to understand how these materials can be designed for different applications it is important to relate their network properties to final performance. In this paper we will discuss some rheological techniques that are used to characterize both the curing behavior and end viscoelastic and mechanical response of these systems. A unique, two stage curing behavior will be demonstrated for some model systems. Using dynamic mechanical analysis, the response of systems with different network properties will be compared. Final properties of several systems will be discussed. This work has enabled us to develop systems that are already being considered for novel comfort applications. The properties of these developmental systems will also be discussed.

## INTRODUCTION

Due to the latitude of formulations, the properties of the polyurethane elastomers can vary over a very wide range, both in terms of hardness or modulus and density. Full density elastomers and elastomer-like materials can vary from gel type materials to hard tough products, with hardness spanning a number of scales from Shore OO or lower to Shore D. In recent years, those products at the low end of the scale, i.e. Shore A 30 or less have received increased attention because they can be formulated to make products with very soft tact or even liquid-like properties that find use in comfort and pressure relief applications. A gel can be described as a colloidal system with liquid like characteristics. Polyurethane gels can be produced by a number of routes. Gels have been extensively investigated for insert applications in furniture, sports articles, office support pads and medical applications. Many polyurethane gels are obtained by incorporating a plasticizer into a soft elastomer; several options have been developed to produce very soft gels without the use of plasticizers. One of these approaches is to choose materials of a particular functionality and combine them a low index to produce a combination of a network and multiple loose chain ends [1]. Huntsman has developed patented technology using special monol polyol combinations that allows the production of very soft materials even at index ratios of 1.0 (ratio of isocyanate to hydroxyl equivalents) and without the presence of any plasticizer or other migrating products [2].

On the higher end of the scale we encounter very soft elastomers that span the range between these gel-like products and conventional soft elastomers such as those described by Tuinman et al. [3]. These materials, and many others studied in the literature, however, (see for instance reference [4]) are more conventional elastomers produced by combinations of short chain diols and flexible polyols, most of these systems having a typical  $[AB]_n$  block copolymer composition and typical phase separated morphology [5]. Perhaps worth mentioning in this area is the work of Chang et al. [4] because they systematically studied the presence of crosslinking points, in the hard and soft phase and found that soft phase crosslinking was preferable in terms of performance to hard phase crosslinking. All the materials just described have hardness typically in the Shore A scale of 30 or higher.

Of particular interest in this work was the study and characterization of elastomers with hardness values below ca. 30 in the Shore A scale but above ca. 40 in the Shore OO scale. In order to achieve lower hardness in elastomers it is useful to understand that conventional hard block, soft block combinations achieve a practical lower limit. To further lower the

hardness we need to approach these systems as conventional elastomeric networks and apply traditional network properties to describe them. Thus, instead of looking at variables such as hard block content, we focus our attention on crosslink density and other related parameters such as molecular weight between crosslinks,  $M_c$ . Also important, as described elsewhere [6, 7] is the effect of monol species in the formulation. Lee et al. [6], for instance have used some simple systems to show that the concentration of dangling chains in a polyurethane elastomer can significantly affect viscoelastic properties of the material. A higher concentration of dangling chains leads to more viscous losses as determined from higher  $\tan \delta$  values and lower storage modulus in dynamic mechanical analysis, DMTA, data.

Earlier findings of the present work were reported earlier [8]. As such, we will first review this work briefly. We extended these principles to a series of products where the network properties were varied by choice of polyol components and isocyanate functionality. We show that both studies are consistent with our approach of treating these systems as elastomeric networks.

## KINETIC AND RHEOLOGICAL CHARACTERIZATION OF MODEL GELS

The initial work was conducted on a simple model system consisting of a polyether triol and a quasi-linear isocyanate prepolymer. A small amount of a standard amine catalyst, JEFFCAT<sup>®</sup> TD-33A, was used to control the speed of curing). The polyol was JEFFOL<sup>®</sup> G31-55 having an estimated functionality of 2.8, and the isocyanate was RUBINATE<sup>®</sup> 1209, with an actual functionality of about 2.1. All of the above products are produced by Huntsman. To simplify the analysis, the system was modeled as the reaction of a difunctional monomer,  $A_2$  with a trifunctional one,  $B_3$ . Branching theory and simple kinetic models were applied to analyze the data [9-11].

The curing and relaxation rheology of the system was studied as function of index ratio ( $r$ ) defined as the ratio of NCO groups to OH groups in the formulation. A TA Instruments AR-2000 rheometer was used for the studies with index  $r$ , varying from 0.4 to 1.0. Storage modulus ( $G'$ ), loss modulus ( $G''$ ) and phase angle ( $\delta = \tan^{-1}(G''/G')$ ) were monitored during curing at 50°C with 1% strain and 1 rad/sec frequency ( $\omega$ ). The curing time ranged from 2 hours to 5 hours. For each cured sample, dynamic frequency sweeps (0.1 – 600 rad/s) were conducted with 1% strain at 30°C, 50°C and 70°C, respectively. Master curves were built at a reference temperature of 50°C by horizontally shifting isothermal frequency sweep data [12].

If the index of the above system is reduced gradually from the stoichiometric condition,  $r = 1$ , there is a critical minimum value below which the system does not chemically gel. The critical index can be estimated following the critical gel conversion equation from Miller and Macosko [10], setting  $p_c = 1.0$ :

$$p_c = \frac{1}{\sqrt{r(f_A - 1)(f_B - 1)}} \quad (1)$$

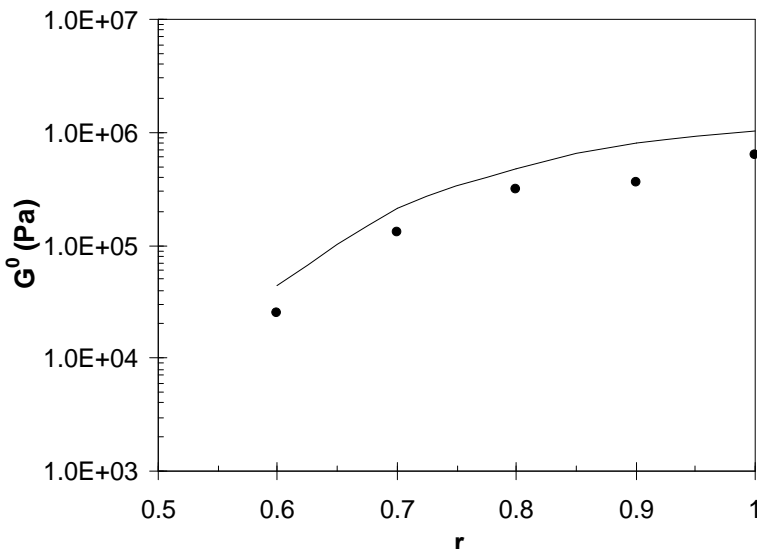
In equation (1),  $r$  is the index ratio,  $f_A$  is the average isocyanate functionality and  $f_B$  is the average polyol functionality. The critical index for the model system studied here is calculated at 0.5. At  $r = 0.4$ , as predicted, the system never achieved gelation but behaved as a viscous liquid during the curing stage.

The main findings of this work were:

- 1) A simple second order kinetic model was adequate to describe the progress of the reaction.
- 2) Calculations from classical rubber elasticity [9] agree well with the plateau storage moduli measured by dynamic mechanical analysis using frequency sweeps at multiple temperature and classical time-temperature superposition shifts [12]. This is illustrated in Figure 1, where measured and calculated values are compared. This implies that classical network theory can be used to describe these systems.
- 3) As the index was increased from 0.5 (critical index value) to 1.0, three types of behavior were observed:
  - a) At  $r = 0.5$  a critical gel condition is encountered.  $G' = G''$  and thus the system behaves both as a liquid and a solid. The shift angle ( $\delta$ ) has a value of 45°.

- b) From  $r = 0.6$  to  $r = 0.8$  the systems can be described via a single master curve that scales with approximately the square root of the frequency. This situation corresponds to fully formed polymer networks containing also a large number of unreacted loose ends or dangling chains.
- c) At  $r = 0.9$  and  $r = 1.0$  a new relaxation mechanism appears and it is not possible any longer to create a single master curve. The relaxation behavior is both frequency and temperature dependent. This unique behavior, typical of full polyurethane networks with low concentration of dangling chains still needs to be investigated further.

Main results from this earlier work are summarized in figures 2 and 3.



**Figure 1.** Effect of index on the plateau modulus,  $G'$  for cured samples of the A2 + B3 model system. Line is calculated from rubber elasticity predictions. Circles represent experimental data from  $G'$  plateau modulus at  $50^\circ\text{C}$ .

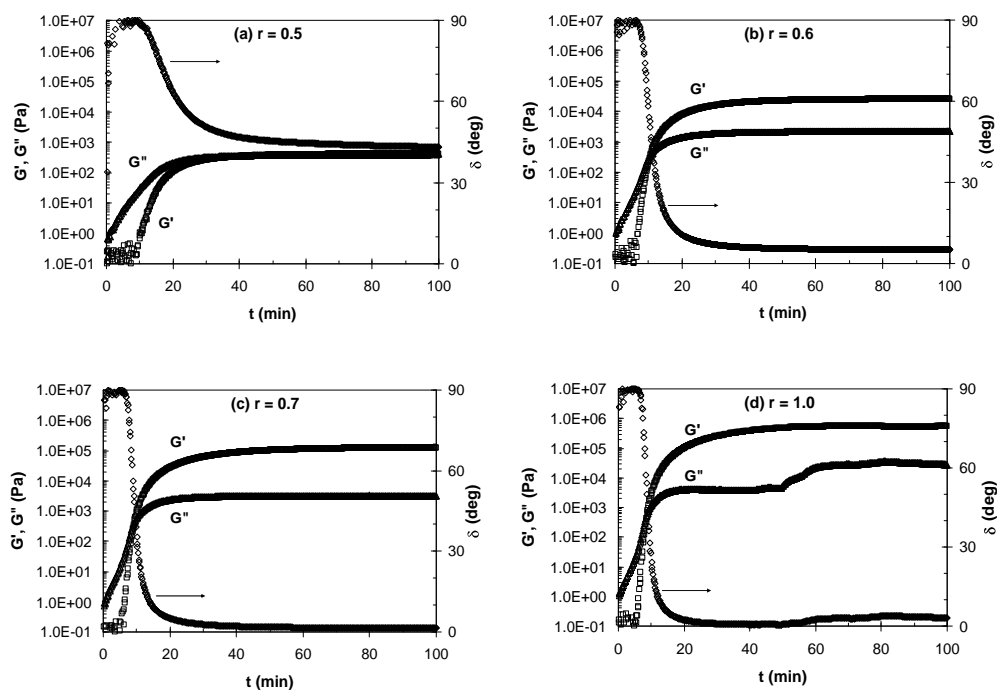
## RHEOLOGY AND MECHANICAL CHARACTERIZATION OF SOFT ELASTOMERS

### EXPERIMENTAL

**Materials.** A series of twelve samples was prepared from a combination of three different polyol blends and four different isocyanates. The polyol blends are proprietary containing a blend of flexible polyols and catalysts to achieve reasonably high cure speeds and short demold times. We will designate these polyol blends as Polyol A, Polyol B and Polyol C. The number average functionality of these blends along with other parameters, including % moles with one functional group (monol) is listed in Table 1. The four isocyanates ranging in number average functionality from 2.0 to 2.3 were prepared by blending a commercial prepolymer, SUPRASEC<sup>®</sup> 2445,  $f_n = 2.0$  and 16% NCO, with RUBINATE<sup>®</sup> 8700,  $f_n = 2.7$  and 31.2% NCO. These isocyanates have been designated for convenience “Iso 2.0”, etc. where the number corresponds to the number average functionality ( $f_n$ ). Typical open time of these systems is  $\sim 1$  minute and demold times are 4 to 5 minutes. All polyol blends were degassed under vacuum ( $< 1$  mm Hg) for at least four hours prior to use. All systems were run at a fixed index ratio of 0.87. Polyol and isocyanate were blended for 10 seconds at 25,000 rpm in a centrifugal mixer (FlackTek, Inc.) and then transferred to a set of parallel plates for curing and rheology studies, or poured into molds at  $50^\circ\text{C}$  to be cured into specimen slabs.

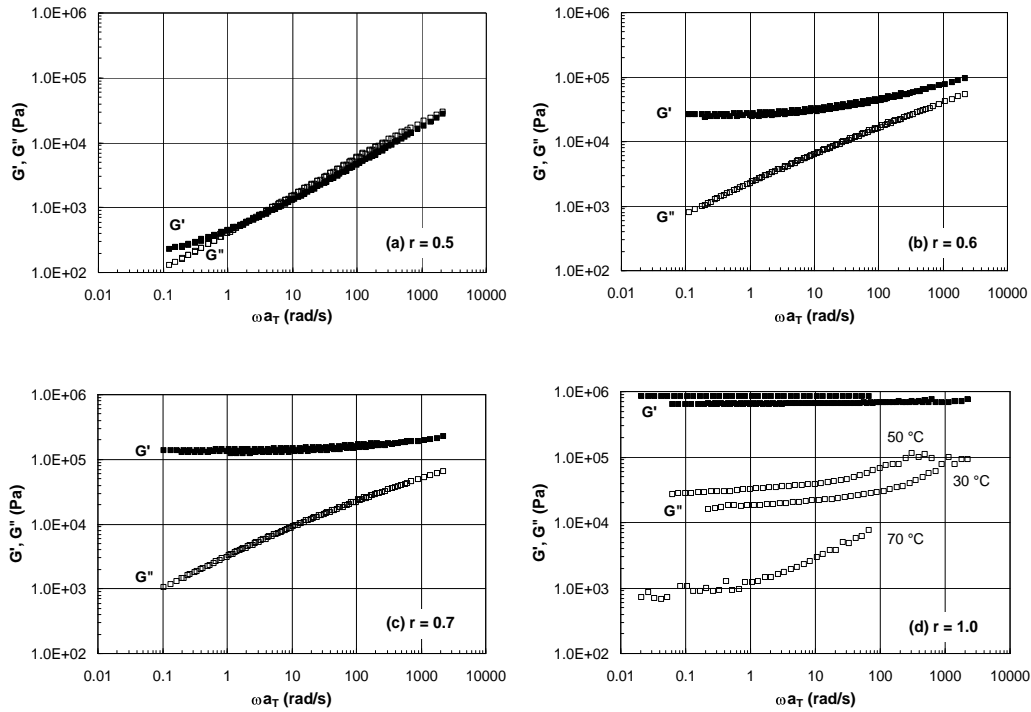
**Rheology Characterization.** All rheological measurements were conducted in a TA Instruments AR-2000 rheometer using a parallel plate configuration and oscillatory mode. For dynamic mechanical thermal analysis, DMTA, the samples were run from  $-50^\circ\text{C}$  to  $+150^\circ\text{C}$  at a frequency of 6.26 rad/sec (1 Hz) and the temperature was ramped at the rate of  $3^\circ\text{C}/\text{minute}$ . Because of significant sample hardening at low temperatures, data below  $-40^\circ\text{C}$  displayed a great deal of noise and will not be presented here. It is important to note however that above this temperature no significant transitions took place and the glass transition temperature of all samples studied falls below  $-40^\circ\text{C}$ , probably as low as  $-50^\circ\text{C}$  or lower. For curing studies, all work was done at  $50^\circ\text{C}$  but the data was not analyzed quantitatively and will not be reported here. Curing was used to

monitor the extent of the reaction and to determine when the materials reached a steady reading in the main parameters, namely shear storage modulus ( $G'$ ) shear loss modulus ( $G''$ ) and shift angle ( $\delta$ ) or loss tangent ( $\tan \delta$ ). Once the samples reached a steady state in the above parameters, typically after about 10 minutes, a dynamic frequency sweep, DFS, was conducted at three different temperatures, 30 °C, 40 °C and 50 °C with frequencies ranging from 0.1 to 100 rad/second. The resulting data was used to build master curves for each polymer by using a classical time-temperature shift factor, and determining the dependency on frequency,  $\omega a_T$  [12]. The reference temperature for these shifts was 40 °C.



**Figure 2.** Comparison of curing profiles for a series of  $A_2 + B_3$  elastomers at different index ratio,  $r$ . Curing temperature was 50 °C

<b>Table 1. Summary of materials and properties</b>						
<b>Polyol Type</b>	<b>Isocyanate Type</b>	<b>Isocyanate fn</b>	<b>Polyol fn</b>	<b>Polyol OH [mg KOH/g]</b>	<b>Monol Content [molar %]</b>	<b>Mc/1000 [g/mole]</b>
Polyol A	Iso 2.0	2.00	2.16	53	14.0%	15.40
Polyol A	Iso 2.1	2.10	2.16	53	14.0%	13.60
Polyol A	Iso 2.2	2.20	2.16	53	14.0%	12.40
Polyol A	Iso 2.3	2.30	2.16	53	14.0%	11.40
Polyol B	Iso 2.0	2.00	2.28	51	9.0%	16.40
Polyol B	Iso 2.1	2.10	2.28	51	9.0%	14.40
Polyol B	Iso 2.2	2.20	2.28	51	9.0%	13.10
Polyol B	Iso 2.3	2.30	2.28	51	9.0%	12.10
Polyol C	Iso 2.0	2.00	2.35	51	5.0%	15.50
Polyol C	Iso 2.1	2.10	2.35	51	5.0%	13.80
Polyol C	Iso 2.2	2.20	2.35	51	5.0%	12.60
Polyol C	Iso 2.3	2.30	2.35	51	5.0%	11.60



**Figure 3.** Comparison of master curves for a series of model soft elastomers of the type  $A_2 + B_3$  with a reference temperature of  $50^\circ\text{C}$ . Data was collected at  $30^\circ\text{C}$ ,  $50^\circ\text{C}$  and  $70^\circ\text{C}$  and shift factors  $a_T$  then calculated.

**Mechanical Properties.** Molded slabs of the different samples were conditioned for at least 7 days and tested for tensile properties (ASTM D412), tear strength (ASTM 1938), ball rebound (ASTM 3574) and Shore OO hardness (ASTM 2240) at  $23^\circ\text{C}$  and 50% relative humidity. All the properties were correlated against a calculated molecular weight between crosslink,  $M_c$  parameter. The  $M_c$  calculation was done using the expression:

$$M_c = (\text{Total Polymer Weight}) / \frac{1}{2} (\sum \text{Equiv. reacted with } f \geq 3) \quad (2)$$

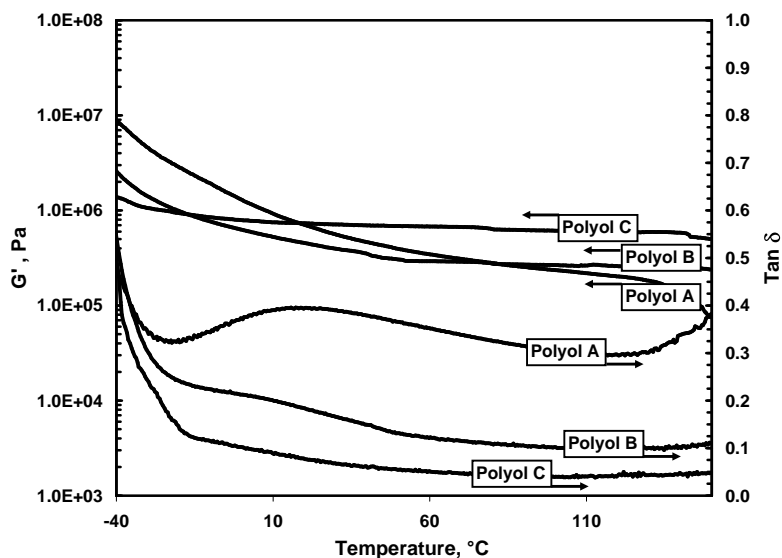
The above expression does a reasonable job but it under predicts the  $M_c$  values for situations that are close to critical gel condition. Because of the complexity of the system studied in this work (i.e. multiple monomers with multiple functionalities), more accurate expressions to predict crosslink density or  $M_c$  are too complex and have been avoided. In any case the expression above can help us visualize the effect of crosslink density on some properties and rheological behavior of these systems with reasonable accuracy.

## RESULTS AND DISCUSSION

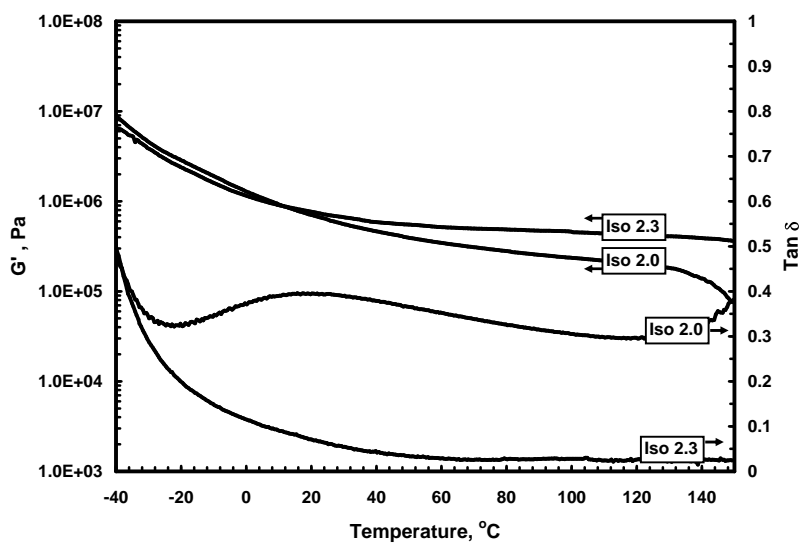
**Dynamic mechanical analysis.** Comparative DMTA data for three systems based on a difunctional isocyanate are shown in Figure 4. Increasing the functionality of the polyol blend increases crosslink density and reduces loose chains. This creates a more perfect network structure and the storage modulus becomes flatter while  $\text{Tan } \delta$  is reduced. This implies that the samples achieve higher elasticity. It looks like the functionality in Polyol C is enough to create a good network structure at much lower isocyanate functionalities. This will be confirmed with other data below.

Figure 5 shows the data for Polyol A with the lowest functionality and two isocyanates of different functionality. The results are consistent with those presented above. As the isocyanate functionality increases, the crosslink density is again increased, the network reduces loose ends and both the rubbery plateau becomes flatter and  $\text{Tan } \delta$  becomes smaller. By contrast, with two phase elastomers where the degree of phase separation plays a significant role in determining elasticity, in these systems the completeness of network formation is the determining factor. These results are also consistent with those reported earlier by Lee et al. [6].

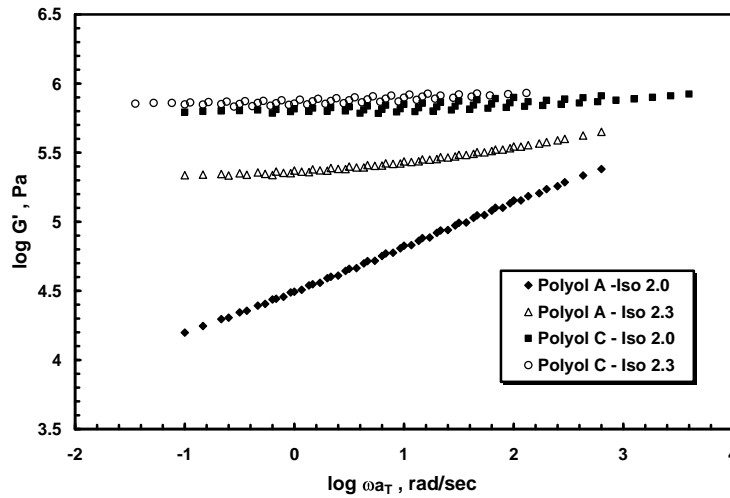
**Viscoelastic response.** Master curves at a reference temperature of 40°C for the storage modulus,  $G'$ , are shown in Figure 6 for Polyols A and C at the highest and lowest isocyanate functionalities, Iso 2.0 and Iso 2.3. The master curves for Polyol A have a much lower modulus response and higher frequency dependence than those for Polyol C that are very similar. From the  $M_c$  calculations, the difference in values for the two Polyols with the same higher functionality isocyanate is small and cannot account for the differences seen here. It must therefore be concluded that the much higher monol concentration in Polyol A is responsible for the different viscoelastic response and confirms the behavior of the temperature sweep curves. Although introducing a higher isocyanate functionality creates a tighter network, the chain termination effect of monol species cannot be overcome.



**Figure 4.** DMTA data of multiple soft elastomer systems produced with a difunctional isocyanate and polyols of increased functionality.

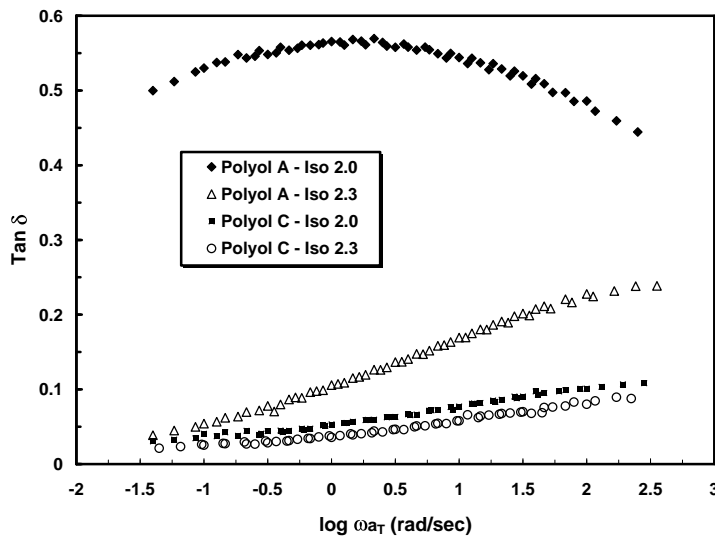


**Figure 5.** DMTA curves for Polyol A with two isocyanates of different functionality.

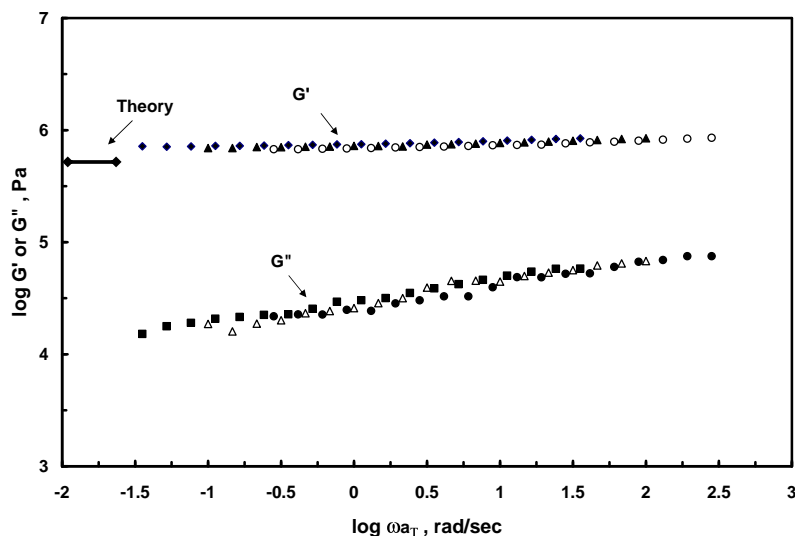


**Figure 6.** Master curves at 40°C reference for soft elastomers produced by blends of materials of different functionality.

Figure 7 shows  $\text{Tan } \delta$  data for the similar series of samples. This data confirms that while the samples made from Polyol A have a much higher loss, i.e. less elastic, those made from Polyol C display a much lower  $\text{Tan } \delta$  set of values. Again, these properties will be correlated to mechanical data later on. Figure 8 shows the frequency dependence of the master curves for Polyol C with Iso 2.3. This system has the highest crosslink density and lowest monol content of the series. This results in a  $G'$  modulus that is almost independent of frequency and a  $G''$  that scales with approximately  $\omega a_T$  to the 0.3 power. This frequency dependence is lower than the one reported in our earlier work [8] for the second type of systems. A theoretical value for the plateau modulus calculated from rubber elasticity theory agrees reasonably well with the experimental data for this system. We extended the range of temperatures to 70°C for this sample, the highest temperature studied in the previous work with the model systems but saw no evidence of any temperature transition that results in temperature dependent relaxation behavior.



**Figure 7.**  $\text{Tan } \delta$  as a function of frequency for several soft elastomers with varying network properties.



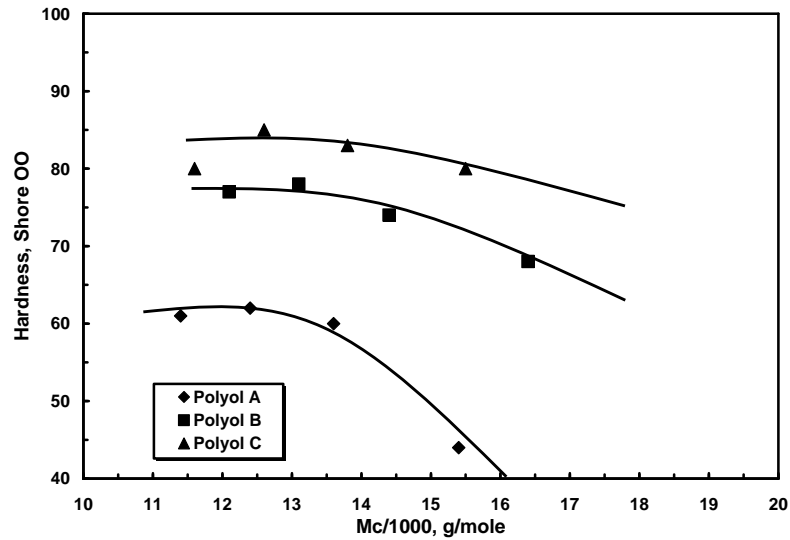
**Figure 8.** Master curves with reference temperature 40°C for a soft elastomer (Polyol A + Iso 2.3)

**Mechanical Property Data.** All results for mechanical property data were plotted against a calculated  $M_c$  as per Equation (2) given earlier. Figure 9 shows the dependence of hardness, Shore OO on  $M_c$ . As expected, hardness increases with crosslink density. However it appears to level off at low values and even achieve a maximum value at approximately 4,000 g/mole. One would expect that, as  $M_c$  becomes smaller hardness should continue to increase but the present work can not confirm this expected trend. Very early work by Pigott et al. [13] was also inconclusive on the effect of  $M_c$  on hardness. The elastomers of that study, however, were significantly different from the ones studied here.

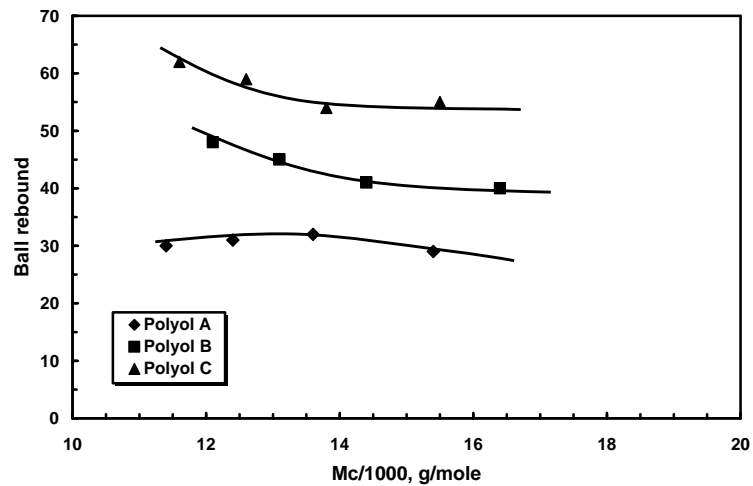
Ball rebound data is presented in Figure 10. There is a very significant effect of the type of polyol on ball rebound with individual values ranging from about 30% for Polyol A to approximately 60% for Polyol C based elastomers. This data is very consistent with the rheology data presented earlier. In fact, we have found a very good correlation between ball rebound and  $\tan \delta$  at the same temperature for this type of systems. It appears that monol content plays a significant role on the elastic behavior of these polyurethane elastomers.

Figures 11 and 12 show the tensile properties of these elastomers as a function of  $M_c$ . Not unexpectedly, both tensile strength and elongation increase with increase in  $M_c$ . It is important to observe that the dependence also appears to be related to the type of polyol used. Polyol A having lower functionality and higher monol content appears to have better elongation, i.e. higher values, and lower tensile strength than either Polyol B or Polyol C at equivalent  $M_c$ . This is an interesting result because it illustrates the poor correlation between high tensile properties and high resiliency that is normally associated with better elastic behavior. Tear strength, Figure 13, shows that it increases with increasing  $M_c$ . Elongation effects appear to dominate tensile strength effects in determining the tear properties of these systems. The data shown here is in good agreement with the data of Pigott et al. that also found a similar dependence of tensile and tear properties on  $M_c$ . Also worth mentioning, the dependence of elongation on  $M_c$  seems to be stronger for Polyol A than Polyol B or Polyol C (Figure 12).





**Figure 9.** Hardness of soft elastomer networks as function of molecular weight between crosslink,  $Mc$ , for a series systems based on different polyols and isocyanates.

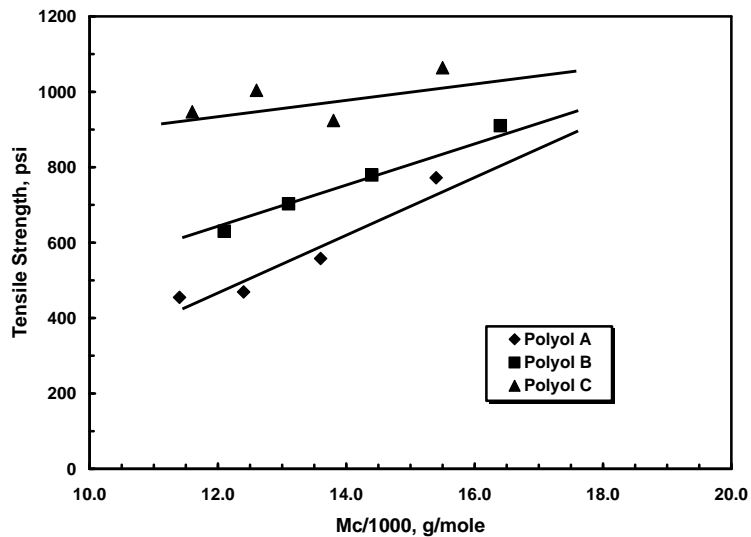


**Figure 10.** Ball rebound (resilience) of soft elastomer networks as function of molecular weight between crosslink,  $Mc$ , for a series systems based on different polyols and isocyanates.

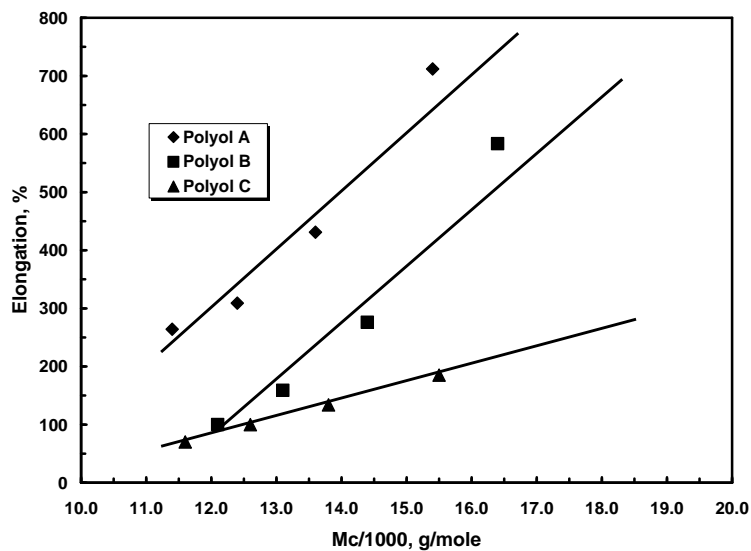
## CONCLUSIONS

Curing behavior, rheological properties and final mechanical properties of a series of very soft elastomers, i.e. with hardness values in the Shore OO scale have been studied. To achieve the very soft hardnesses, conventional two phase approaches are not suitable. Instead, we need to approach these systems as pure polymer networks and apply principles related to classical network theory. Working with a simple model system, we have demonstrated that this theory adequately describes the behavior and properties of these systems. Isocyanate and polyol functionality play an important role in determining the network properties of these systems that can be described in terms of molecular weight between crosslinks or crosslink density. For systems of compositional complexity such as the ones studied here, approximate treatment works reasonably well.

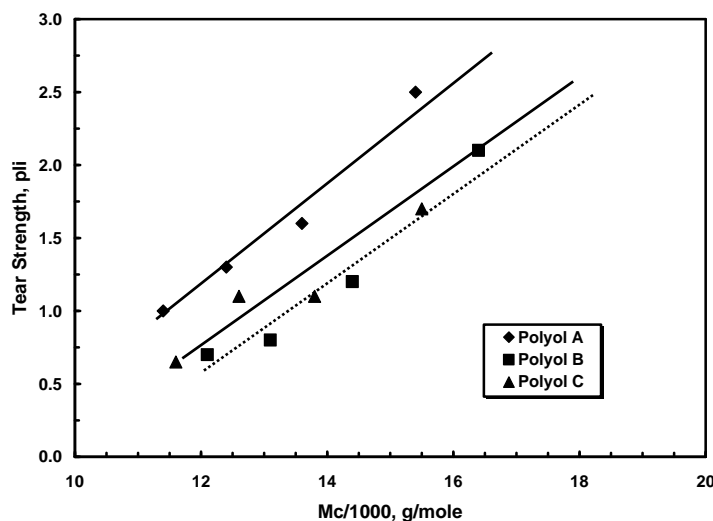
Considering the wide range of properties that we have reported, a solid platform has been established that allows us to fine tune properties of soft elastomers for different requirements that support the growth of polyurethane materials in new markets and applications.



**Figure 11.** Tensile strength of soft elastomer networks as function of molecular weight between crosslink,  $M_c$ , for a series systems based on different polyols and isocyanates.



**Figure 12.** Elongation at break of soft elastomer networks as function of molecular weight between crosslink,  $M_c$ , for a series systems based on different polyols and isocyanates.



**Figure 13.** Effect of  $M_c$  on tear strength of soft polyurethane elastomers.

## ACKNOWLEDGEMENTS

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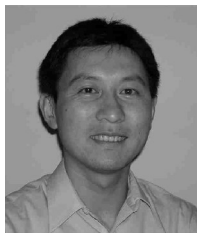
## BIOGRAPHIES

### Emilie Smith-Heberer



Emilie Smith-Heberer received her M.S. in Polymer Science from the University of Akron in 1993. She joined Huntsman Polyurethanes in 2005 in the Elastomers Business Development Group as a Senior Technical Specialist. She has been involved in projects related to spray elastomers, gels and microcellular high performance elastomers for multiple market areas. Prior to Huntsman she has worked in a variety of areas including solvent, waterborne and radiation curable coatings and inks.

### Lifeng Wu



Lifeng Wu is currently a Senior Technical Specialist in Americas Business Development Team of Huntsman Polyurethanes at Auburn Hills, Michigan. Since joining in 2005, he has been involved in various projects including TPU, PU cast elastomers and rigid foams. He received his Ph.D. in Chemical Engineering from University of Minnesota in Minneapolis, and M.S. degree in Chemical Engineering from Tsinghua University in Beijing.

### Rafael Camargo



Rafael E. Camargo is currently the Elastomers Development Manager for the Americas Business Development Team in Auburn Hills, Michigan. He is responsible for new developments in multiple areas of polyurethane elastomers and related technologies. Dr. Camargo has over 20 years of experience in numerous polyurethane applications. He has been part of the Polyurethanes business at Huntsman since 1987 and has held a number of commercial and technical positions. Dr. Camargo has a Chemical Engineering Diploma from Universidad Pontificia Bolivariana in Medellin, Colombia and a Ph.D. in Chemical Engineering and Materials Science from the University of Minnesota in Minneapolis.