DYNAMIC MECHANICAL ANALYSIS FOR EVERYONE

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ABSTRACT

Interest in the dynamic properties of urethane elastomers is becoming increasingly important as fabricators and end users push the window for use of these materials. An indication of the importance of this information is the fact that the PMA has compiled a series of articles on the design of elastomers with emphasis on dynamic properties. Dynamic Mechanical Analysis (DMA) is an analysis technique used to determine the dynamic properties of elastomers by applying an oscillating stress to a test specimen and resolving the resultant strain into a viscous and elastic component. It is the presence of these viscous and elastic components that defines an elastomer, so it is important to be able to measure them, and a method of comparing one elastomer to another. Knowledge of these components enables a researcher to determine the ability of the elastomer to absorb energy, and to resist hysteresis or heat build up. This paper will attempt to define these components on a fundamental level, describe the operation of the instrumentation and test methodology, and demonstrate the effect of various polymer compositional structures on the dynamic mechanical properties.

INTRODUCTION

Polyurethane elastomers have long been used successfully in such dynamic applications as roll coverings and tires. As speed, load requirements, and temperature of operation for these applications increase, the dynamic requirements of the material also increase and the ability to determine dynamic properties on a small sample becomes extremely cost effective. Dynamic mechanical testing is a method developed to assist in the determination of the dynamic properties of various materials, most notably elastomers and takes advantage of the viscoelastic nature of elastomers. Viscoelasticity is observed in materials when the mechanical response to an

excitation is not instantaneous, but rather is time, rate, and temperature dependent. DMA testing relies on the ability of the instrumentation to apply an oscillating stress to a test specimen, and to resolve the resultant strain generated into a viscous and an elastic component. It is the presence of these two responses, which arise from the phase separation of the long flexible chains and the hard crystalline blocks (Figure 1), that defines an elastomer. The combination of these two components responding to an applied force has been represented diagrammatically as a combination of a spring and dashpot either in series (the Maxwell diagram, Figure 2) or parallel (Voight diagram, Figure 3). In these diagrams the spring represents the elastic component while the dashpot represents the viscous component.

VISCOELASTIC PROPERTIES

The elastic component, of the resultant strain, is also referred to as the storage modulus, and represented as E' in tension or flex, and G' in shear. It is a quantitative measure of the material's elastic properties, and a qualitative measure of a material's stiffness, and to a lesser degree to its hardness. Storage modulus is defined as the ratio of the stress in-phase with the strain, to the magnitude of the strain. It is characterized as being linear, in that if twice the stress is applied, the resultant strain will be doubled. It is 100% efficient, in that it always returns to its initial configuration when the stress is removed. It is not time or rate dependent as demonstrated by the resulting strain always being the same no matter at what rate the stress is applied, but in the case of elastomers, it is temperature dependent. If we look at a plot of the storage modulus versus temperature (Figure 4) beginning at a very low temperature, we see the storage modulus at a high value corresponding to a hard possibly brittle material resulting from the immobility of the polymer chains. As the temperature increases, a transition is seen where the long flexible chains

achieve mobility within the elastomer, and the Glass Transition temperature (Tg) is reached. This is observed as a rapid drop in the storage modulus. Some insight into the phase separation can be gained by observing this transition; a long gradual transition represents poor phase separation, while a sharp transition is associated with good phase transition. After passing through the transition temperature a long rubbery plateau is observed wherein the phases separate, and the material demonstrates its true elastomeric characteristics. As even higher temperatures are reached, the hard crystalline blocks begin to dissociate, the elastomer loses its integrity, and softens to a non-useable material. The storage modulus is affected by the amount of hard segments in the elastomer, the crosslink density of the elastomer, and the backbone structure of the prepolymer, and in turn of the polyol used in preparing the elastomer.

The viscous component of the resultant strain, or loss modulus, is represented by E" in tension or flex and G" in shear. It is a quantitative measure of energy dissipation, and is defined as the ratio of stress 90° out of phase with oscillating strain to the magnitude of the strain. It is 0% efficient, in that when the stress is removed, a second stress or force must be applied to return the material to its original configuration. The loss modulus is also time, rate, and temperature dependent, with the strain changing when the stress is applied at different temperatures, time spans, and rates. Higher frequencies of applied stress will increase the loss modulus. If one plots the loss modulus as a function of temperature (Figure 5), again running from low to high temperature, one observes an initial high loss modulus at low temperature when the long flexible chains are frozen into a rigid configuration. As the temperature is increased the chains begin to achieve mobility at the Glass Transition temperature and a peak is observed in the loss modulus curve. As the temperature continues to increase, the loss modulus decreases into a long plateau, followed by a

rapid increase at the temperature when the hard segments dissociate and more mobility is achieved. The loss modulus is affected by the molecular weight of the polyol used in preparing the prepolymer, the backbone of the prepolymer, the crosslink density and the frequency of the applied stress.

Other dynamic properties that can be determined include the Tan δ, which is a measure of the damping ability of the elastomer. The Tan δ can be used as a qualitative tool to estimate the hysteresis or heat build up in an elastomer during dynamic flex. Tan δ is defined as the ratio of the viscous or loss modulus to the elastic or storage modulus, and from this definition it is apparent that any effort to increase the loss modulus will increase the Tan δ, while increasing the storage modulus will decrease the Tan δ. The Tan δ curve (Figure 6) has a low value below the Glass Transition temperature, passes through a maximum at the Glass Transition temperature, followed by a decrease as the transition region is ending, and a long usually upward-curving slope with another sharp upcurve at the prepolymer decomposition temperature. The hard segment content, effects the height of the Tan δ curve, while the polyol backbone structure effects the location of the Tan δ peak, and phase separation effect the width or breath of the Tan δ peak.

The loss compliance, or power loss, quantifies the heat generation during dynamic loading. It represents the power, per unit volume, that is transformed into heat through hysteresis, and is defined as the product of energy loss and frequency. Loss compliance can be used to determine the ability of an elastomer to give back heat to the environment. Lower values of loss compliance demonstrate an elastomer's ability to build up less heat internally, and thus suffer fewer failures due to hysteresis. Figure 7 is the loss compliance curve for ANDUR® 90AP a 90 Shore A PTMEG elastomer.

INSTRUMENTATION and METHODOLOGY

When discussing instrumentation for dynamic mechanical testing, a number of acronyms are used to describe analogous equipment and techniques. These include Dynamic Mechanical Analysis (DMA), Dynamic Mechanical Spectroscopy (DMS), Dynamic Mechanical Rheological Testing (DMRT), and Dynamic Mechanical Thermal Analysis (DMTA). Typical instrumentation (Figure 8 & 9) for the determination of dynamic properties consists of a sample holder, thermo-stated sample chamber and the necessary instrumentation to vary the applied stress force and frequency and then measure the resulting strain. The oscillating stress can be applied in tension, compression, flex, or twisting (Figure 10), and the equipment has the ability to apply the stress at different frequencies. Different manufacturers have different test fixtures, with three point bending, torsion or twisting, dual cantilever, tension, and compression being common.

An analysis run can consist of varying the temperature at a fixed frequency and observing the resultant dynamic properties. Frequency can also be varied over a fixed temperature range and the dynamic properties observed. Critical to good results is good sample preparation, and in the case of a temperature sweep, increasing the temperature at a slow enough rate to allow the material to equilibrate during the run. Three to four degrees per minute temperature ramping is considered a maximum for good dynamic results.

STRUCTURE/PROPERTY RELATIONSHIPS

Before beginning a discussion of the structure/property relationship, let me comment that such a discussion could be almost infinite. We chose to study backbone structure at a constant hardness, stoichiometry, backbone polyol structure and molecular weight at constant hard

segment content, constant polyol content at varying hard segment, and isocyanate type. We did not study polyester composition, fillers, curative type, or any processing conditions such as mold temperature, or post cure time and temperature. All of these parameters can be seen to have an effect on, and can be used to alter both the static and dynamic properties of urethane elastomers. With such variation possible it becomes critically important for the prepolymer manufacturer, elastomer fabricator, and end user to work together to identify the best material for a given application.

The first consideration of the effect of elastomer structure on dynamic properties should be given to the polyol backbone used in the preparation of the prepolymer. If one looks at 90 Shore A elastomers prepared from polyester (4.15% NCO), PTMEG ether (4.2% NCO), and PPG ether (5.15% NCO), one observes that the PTMEG ether has the lowest storage modulus (Figure 11), and lowest Glass Transition temperature. This is most likely due to the mobility of the PTMEG ether chains, which would require a lower temperature to crystallize. Both the PPG ether with its methyl branching, and the polyester backbone with its high level of polar ester linkages would have reduced mobility in the polymer chain segments, and thus show higher storage modulus values in the low temperature region. As the temperature is increased, one observes that the PTMEG has a slight upward slope actually crossing over the polyester and PPG ether, this might be due to the increasing flexibility of the PTMEG chains. The loss modulus (Figure 12) demonstrates the reverse effects as those observed in the storage modulus. The PPG ether with its poor regularity exhibits the highest loss modulus, followed by the PTMEG and then the highly polar and regular polyester. Tan δ of these materials (Figure 13) follows the same trends with the PTMEG based material having a lower peak temperature then the PPG or polyester based

prepolymers again most likely caused by the increased mobility of the PTMEG backbones. The loss compliance curves (Figure 14) are interesting in that the PTMEG has a higher value then the polyester, which would indicate it is more susceptible to hysteresis and failure due to internal heat build-up and melting. This will need to be verified to determine if this is related to the test, or an effect of the polyester backbone. A comparison of the ester-based TDI prepolymer (80/20 2,4/2,6 Toluene diisocyanate ratio) versus a TDS prepolymer (100% 2,4 Toluene diisocyanate) indicates the TDS with its single isomer yields somewhat higher modulus values through the transition region resulting in a lower peak Tan δ, this is most likely caused by the regularity of the TDS molecule.

The effect of polyol structure on dynamic properties, was observed by preparing prepolymers to a constant %NCO (3.2-3.4) from PTMEG, Polycaprolactone, and PPG of comparable molecular weight. TDI 80/20 was used as the isocyanate, and these prepolymers were cast using CURENE® 442 (MOCA) as the curative and tested. Hardness was allowed to vary for these materials but can be reported as 84 Shore A for the PTMEG based product, 80 Shore A for the Polycaprolactone, and 64 Shore A for the PPG based elastomer. Again we see the general trend that the PTMEG based prepolymer yields lower storage modulus, and higher loss modulus (Figure 15 & 16). As before this is most likely related to the mobility of the tetramethylene ether chains. Of particular note is the significant difference in the Tan δ curves (Figure 17) for the three compositions with the PTMEG having a significantly lower and broader curve then the polycaprolactone or PPG. This might be caused by a wider molecular weight distribution in the PTMEG used in the preparation of the prepolymer. Also here we see that at temperatures above the T_g the

loss compliance (Figure 18) of the PTMEG is below that of the polyester, so perhaps the earlier observation was truly based on the particular structure of the polyester used in that study.

The effect of stoichiometry was studied by casting a 95 Shore A PPG ether/TDI prepolymer with CURENE® 442 at 85, 95 and 105% stoichiometry. This study indicates that the dynamic properties (Figure 19 - 22) appear to have a peak at 95% stoichiometry. This would support the long held conviction that 95% stoichiometry is the optimum level, and arise from the fact that 95% produces the most linear structure, whereas 85% would result in additional branching and crosslinking while 105% would reduce crosslinking and result in plasticizing of the elastomer by end-capped chains.

Observing the effect of the hard segment content, by using comparable polyols (PPG ether) and altering the %NCO of the prepolymer shows that the storage modulus, (Figure 23) loss modulus (Figure 24) and loss compliance (Figure 26) increase as the hard segment content increases. The Tan δ (Figure 25) is observed to decrease as the hard segment content increases, as would be expected given the definition of Tan δ being the ratio of the loss modulus to the storage modulus. Here the increasing storage modulus has a greater effect on the Tan δ then does increasing the loss modulus. Also the higher hard segment yields lower loss compliance at higher temperatures.

The effect of the polyol molecular weight distribution on the dynamic properties was observed by using blends of PTMEG to yield an average molecular weight of 1000, and preparing prepolymers to a constant %NCO (4.5) to standardize the hard segment content. Through this work we observe sharper transitions (Figure 27 & 28) when a single molecular weight polyol is used as compared to very broad transitions when a wider molecular materials are blended

together. The most striking example of this is the Tan δ (Figure 29) curve for the mixture of 250 MW and 2000 MW polyol gives a lower Tg and almost a bimodal Tan δ curve.

The effect of isocyanate on the dynamic properties was observed by preparing prepolymers from the same polycaprolactone polyol and using MDI versus TDI. Both prepolymers were made to 3.2-3.4 %NCO to minimize the effect of the hard segment on the properties being observed. The storage modulus (Figure 30) of the TDI material is observe to be higher then that of the MDI indicating more stiffness from the TDI/MOCA segments then from the MDI/butanediol. This is confirmed in a higher loss modulus (Figure 31) for the MDI material. The lower Tan δ (Figure 32) and loss compliance (Figure 33) of the TDI based material suggests it would have less heat build up during usage then the MDI-based product.

CONCLUSIONS

This paper has attempted to present some of the principles of dynamic mechanical testing, and a limited discussion of structure property effects associated with polyurethane prepolymers. As was mentioned at the start of the structure/property discussion, the number of variations of prepolymer structure and their effect on the dynamic properties is almost infinite, so it becomes extremely important for all involved parties to work together to identify the best material for any application. Also it is important to recognize that DMA testing should only be a step in an approval process which should include limited field testing to verify the results of the DMA work prior to full acceptance of any material.

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Understanding Rheological Testing: Rheometrics, Inc.

DYNAMIC MECHANICAL ANALYSIS FOR EVERYONE

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Presented at the 1994 Fall Meeting of the Polyurethane Manufacturers Association
Milwaukee, Wisconsin.

Discussion

- Viscoelasticity and dynamic properties.
- Instrumentation and test methodology.
- Structure/property relationships.

Elastomers are Viscoelastic

- Mechanical response to an excitation is not instantaneous.
- Response is time dependent.
- Response is rate dependent.
- Response is temperature dependent.
- Response can be resolved into two components.
  - Viscous Component
  - Elastic Component
- Results from phase separation of hard and soft segments.

Phase Separation

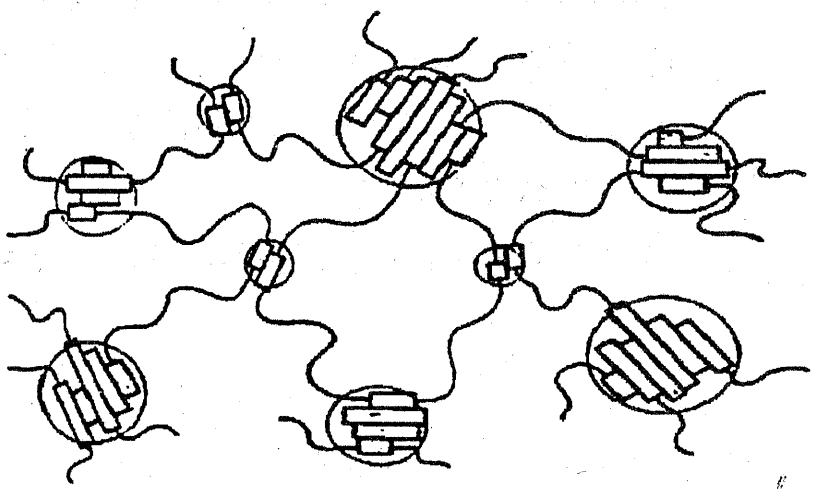

Figure 1

Viscoelastic Properties

- Represented diagrammatically by combining a spring and dashpot.
- Spring represents elastic component.
- Dashpot represents viscous component.
- Maxwell diagram connects spring and dashpot in series.
- Voight diagram connects spring and dashpot in parallel.

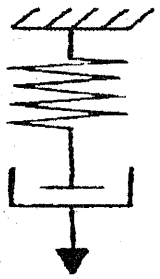

Figure 2

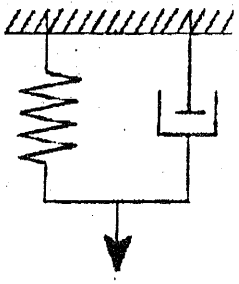

Figure 3

Elastic Component

- **Also referred to as Storage Modulus.**
- **Quantitative measure of elastic properties of the elastomer.**
- **Ratio of stress, in-phase with strain, to magnitude of strain.**
- **Linear.**
- **100% Efficient.**
- **Independent of time or rate of loading.**
- **Dependent on temperature.**
- **Represented by E' in tension or flex, G' in shear.**

Storage Modulus, E'

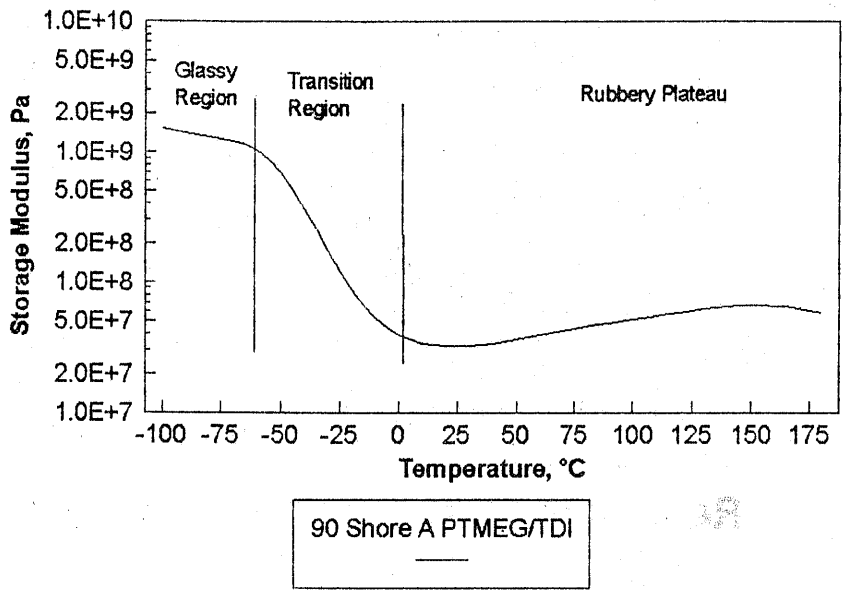

Figure 4

Factors Influencing Storage Modulus

- Crosslink Density
- Polyol Backbone Structure
- Isocyanate

Viscous Component

- Also referred to as Loss Modulus.
- Quantitative measure of energy dissipation.
- Ratio of stress 90° out of phase with oscillating strain to magnitude strain.
- Non linear.
- 0% Efficient.
- Time, rate, and temperature dependent.
- Represented by E" in tension or flex, G" in shear.

Loss Modulus, E"

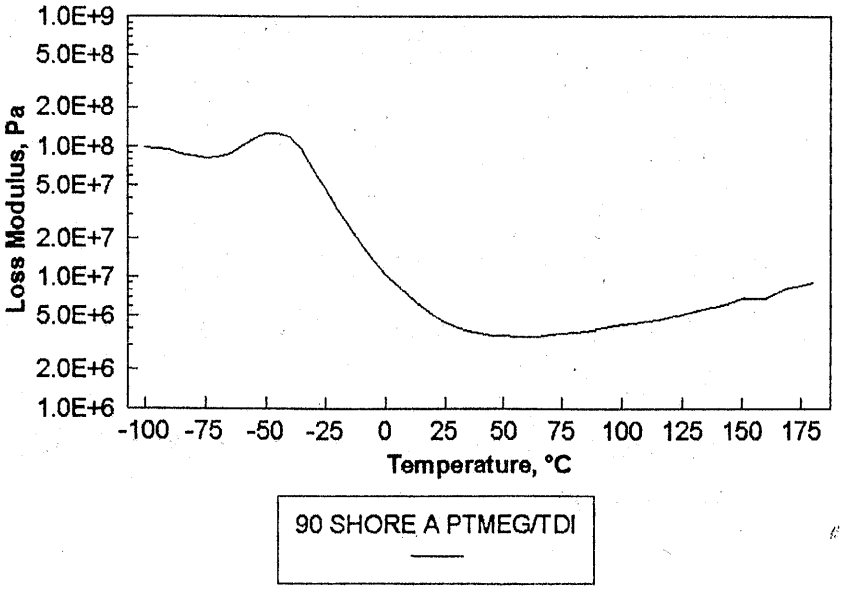

Figure 5

Factors Influencing Loss Modulus

- Frequency of stress
- Backbone
- Crosslink Density

Tan δ

- Measure of damping ability of the elastomer.
- Estimates heat buildup during dynamic flexing.
- Ratio of loss modulus to storage modulus.
- As loss modulus increases Tan δ will increase.
- As storage modulus increases Tan δ will decrease.

Tan δ

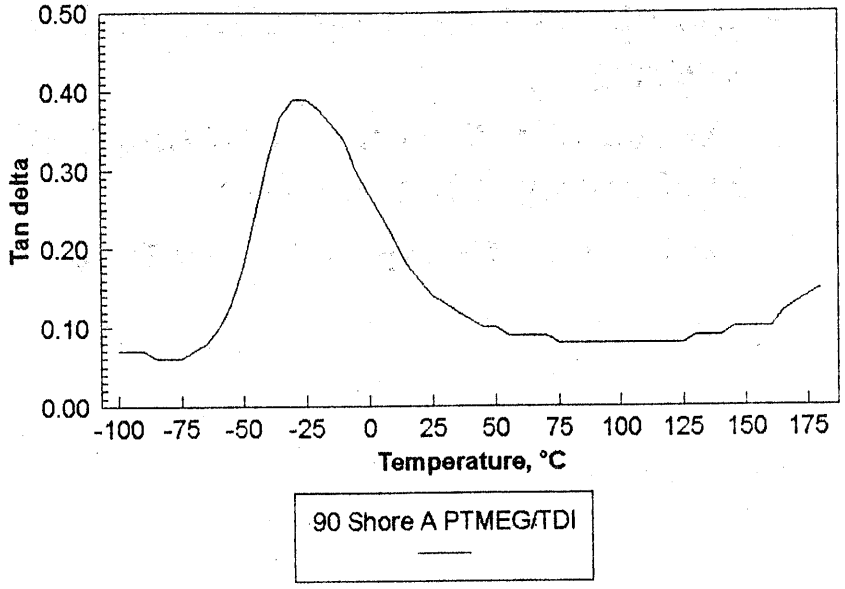

Figure 6

Factors Influencing Tan δ

- Backbone.
- Crosslink Density.
- Level of Hard Segment effects height of Tan δ peak.
- Backbone effects location of Tan δ peak.
- Phase separation effects width of Tan δ peak.

Loss Compliance or Power Loss

- Quantifies heat generation during dynamic loading.
- Represents the energy tranformed into heat through hysteresis.
- Product of energy loss and frequency.

Loss Compliance

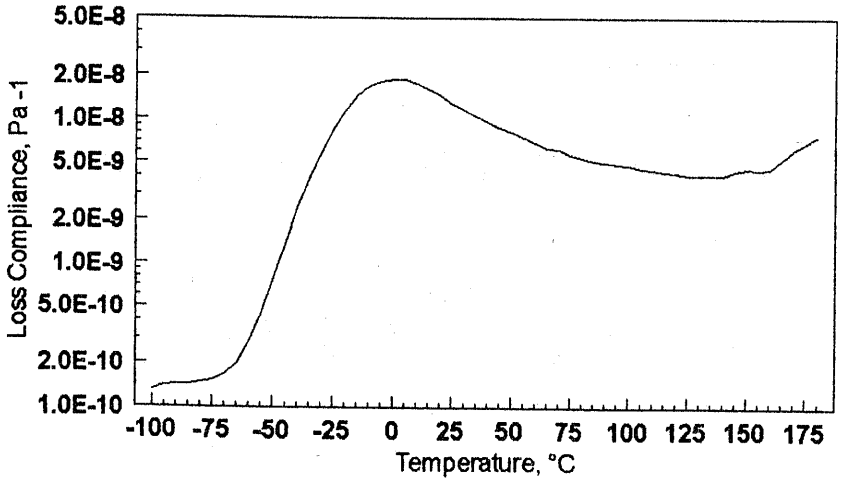

Figure 7

Dynamic Mechanical Testing

- Dynamic Mechanical Analysis, DMA
- Dynamic Mechanical Spectroscopy, DMS
- Dynamic Mechanical Rheological Testing, DMRT
- Dynamic Mechanical Thermal Analysis, DMTA

DMA Instrumentation

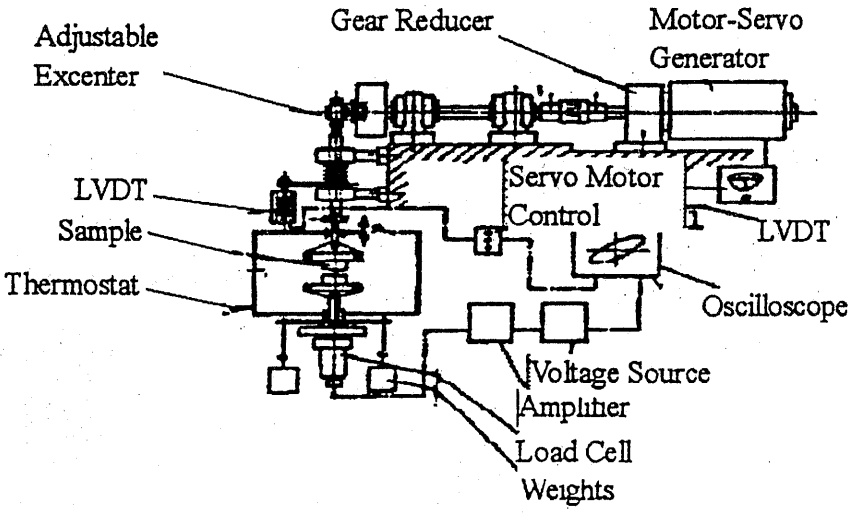

Figure 8

Test Mechanics

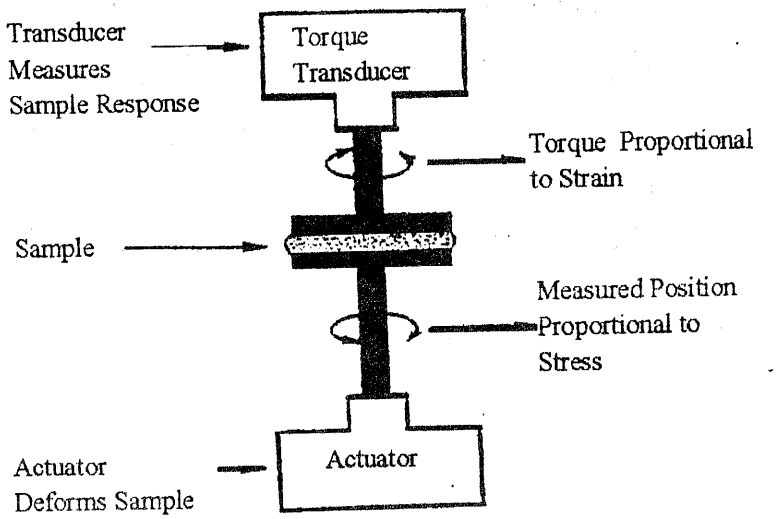

Figure 9 Courtesy of Rheometrics, Inc.

Test Fixture Configurations

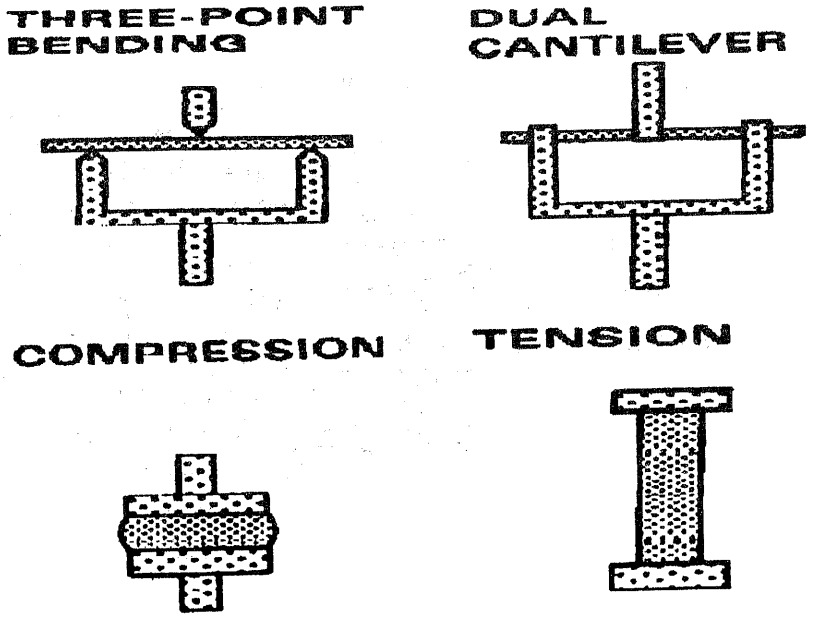

Figure 10

Structure/Property Relationships

- Backbone Structure at Constant Hardness
- Backbone Structure at Constant Hard Segment
- Stoichiometry
- Hard Segment Content
- Polyol Molecular Weight Distribution
- Isocyanate

Effect of Backbone Structure on Storage Modulus

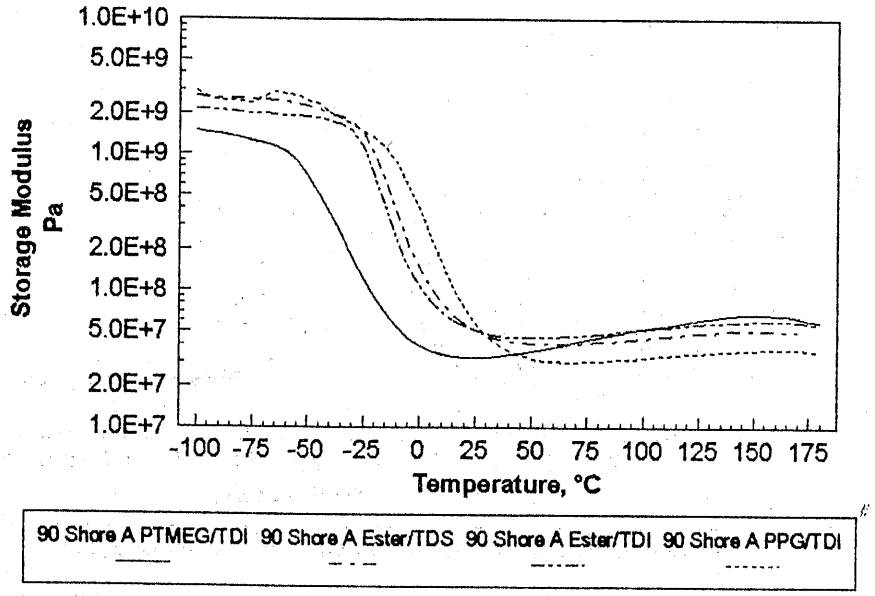

Figure 11

Effect of Backbone Structure on Loss Modulus

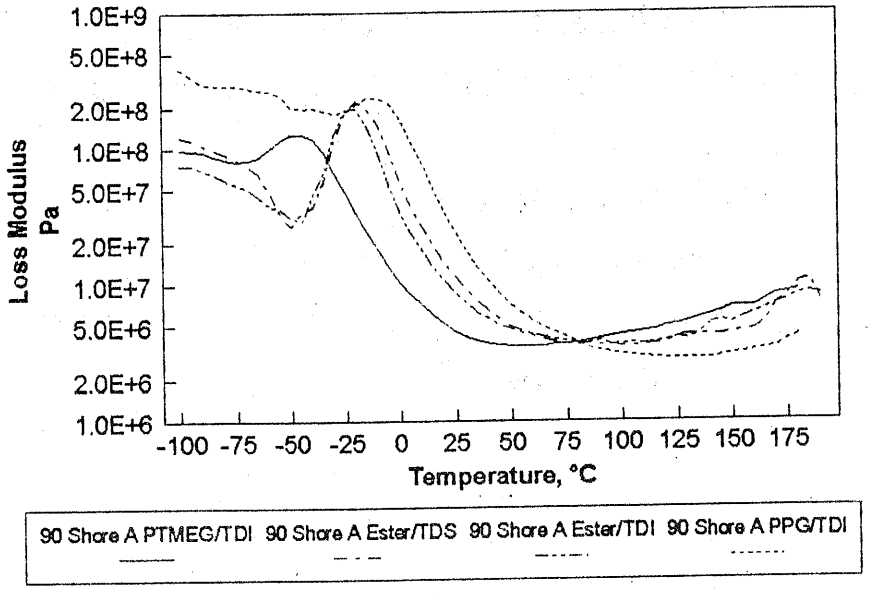

Figure 12

Effect of Backbone Structure on Tan δ

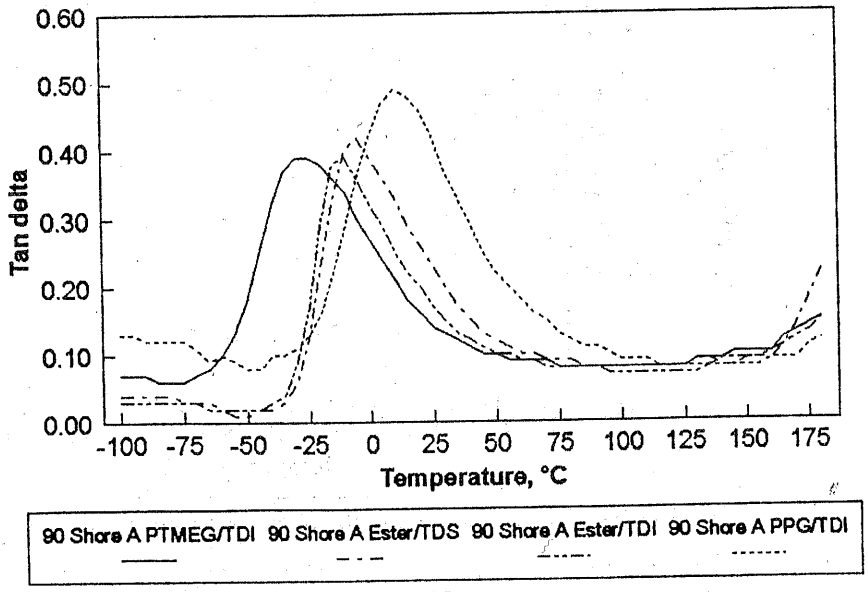

Figure 13

Effect of Backbone Structure on Loss Compliance

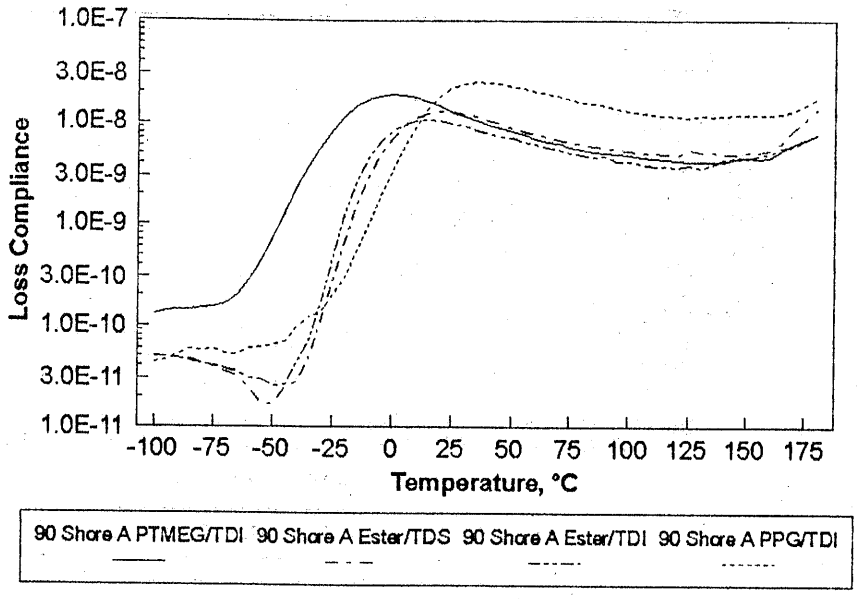

Figure 14

Effect of Polyol Structure on Storage Modulus

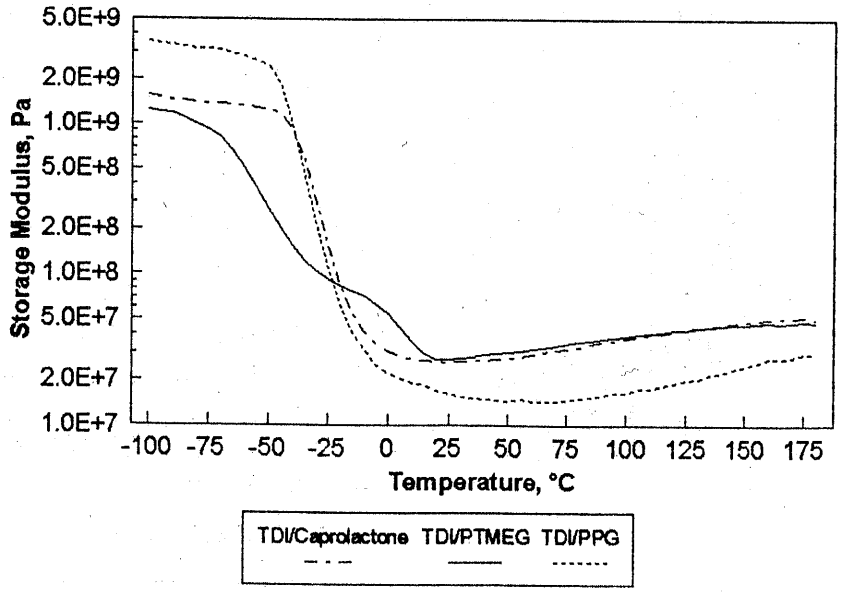

Figure 15

Effect of Polyol Structure on Loss Modulus

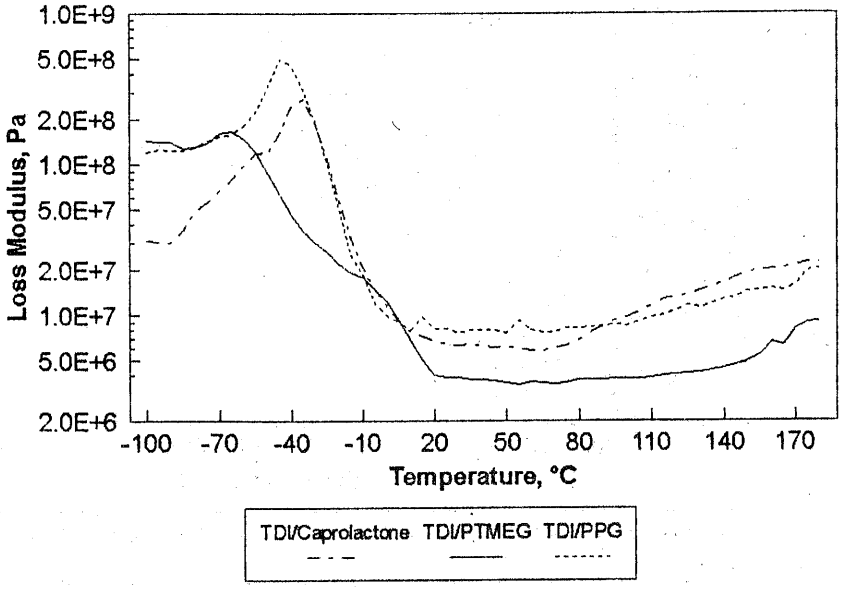

Figure 16

Effect of Polyol Structure on Tan δ

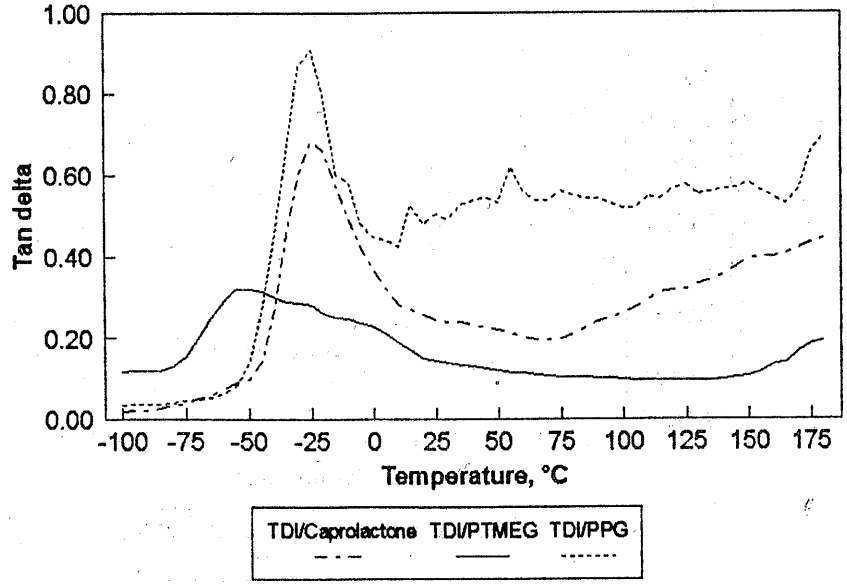

Figure 17

Effect of Polyol Structure on Loss Compliance

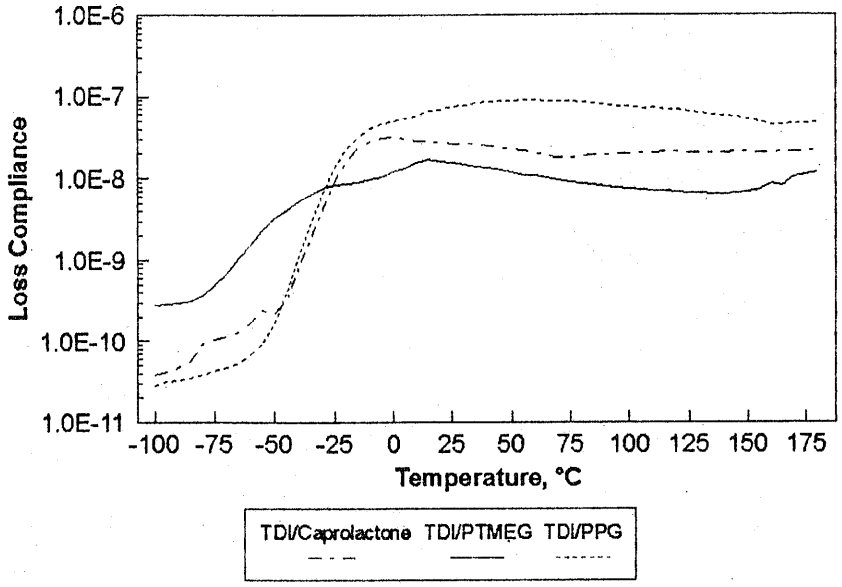

Figure 18

Effect of Stoichiometry on Storage Modulus

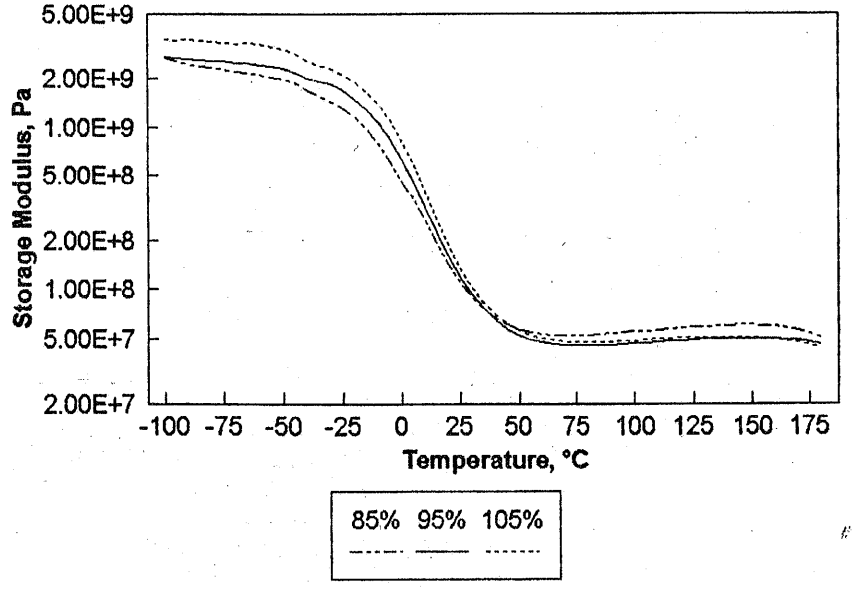

Figure 19

Effect of Stoichiometry on Loss Modulus

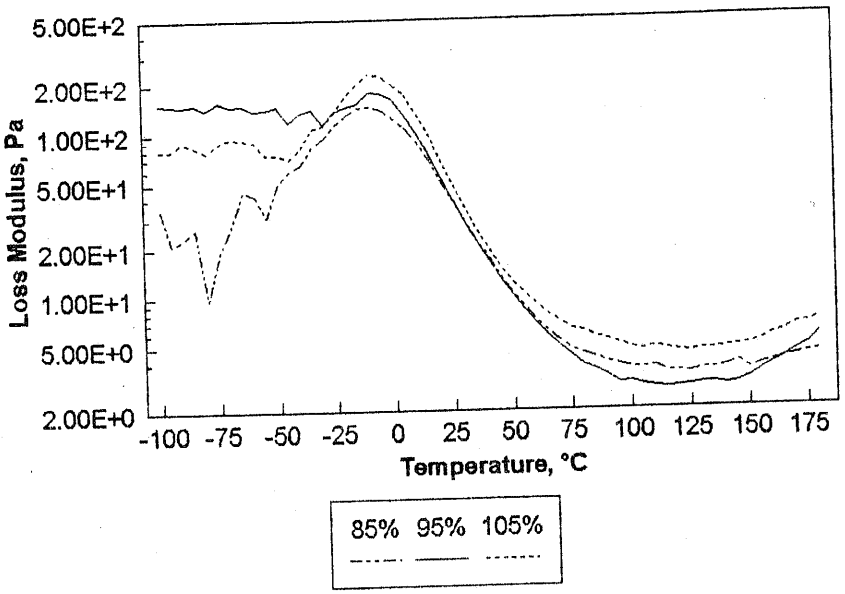

Figure 20

Effect of Stoichiometry on Tan δ

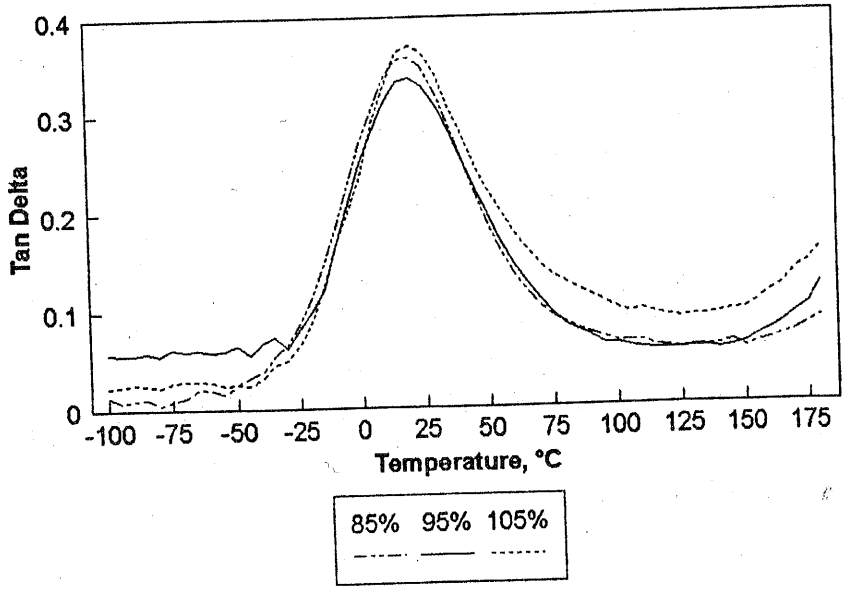

Figure 21

Effect of Stoichiometry on Loss Compliance

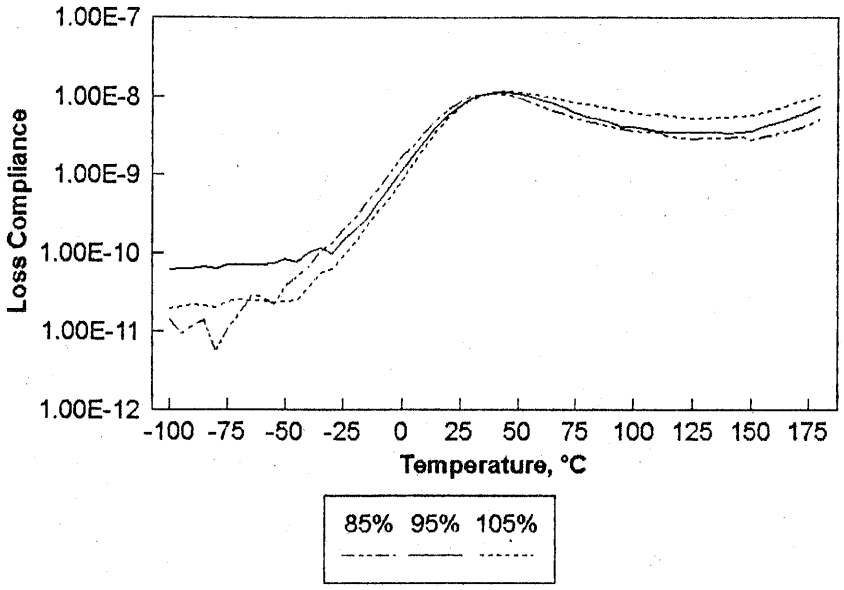

Figure 22

Effect of Hard Segment Content on Storage Modulus

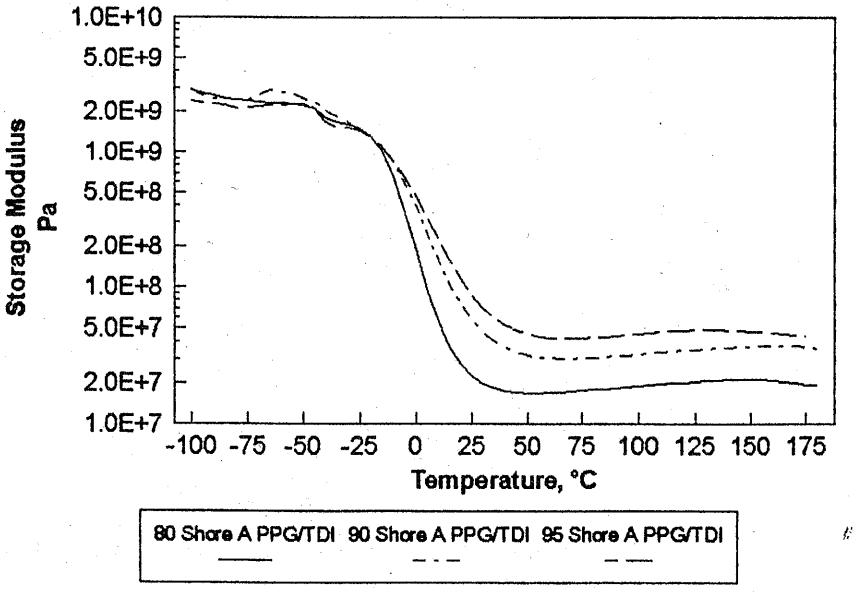

Figure 23

Effect of Hard Segment Content on Loss Modulus

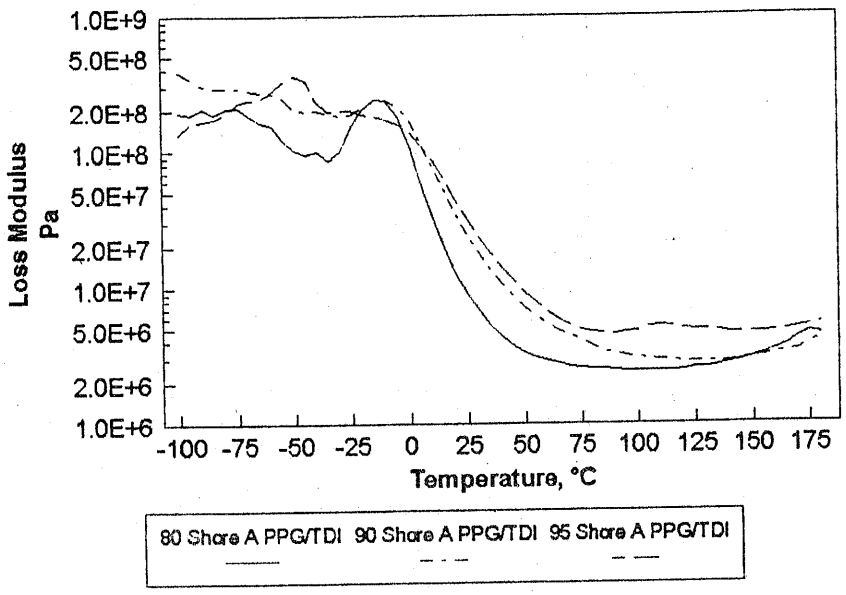

Figure 24

Effect of Hard Segment Content on Tan δ

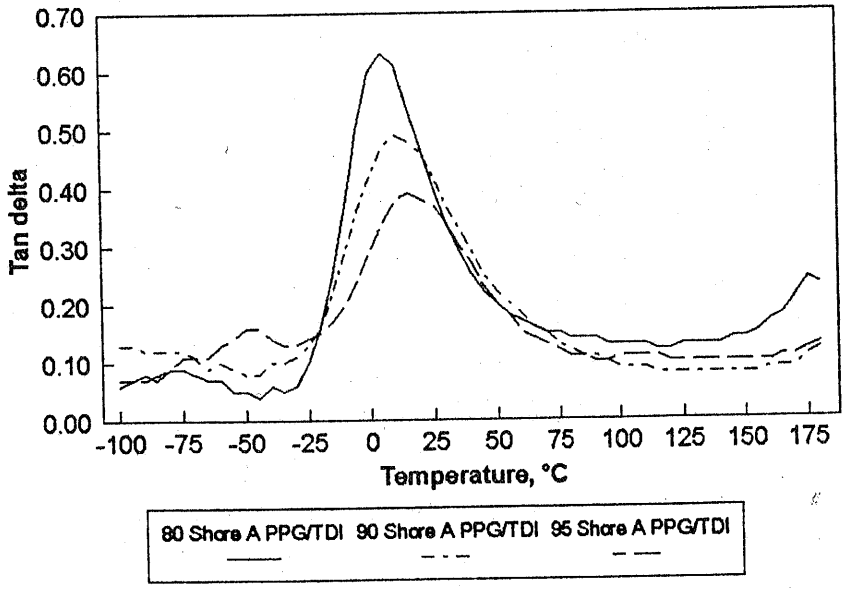

Figure 25

Effect of Hard Segment on Loss Compliance

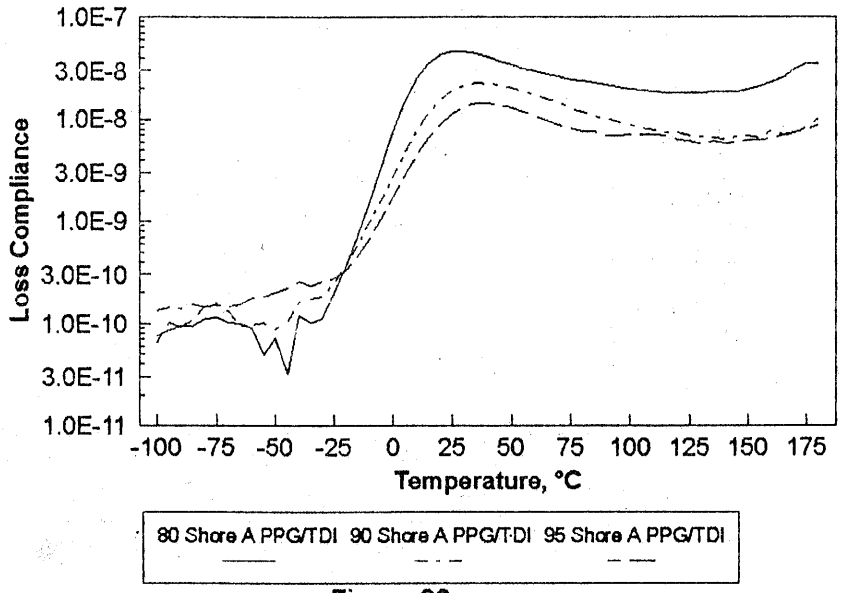

Figure 26

Effect of Polyol Molecular Weight Distribution on Storage Modulus

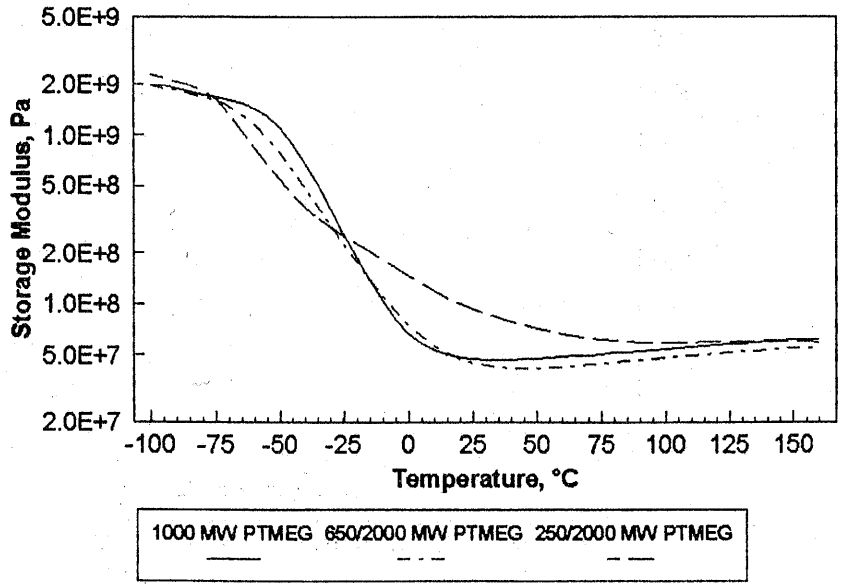

Figure 27

Effect of Polyol Molecular Weight Distribution on Loss Modulus

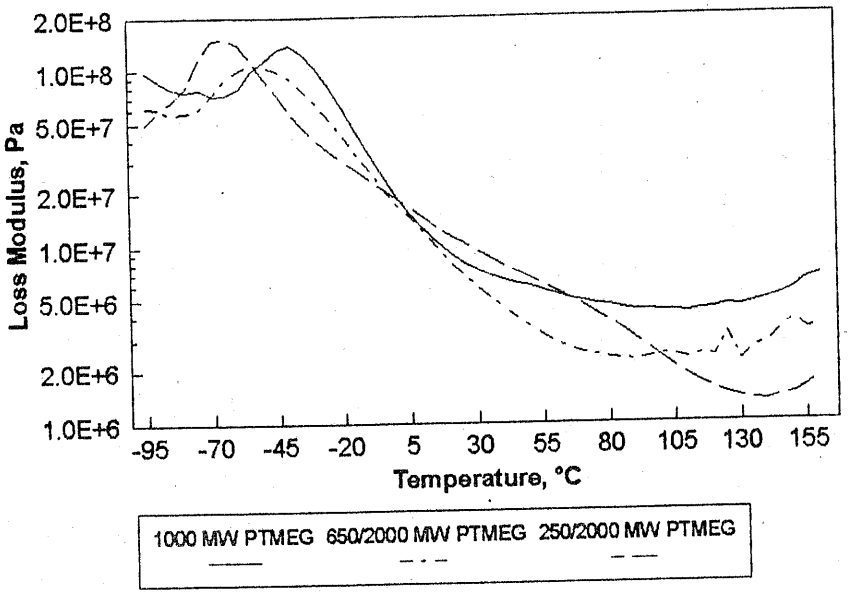

Figure 28

Effect of Polyol Molecular Weight Distribution on Tan δ

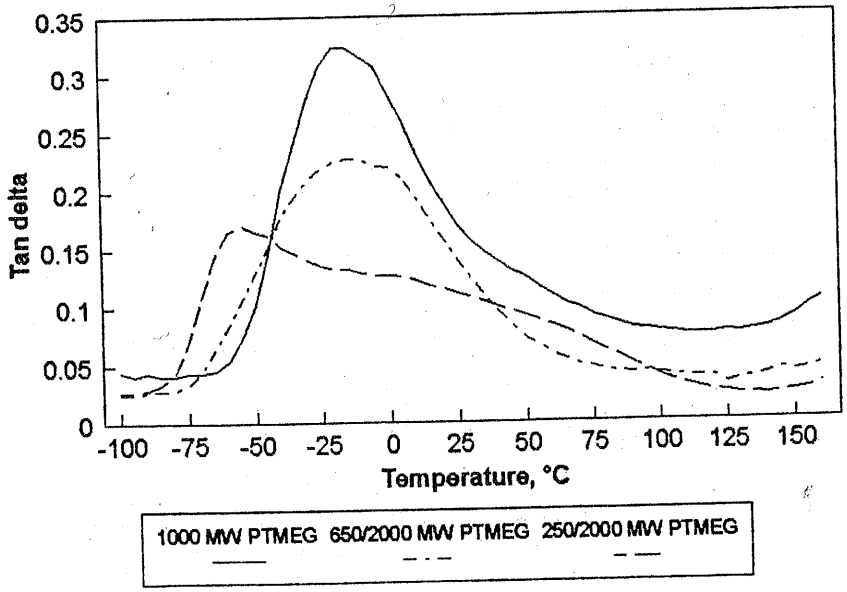

Figure 29

Effect of Isocyanate on Storage Modulus

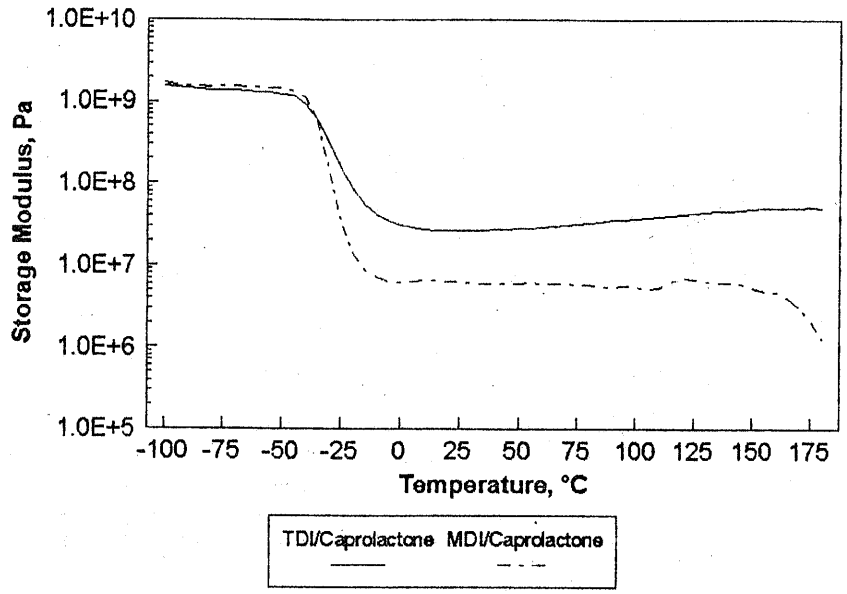

Figure 30

Effect of Isocyanate on Loss Modulus

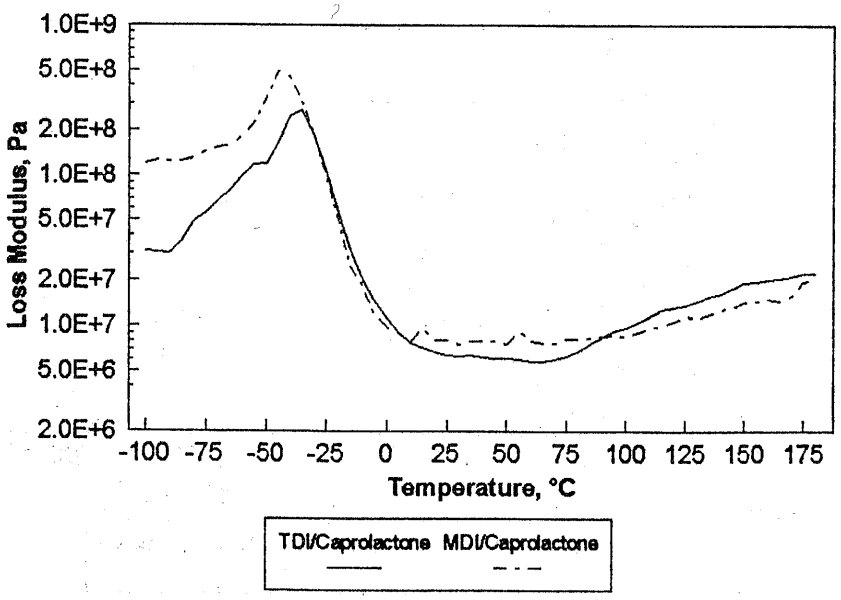

Figure 31

Effect of Isocyanate on Tan δ

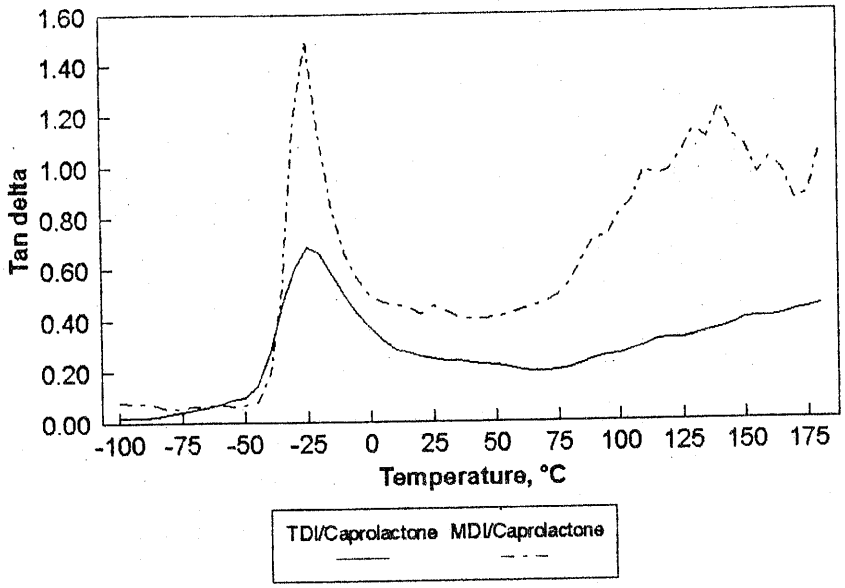

Figure 32

Effect of Isocyanate on Loss Compliance

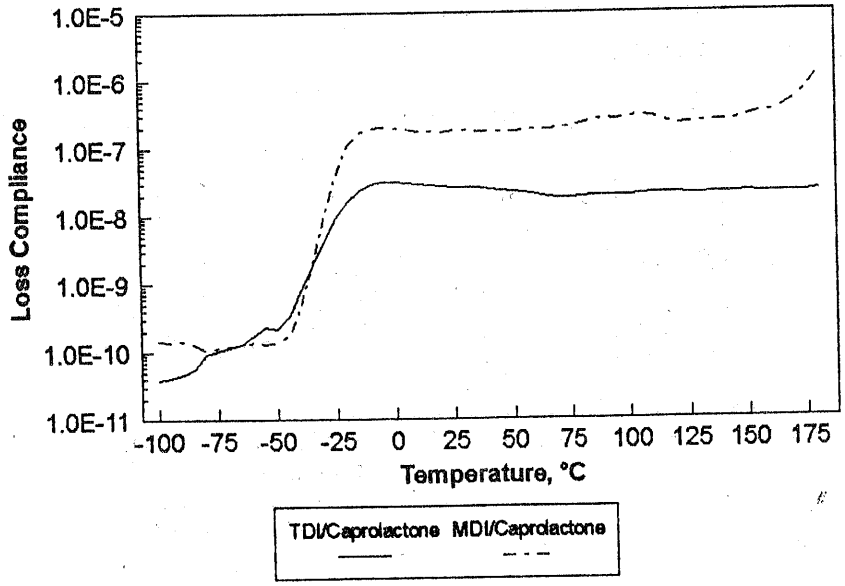

Figure 33

Conclusions

- Dynamic Properties can be varied greatly by many structural changes.
- In order to optimize the dynamic properties for a specific application, the prepolymer supplier, fabricator, and end user should form a team to identify the key parameters required in the material.
- The final test is field performance.