

Cast Polyurethane Elastomers with Improved Dynamic Fatigue Resistance

Rui Xie,¹ Hamed Lakrout,² Gerhard Mueller³

¹The Dow Chemical Company, Polyurethane Application Research and Development, 1881 West Oak Park Way, Marietta, Georgia 30062

²The Dow Chemical Company, New Products, Core R&D, Building 1702, Midland, Michigan 48674

³The Dow Chemical Company, Limited, Polyurethane Application Research and Development, Station Road, Birch Vale, United Kingdom

Received 24 August 2009; accepted 10 January 2011

DOI 10.1002/app.35505

Published online 26 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Cast polyurethane (PU) elastomers have been widely used in dynamic applications, such as rollers and wheels, where a low heat buildup, high-loading resistance, and good cut-growth resistance are desired. Because of their different molecular structure, cast PU elastomers do not perform in the same way in highly demanding dynamic applications. Small variations in the viscoelastic properties can result in significant differences in the longevity of the wheels and rollers that are subjected to a large number of cyclic compressive deformations. Therefore, it is of great interest to understand dynamic performance of urethane elastomers based on various backbones. Dynamic mechanical analysis (DMA) is commonly used to differentiate the dynamic performance of elastomers, but it only provides characterization of the dynamic behavior of a given elastomer at small deformation in the linear viscoelastic regime, where information such as the heat buildup and load-bearing capability of elastomers cannot be obtained. As such, we developed a stress-controlled flexometer on the basis of

the ISO4666/4 method that enabled measurement of the heat buildup and load-bearing capabilities of urethane elastomers in a large dynamic deformation environment. Moreover, a dynamometer was constructed to evaluate wheels based on different urethane elastomers under load at various speeds; this allowed close simulation of the urethane elastomers in a real application environment. In this article, the viscoelastic properties of cast urethane elastomers based on different backbones were studied by DMA. The heat buildup and load-bearing capabilities of the elastomers were investigated via the stress-controlled flexometer, and the performance of the wheels based on various prepolymer systems were evaluated with the dynamometer. Correlations between the material viscoelastic behavior and the heat buildup were established. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 584–594, 2012

Key words: polyurethane elastomers; heat buildup; fatigue; viscoelastic properties

INTRODUCTION

Polyurethane (PU) elastomers are composed of short, alternating polydisperse blocks of soft and hard segments. The use of PU elastomers in wheels and rollers accounts for more than 50% of the total high-performance cast elastomer market. In these applications, PU elastomers are subjected to cyclic deformations of large magnitude and high frequency. Internal heat buildup has been observed in these applications as a result of internal molecular friction during cyclic deformations.^{1–3} The wheel temperature reaches a steady-state after the wheel runs for certain period of time when heat generation balances the heat dissipation. Heat generation is affected by the service conditions, such as the speed and load of the wheels, and the wheel characteristics, such as the wheel size

and shape and urethane viscoelastic characteristics. Heat dissipation depends on the thickness of the urethane on the wheel and the thermal conductivity of the urethane compound.^{4,5} Because common urethane elastomers are poor thermal conductors, the steady-state temperature can be relatively high.

The wheel temperature has an evident effect on the wheel performance characteristics, such as the durability, wear resistance, handling, and traction, and on the rolling resistance. An increase in the wheel temperature is the principal cause of urethane thermal degradation; this leads to fatigue cracking and bond failure over time.⁶ Sometimes, a dramatic heat buildup in the wheels results in the melting of urethane elastomers, commonly referred as *blowout*. A change in the wheel temperature generally affects the viscoelasticity of the urethane compound and can change the rolling resistance, handling, or traction performance. The temperature also affects the strength of urethane elastomers and has a significant effect on the wear resistance and tread block tearing or chunking because the tear

Correspondence to: R. Xie (rxie@dow.com).

strength and abrasion resistance of urethane elastomers are reduced substantially with rising temperature. Other direct physical consequences of the higher temperature include the degradation of the ultimate properties, such as the tensile strength, decreased static and elastic modulus, and increased hysteresis.⁷

Therefore, it is usually desirable to design urethane compounds that can reach a steady-state temperature as low as possible to avoid any of the aforementioned wheel failures. The running temperature often constitutes a limitation in the speed and load at which a wheel can operate, especially for heavy-duty truck tires, off-the-road tires, and high-speed wheels.

Because heat generation is a result of the energy loss of the urethane elastomers under cyclic deformation, the viscoelastic characteristics of the urethane compound play a key role in the temperature rise. The viscoelastic properties of a urethane elastomer depend on the characteristics of its building blocks.⁸ The variation of polyols, isocyanates, and chain extenders can result in a variety of molecular structures of soft and hard segments; this leads to different degrees of phase separation between the hard and soft phases. Abundant literature has shown that phase separation between the hard and soft segments strongly influences the dissipative behavior of PUs. Poor phase separation tends to increase the hysteretic behavior of urethanes under cyclic loading conditions. Therefore, the selection of the right combination of building blocks and the right processing conditions can optimize the viscoelastic properties of an elastomer.

However, selection of the right combination from multiple potential associations to optimize the elastomer properties usually turns into a difficult exercise. There are ample choices in the selection of building blocks, but simple laboratory screening test methods are scarce and often marginal in predicting performance in the field. As a result, wheel performances are often measured directly from real application environments. One popular screening method is dynamic mechanical analysis (DMA). DMA is widely used in the selection of urethane elastomers. However, DMA is designed to probe the mechanical properties of polymers in their linear elastic region; this only provides information on the relative performance of elastomers at small deformation. Therefore, it is often difficult to correlate DMA results to wheel performance in the field, such as those of heat buildup and load-bearing capabilities. In response to the difficulty in correlating DMA to field performance, a number of different approaches have been developed, such as the dynamometer, where the internal temperature of a wheel can be monitored while the speed and load are varied. Although a

dynamometer test directly measures wheel performance and can be easily implemented as a quality-control tool, it is often difficult to use it as a preliminary screening tool because the preparation of the wheels involves a significant amount of effort. A better alternative is to directly observe the temperature rise itself through application of cyclic deformation to a laboratory specimen, as described in ASTM D 623-99. Such dynamic fatigue test consists of a strain-controlled compression fatigue test with a Goodrich flexometer. This method has been widely adopted in the rubber tire industry to directly measure the heat buildup in the laboratory.

Most early work with a flexometer was done on rubber specimens through application of a cyclic strain at a constant amplitude (constant strain deformation). Storey⁹ reported the heat buildup in Buna-type rubber blocks subjected to constant strain deformation. The author also recognized an increasing compression set of elastomers as the final height of the rubber blocks decreased linearly with rising heat-buildup temperature. At moderate temperatures, gradual degradation occurred slowly. At high temperatures, catastrophic failures could cause explosion or blowout.

Studies of the heat buildup in urethane elastomers can be dated back to the mid 1960s. Using a flexometer that was capable of compression and lateral shear, Singh et al.⁶ measured the heat buildup in both polyester- and polyether-based elastomers. The authors emphasized that urethane parts subjected to dynamic stresses or strains generally showed great heat buildup. A temperature rise due to heat buildup could affect the thermal stability of the elastomers and, thus, the service life of the urethane parts. Gianatasio and Ferrari¹⁰ observed that under constant strain deformation, the energy loss escalated with increased hardness and modulus of the elastomers. They also found that the polyether [polyoxytetramethylene glycol (PTMEG)] elastomers generally had a lower heat buildup than the polyester elastomers.

More recently, a stress-controlled flexometer was developed in response to a lack of correlation between the observations from dynamic fatigue testing at constant strain deformation and heat buildup in truck tires. Mouri¹¹ demonstrated that heat buildup in a truck tire was closer to a constant stress deformation than a constant strain deformation, and a flexometer based on a constant stress deformation could better predict the tire temperature rise. Mead et al.¹² used a stress-controlled flexometer to screen PU formulations in high-loading applications, such as rubber pads for military tracked vehicles. They recorded the maximum internal temperature of a 2.5-foot high-PU elastomer cylinder with cycling forces varying between 5000 and 8000 pounds at a

frequency of 6.5 Hz. The ISO 4666 method represents renewed effort in further standardizing and perfecting the stress-controlled test.

In a previous article, the development of a method to determine the resistance of elastomers to heat buildup and their maximum load-bearing capabilities with a stress-controlled flexometer was reported.¹³ This article represents an attempt to correlate the material linear viscoelastic properties of urethane elastomers obtained by DMA with the internal heat buildup measured on a customized stress-controlled flexometer. Such a correlation would help with some fundamental understanding of the heat buildup mechanisms, which in turn, will further drive the development of new urethane elastomers with improved dynamic fatigue resistance or lower internal heat buildup and higher load-bearing capabilities.

INTERNAL HEAT BUILDUP AND MATERIAL VISCOELASTICITY

Heat buildup is an aspect of the dynamic properties of a material. Heat buildup and its associated temperature rise are due to the conversion of some applied mechanical energy into heat. The conversion of the applied mechanical energy takes place at the molecular level. Rapid macroscopic deformations involve fast local motions of polymer chains, chain segments, and crosslinks through the polymer. If the units are forced into new locations more rapidly than vacant sites (holes) are generated by thermal motion of the surrounding molecules, the ordered mechanical motion is converted into random thermal motion of these molecules, that is, heat. The deformation of any material can be resolved into an elastic and a viscous component, often modeled at a first order with a spring and a dashpot attached in series (Maxwell model) or in parallel (Voigt model). When a cyclic sinusoidal strain is imposed on a material, the two viscoelastic components of the material respond at different speeds; this results in the actual stress of the material leading the imposed strain by a phase angle (δ). If the stress is plotted against strain, for a single deformation, a hysteresis loop is obtained. The area within this closed loop is the amount of mechanical energy converted to heat (H) during each cycle, as determined by Eq. (1), where σ is the stress and γ is the strain:

$$H = \int_0^T \sigma(d\gamma/dt)dt \quad (1)$$

where T is time of a single deformation and t is time.

If one assumes that the periodic deformation cycle is sinusoidal, Eq. (1) can be rewritten as

$$H = \pi\sigma_0\gamma_0 \sin \delta \quad (2)$$

where σ_0 and γ_0 are the amplitudes of stress and strain.

Because the loss or viscous modulus (G'') = $\sigma_0/\gamma_0 \sin \delta$, when the deformation is a constant strain process, Eq. (2) becomes

$$H = \pi\gamma_0^2 G'' \propto G' \tan \delta \quad (3)$$

where G' is the storage or elastic modulus. In the case of a constant stress process, the energy loss during one periodic deformation is

$$H = \pi\sigma_0^2 G''/G^* \propto \tan \delta/G' \approx J'' \quad (4)$$

where G^* is the complex modulus and J'' is the loss compliance. Mouri¹¹ proposed a simplified equation for energy loss by using a deformation index (n):

$$H \propto \tan \delta/G'^{n-1} \quad (5)$$

where n ranges between 0 and 2 and is an indication of the mode of deformation. When $n = 0$, Eq. (5) reduces to Eq. (3), which represents a constant strain deformation. When $n = 2$, Eq. (5) reduces to Eq. (4), which represents a constant stress deformation, and a value of $n = 1$ represents constant energy deformation. Equations (3)–(5) offer a better understanding of how viscoelastic properties affect hysteresis, namely, the energy loss. Energy loss due to constant strain deformations is proportional to G'' , and energy loss due to constant stress deformations is proportional to $\tan \delta$, although it is inversely proportional to G' . Energy loss due to constant energy deformations is independent of modulus and merely a function of $\tan \delta$.

Equations (3)–(5) suggest that the hysteresis of a given urethane elastomer depends on the type of deformations it is subjected to. With this in mind, equations (3)–(5) can really direct effort in the design of urethane elastomers to minimize heat generation. For example, for applications under constant strain deformations, one should minimize G'' , whereas for applications under constant stress deformations, minimizing $\tan \delta$ and maximizing G' would increase the durability of the elastomers.

Using Eq. (5), one can empirically determine n or the type of deformation to which a material is subjected in an application environment. Futamura¹⁴ found that n for wet traction was $n = 0$, a constant strain deformation process, whereas dry traction was a constant stress deformation process, where $n = 2$. Summer et al.¹⁵ demonstrated that belt-edge separation is a constant stress deformation and sidewall ozone cracking is a constant strain deformation. Mouri¹⁶ found that truck tire rolling resistance was closely approximated to constant stress deformation. By using a flexometer based on constant stress deformation, Mouri¹¹ also demonstrated that truck

TABLE I
Prepolymer Systems Used in the Study

Sample	Product name	Chemistry	NCO content (%)
A	Hyperlast T840/95A	Reaction product of TDI and PTMEG	6.35
B	Hyperlast T140/95A	Reaction product of TDI and PTMEG	6.30
C	Diprane T940/95A	Reaction product of TDI and polyester polyol	5.75
D	Experimental	Reaction product of TDI and PTMEG	5.25
E	Experimental	Reaction product of TDI and PTMEG	5.25
F	Diprane T950/95A	Reaction product of TDI and polycaprolactone polyol	5.75
G	Low free TDI PTMEG prepolymer 95A	Reaction product of TDI and PTMEG	6.30

tire heat generation was closer to constant stress deformation than constant strain deformation. Because of the similarity of running truck tires and urethane wheels, in this work, heat generation in a urethane wheel was considered as a result of constant stress deformation.

EXPERIMENTAL

Preparation of the elastomer specimens and wheel samples

Elastomer specimens were prepared via a two-step prepolymer process. Various polyols were reacted with toluene diisocyanate (TDI) form prepolymers. VORANATE T80 type I TDI was obtained from The Dow Chemical Co., Midland, MI. Prepolymers A, B, C, and F were commercial products of the Dow Chemical Co., whereas prepolymers D and E were experimental compositions that were primarily based on PTMEG with a weight-average molecular weight of 2000. Prepolymer G was a commercial TDI-PTMEG prepolymer, which contained less than 0.1% monomeric TDI content. All of the reactions were conducted in a glass reactor under nitrogen protection at 80°C with stirring. The extent of the reaction of the hydroxyl groups with isocyanate was determined by an amine equivalent method. The

NCO contents of the prepolymers are listed in Table I. After the reaction finished, the prepolymers were degassed at 70°C *in vacuo*. The chain extender, 4,4'-methylene bis(2-chloroaniline) (MOCA), was melted at 115°C and mixed with the prepolymers at about 70°C at 95% stoichiometry ($[\text{NH}]/[\text{NCO}]_{\text{Prepolymer}} = 0.95$). The mixture of the components was achieved via a Speedmixer DAC 400FV by Hauschild (Hamm, Germany) at 2200 rpm for 60 s. The mixtures were then poured into an aluminum mold preheated at 110°C. After curing at 110°C for 30–45 min, the samples were removed from the mold and further post-cured at 110°C for 16 h. A variety of elastomers at 95–97 A free from defects, such as entrapped air bubbles, were obtained after postcure. The details of the elastomer samples are shown in Table I.

The PU wheels were manufactured via the standard open-casting process. Steel wheel hubs 5.4 in. in diameter and 2 in. wide were first sand-blasted to create a fresh, rough surface and then cleaned with isopropyl alcohol. Two coats of Thixon 405 (The Dow Chemical Co.) were applied to the wheel surface. After it was dried at room temperature for about 2 h, the surface-treated steel hub was placed in an oven at 120°C for at least 2 h before it was assembled in a wheel mold that was preheated at 110°C, as shown in Figure 1(a). The prepolymers and MOCA were mixed according to the process

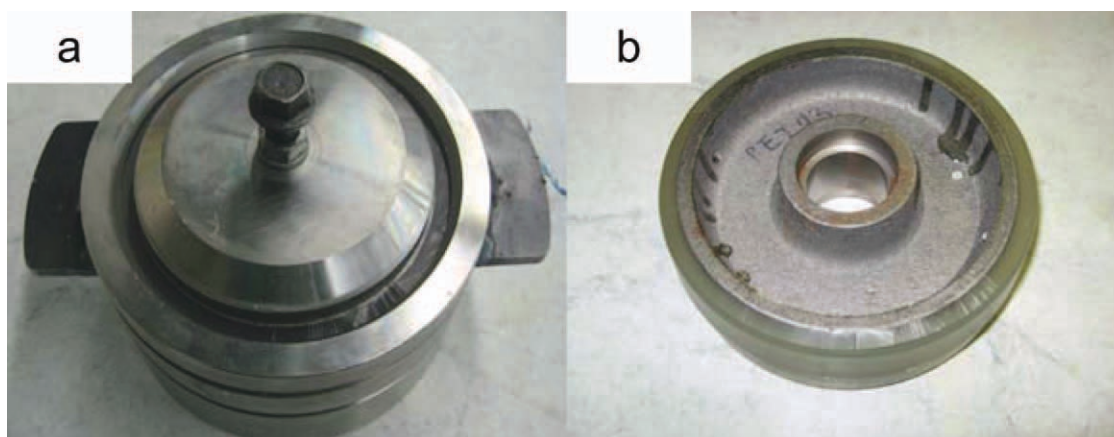


Figure 1 (a) Mold assembly and (b) PU-coated wheel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

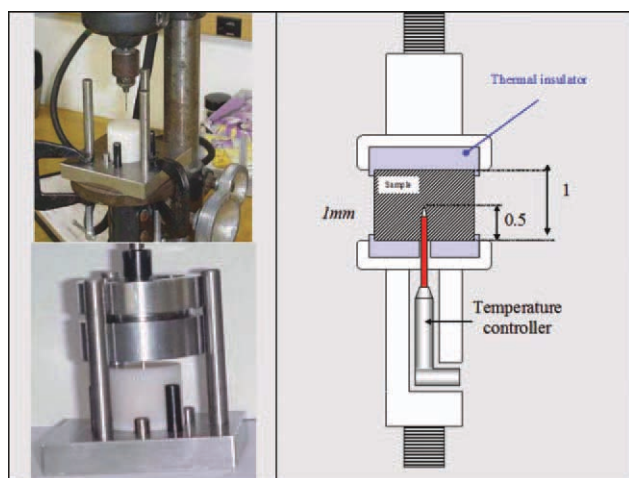


Figure 2 Drilling and the insertion operation of the temperature probe in the cylinder. The setup was then installed in the custom apparatus represented on the right-hand side. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

described previously, and mixtures of the prepolymers and chain extenders were poured into the mold to form a PU-coated wheel with a thickness of the PU layer at 0.3 in., as shown in Figure 1(b). After curing at 110°C for about 30 min, the wheel was removed from the mold and trimmed before it was further postcured at 110°C for 16 h. The wheels were subjected to dynamometer testing, described later, after they were conditioned at room temperature for about 4 weeks.

DMA and compression fatigue test

After the specimens were aged at room temperature for about 2–4 weeks, their viscoelastic properties were characterized by DMA. The analysis was performed on a Rheometrics RSA II in tension mode between –100 and 250°C in air while the specimens were heated at 2°C/min. The imposed strain and frequency were 0.1% and 10 Hz, respectively.

The dynamic fatigue properties of the specimens, including the internal heat buildup and maximum load capabilities, were measured by a stress-controlled flexometer. The stress-controlled dynamic fatigue test was built on a servo-hydraulic machine made by MTS Systems Corporation, Eden Prairie, MN capable of recording the internal and surface temperatures of the elastomeric cylinder specimen 30 mm in diameter and 25 mm high. The internal temperature was measured through an internal probe. A small hole (1 mm in diameter) was drilled at the center of the specimen. The temperature probe was inserted into the center of the specimen, and the hole was then sealed with heat-conductive urethane adhesives. Because of the size of the hole and the fact that the hole was sealed afterward, its impact on the

viscoelastic properties of the specimen was believed to be negligible. Force, displacement, and time were also recorded. The tests were conducted at ambient temperature at 20 Hz. A specific procedure was developed to evaluate the load-bearing and temperature capabilities of different PU formulations.¹³ Successive sequences of 25 min each with a load increment of 500 N were applied until the sample failed. Failure was detected as sudden increases in the compression set and internal temperature of the cylinder specimen, which occurred because of melting or blowout. Median test results of three specimens of each composition were reported as the maximum load of the PU composition. Figure 2 showed the test apparatus.

Wheel dynamometer testing

The performance of the wheels was evaluated by a wheel dynamometer. The wheel dynamometer was constructed and equipped with LabView 8.2 software, which was capable of measuring the wheel speed, wheel temperature, wheel deflection, driving torque, and load. Tests were conducted at ambient temperature. A specific protocol was developed to evaluate the wheel performance at a given speed of 10 km/h. Successive sequences of 30 min each with a load increment of 100 kg were applied until the wheel failed. The wheel failure was detected by a sudden increase in the wheel deflection and driving torque due to melting of the PU or delamination of the PU from steel hubs. Median test results of the three wheel samples were reported as the maximum load-bearing capability of the wheel.

RESULTS AND DISCUSSION

Viscoelastic behavior of the urethane elastomers

A material's viscoelastic properties can be characterized in terms of G' , G'' , and G^* . Alternatively, the dynamic properties can be expressed in terms of the *compliance*, the response to stress rather than to strain. This is represented as J , which is a reciprocal of G^* .

Elastomers, by definition, are used in the rubbery state, that is, at a temperature that is higher than the glass-transition temperature but lower than the softening temperature, where modulus decreases rapidly with increasing temperature. In this rubbery region, well above the glass-transition temperature, the viscoelastic properties are primarily affected by differences in the molecular friction coefficient among elastomers. As heat generation in urethane elastomers is not a primary concern before it results in significant material deterioration at a temperature well above the glass-transition temperature, in this article, only the viscoelastic behavior of urethane

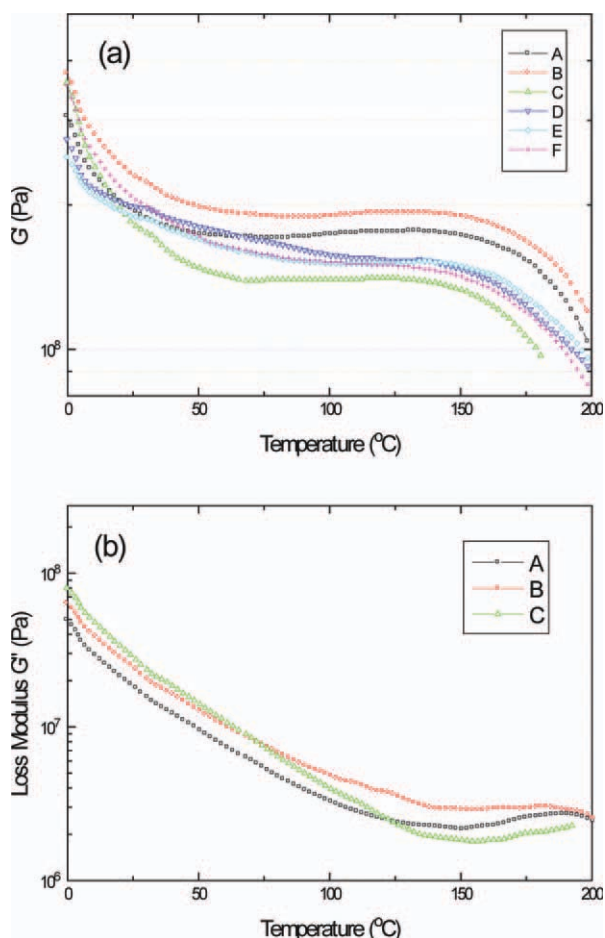


Figure 3 (a) Elastic modulus of 95A elastomers in a normal operation temperature window between 0 and 200 $^{\circ}\text{C}$. (b) G'' values of the A, B, and C elastomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

elastomers in the rubbery state or in the plateau region of the elastic modulus are discussed.

Figure 3(a) shows the elastic modulus of different 95A urethane elastomers between 0 and 200 $^{\circ}\text{C}$. The moduli of the elastomers were slightly different from each other, although their hardnesses were about the same. All of the samples exhibited a plateau between 50 and 150 $^{\circ}\text{C}$. However, the slope of the plateau was different. Sample A demonstrated the flattest slope, and sample F showed the highest slope. As the elastic modulus of an elastomer represents its sustainability under a work load, it is highly desirable to have a constant elastic modulus over a wide temperature window.

According to eqs. (3) and (4) in the earlier discussion, an elastomer with a higher G' but the same $\tan \delta$ generates more heat under constant strain deformations, whereas under constant stress conditions, it would undergo less deformation and generate less heat. In this case, under constant strain deformations, heat buildup in the elastomers should have

followed the order $H_B > H_A > H_D \approx H_E \approx H_F > H_C$, whereas under constant stress deformations, the sequence would be reversed. However, rarely, two different elastomers have the same $\tan \delta$ value. It could be risky to draw a conclusion solely the basis of the performance of elastic modulus. For example, in Figure 3(b), the G'' values of elastomers A, B, and C are plotted against the temperature. G'' of sample A was consistently lower than that of sample B across the temperature range and lower than that of sample C when temperature was lower than 125 $^{\circ}\text{C}$. Because heat buildup in elastomers is proportional to G'' [Eq. (3)] under constant strain deformations, one might conclude that the heat generation in elastomer A would be less than that in elastomers B and C, that is, $H_B > H_A$ and $H_C > H_A$. Although $H_B > H_A$ was in agreement with the earlier prediction from G' , $H_C > H_A$ was contradictory to the prediction. The discrepancy could be attributed to the difference in $\tan \delta$ among the elastomers.

$\tan \delta$ has been widely used to gauge the performance of elastomers in dynamic applications. As demonstrated in eqs. (3) and (4), heat buildup is proportional to $\tan \delta$, regardless of the mode of deformation. This consideration is of great practical importance in the formulation of urethane elastomers. However, as $\tan \delta$ is a ratio of G'' to the elastic modulus, it does not give information on the load-bearing capability of an elastomer. Figure 4 shows the $\tan \delta$ values of the 95A elastomers between 0 and 200 $^{\circ}\text{C}$, measured at 10 Hz. For all samples, $\tan \delta$ decreased with increasing temperature and was minimized at about 150 $^{\circ}\text{C}$. However, it appeared that there were distinguishing differences in the viscoelastic behavior among the elastomers. For example, the $\tan \delta$ value for sample A was lower in a wide temperature range compared to the other specimens, and those of samples D and E were

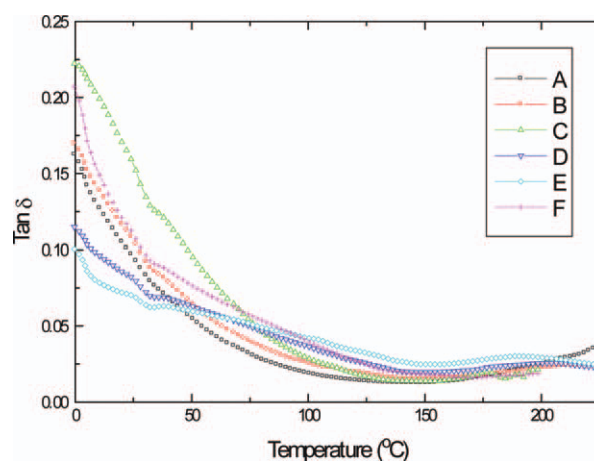


Figure 4 $\tan \delta$ of the elastomers between 0 and 200 $^{\circ}\text{C}$, obtained via DMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

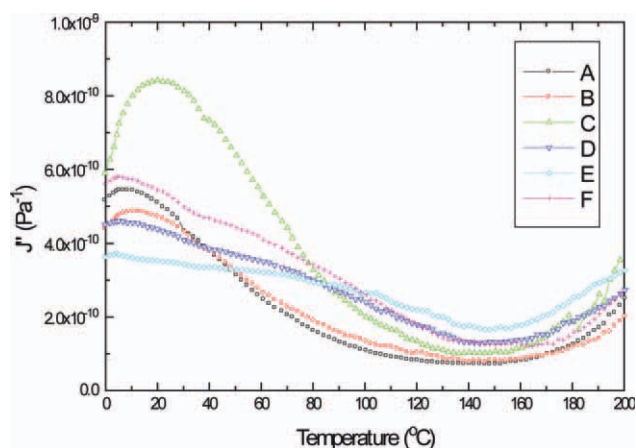


Figure 5 J' values of the 95A elastomers between 0 and 200°C, obtained via DMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

consistently higher than those of the rest samples at higher temperatures (>100°C).

Figure 5 shows the J' values of the 95A elastomers between 0 and 200°C. The J' values of all of the elastomers decreased with increasing temperature and bottomed out between 140 and 160°C. In particular, samples A and B and samples F and D exhibited similar J' profiles between 120 and 160°C. According to Eq. (4), the dynamic heat buildup is proportional to J'' under constant stress deformation; it is interesting and practically useful to correlate the heat buildup measured by a stress-controlled flexometer to the viscoelastic behavior of the elastomers, such as J'' .

Heat buildup and load-bearing capabilities of the urethane elastomers

Although DMA provides a characterization of the viscoelastic properties of materials in the linear regime, it cannot address the large deformation behaviors often observed in field applications. As a result, it is difficult to correlate the viscoelastic behavior observed by DMA to material performance in the field.

In this study, we tried to correlate the viscoelastic properties of urethane elastomers with their heat buildup and load-bearing capabilities, as measured by a stress-controlled flexometer. Tests on a flexometer can be conducted at conditions that closely simulate what an elastomer would experience in a real application environment, including properties such as the load, speed, temperature, and moisture level. Thus, it offers a more direct measurement of elastomers operating in a dynamic environment.

Figure 6 shows the compression set and internal temperature of elastomer D during a 25-min testing period under different loads. Both the compression

set and internal temperature increased with increasing load and leveled off over the testing period at a given load until the specimen was subjected to a critical load, in this case, 5.0 kN. At the critical or maximum load, sudden increases in the compression set and internal temperature were observed; this indicated a structural disruption in the elastomer due to melting or blowout. Similar behavior was observed in all of the elastomers tested.

In Figure 7, the internal temperatures of the elastomers at the end of each of the 25-min testing periods are examined as a function of the load. Clearly, internal heat buildup was a linear response to the load. However, the rate of temperature rise changed abruptly at about 100°C. The internal temperature rose slowly with the load at temperatures lower than 100°C and rapidly when the temperature exceeded 100°C. The amount of load required to reach 100°C was different from one specimen to another. Interestingly, all of the specimens exhibited a similar rate of temperature rise when the internal temperature of the elastomers went beyond 100°C,

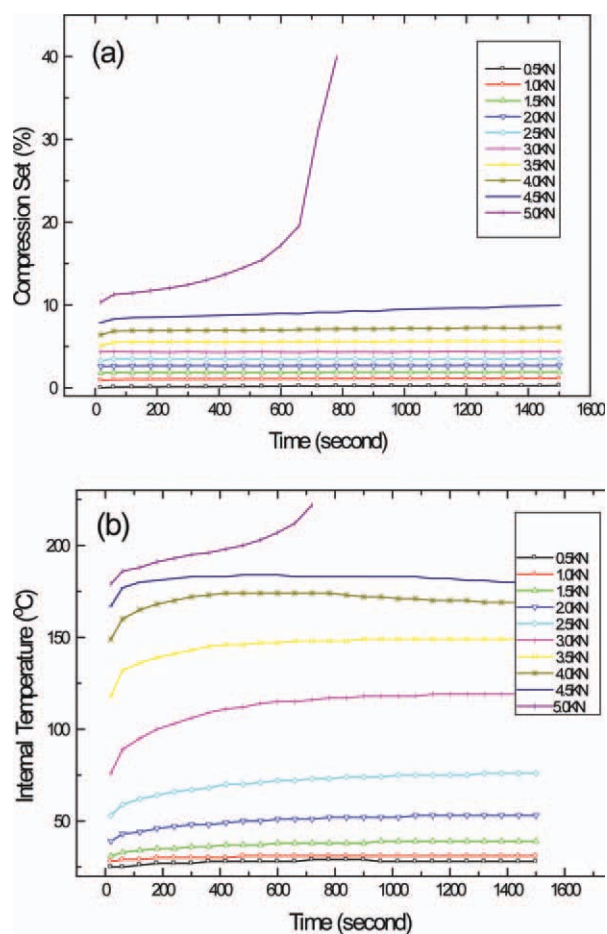


Figure 6 (a) Compression set and (b) internal temperature of elastomer D under various loads, obtained via a stress-controlled flexometer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

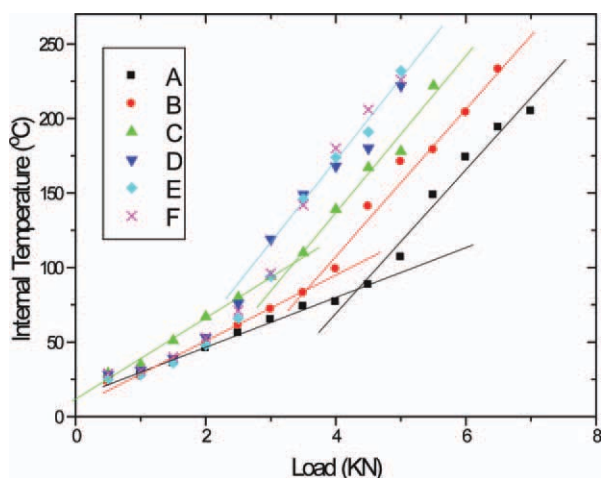


Figure 7 Internal temperature of the elastomers as a function of the compression load. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as evident by the slopes. The fundamentals behind this phenomenon remain to be investigated.

Figure 8 shows the maximum load of the specimens and other 95A elastomers obtained from the market. Among the other 95A elastomers, A' and B' were based on TDI-PTMEG prepolymers chain-extended by MOCA, and C' was based on a TDI-polyester prepolymer cured by MOCA. The three elastomers were tested side by side with the Dow elastomers and used as benchmarks of the study. They were selected because of their excellent heat buildup and load-bearing capabilities and proven performance in wheel and roller applications. The *maximum load* was defined where permanent disruption to the elastomers occurred, as discussed earlier. The maximum load of the three benchmarks ranged from 4.0 to 5.5 kN, whereas the Dow elastomers achieved maximum load between 5.0 and 7.0 kN. Hyperlast T840/95A and T140/95A exhibited signifi-

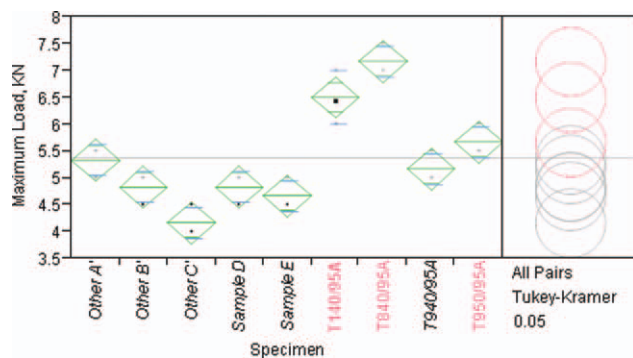


Figure 8 Maximum load of various Dow elastomers and elastomers from the marketplace, obtained by a stress-controlled flexometer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cantly improved load-bearing capabilities versus samples A', B', and C'. It is expected that a lower heat buildup, higher load-bearing capability, and longer service life will be achieved out of wheels made from these elastomers.

Correlation of the heat buildup and elastomer viscoelastic properties

As mentioned earlier, it is often challenging to correlate the viscoelastic properties observed by DMA with dynamic performance in the field. There are a few factors that have contributed to the complexity. First, cyclic deformation may vary from application to application. According to eqs. (3)–(5), the heat buildup in elastomers depends on the type of deformation, and it usually requires detailed work to define *n* for a given application.^{14–16} Second, the viscoelastic properties are functions of

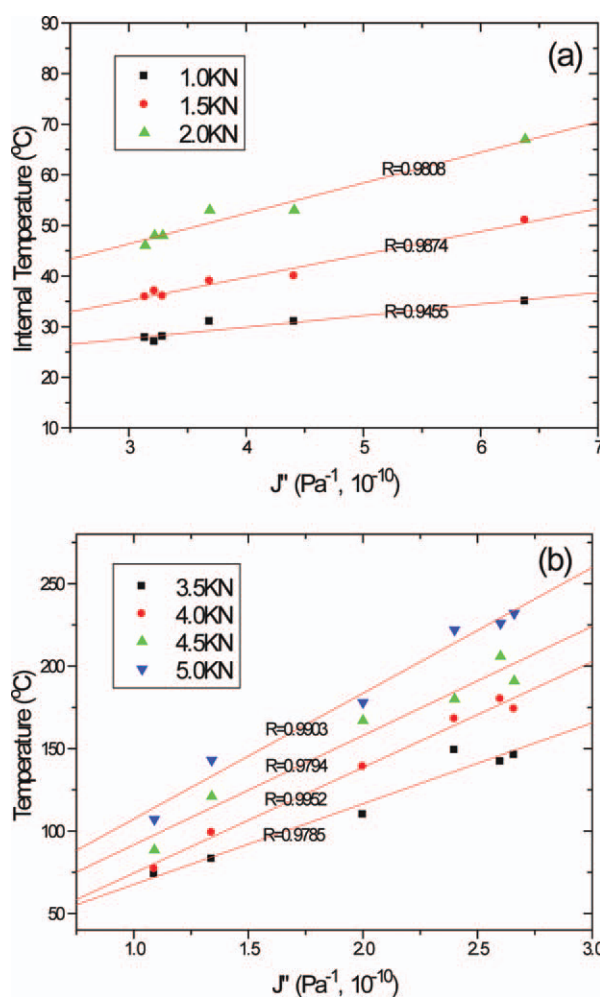


Figure 9 Internal temperatures of the elastomers at (a) 1.0–2.0-kN loads as a function of J'' at 50°C and (b) 3.5–5.0-kN loads as a function of J'' at 100°C. A strong linear correlation was observed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

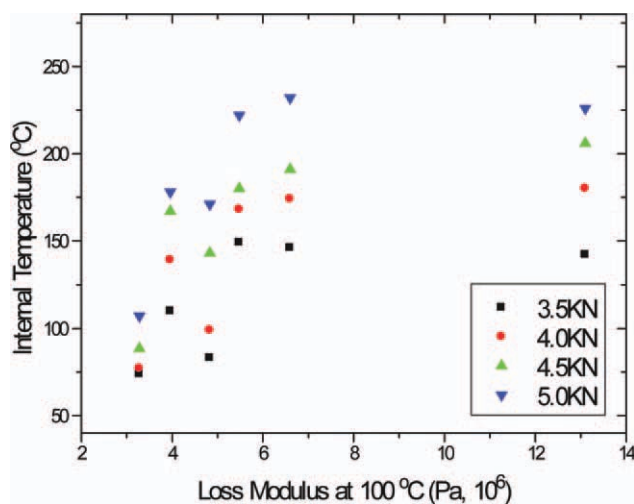


Figure 10 Internal temperature of the elastomers at a load of 3.5 kN as a function of G'' . No correlation was observed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the temperature. Heat buildup causes a temperature rise in the elastomers, and a temperature rise affects a material's viscoelastic behavior. Thus, it is difficult to define a temperature or a temperature window in which viscoelastic behavior would be critical in determining heat buildup in the materials.

In this study, we attempted to correlate the heat buildup in the elastomers measured by a stress-controlled flexometer with their viscoelastic properties determined by DMA, or more specifically, J'' . Figure 9(a) shows the internal temperature of the elastomers under loads of 1.0–2.0 kN as a function of J'' at 50°C, and Figure 9(b) shows the internal temperature of the elastomers under higher loads as a function of J'' at 100°C. A strong linear correlation between J'' and the internal temperature was observed. The internal temperature was found to be proportional to J'' ; this was in good agreement with Eq. (4). As expected, the internal temperature was proportional to J'' at 50°C when the load was low and was proportional to J'' at 100°C when the load was high. As demonstrated in Figure 7, a lower load corresponded to a lower internal temperature, whereas a higher load resulted in a higher internal temperature.

The strong correlation shown in Figure 9 was encouraging, as it established a simple link between the dynamic heat buildup and the elastomer viscoelastic behavior, J'' . The correlation, in turn, proved Eq. (4), which was derived from a simple model of spring and dashpot that has been widely used to describe the viscoelastic behavior of elastomers. For comparison, the internal temperatures of the elastomers at higher loads were plotted against G'' at

100°C and are shown in Figure 10. As expected, no correlation of any sort was observed.

Dynamic performance of the wheels based on various prepolymer systems

It is evident from the previous results that the heat buildup was correlated to the viscoelastic properties

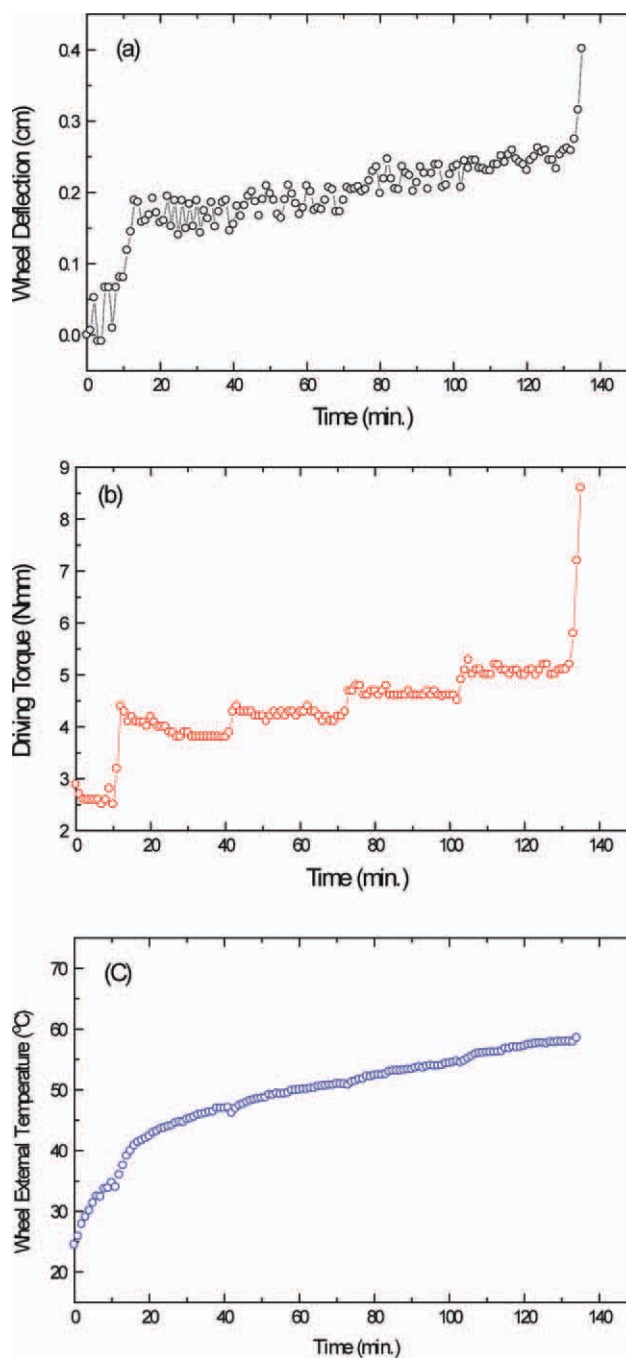


Figure 11 (a) Wheel temperature, (b) driving torque, and (c) wheel deflection increase with load increases over time. The wheel was based on Hyperlast T840/95A. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the PU elastomers. However, it has been widely discussed in recent years how the PU viscoelastic properties may affect the service life of PU wheels and rollers. The question is what kind viscoelastic profile, as measured by DMA, is required to enhance the longevity of PU wheels and rollers, especially in harsh application environments. There is a need for PU wheels to operate at higher speeds under higher loads for extended periods of time. To better understand the problem, PU wheels based on different prepolymer systems were made and subjected to the same testing protocol with a dynamometer. Figure 11 shows the changes of wheel deflection, driving torque, and external temperature of a PU wheel running at a fixed speed of 10 km/h as the load increased over time. The wheel was made of Hyperlast T840/95A. It is evident from Figure 11 that the wheel deflection, driving torque, and external temperature increased over time with increasing load. Step increases in the deflection and driving torque were observed when the wheel failed. The onset of the steep increase was used to determine the maximum load of the PU wheel.

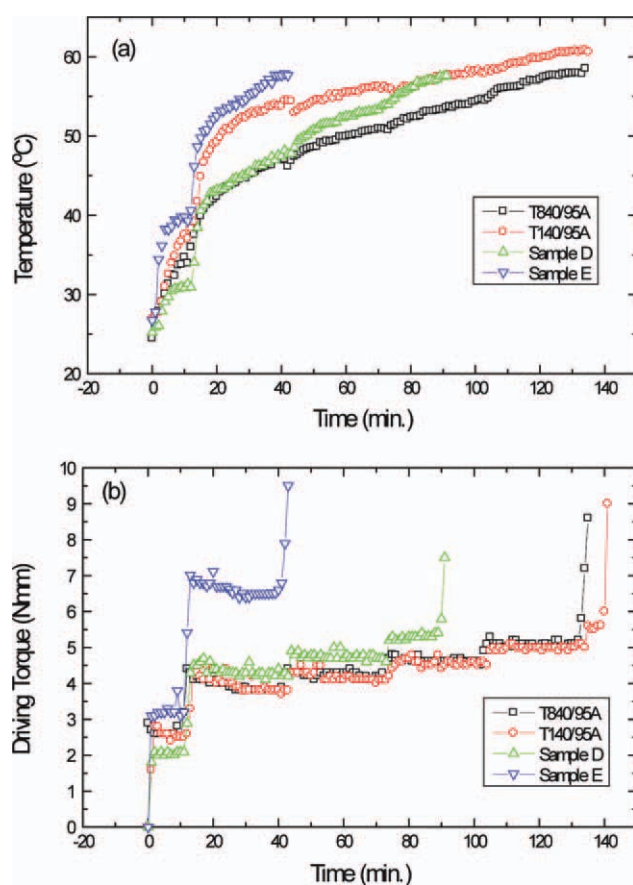


Figure 12 Effects of the prepolymer systems on the (a) wheel temperature and (b) driving torque with load increases over time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

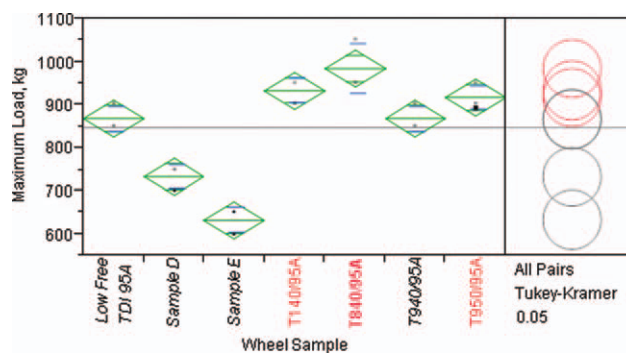


Figure 13 Comparison of the maximum load for wheels based on various prepolymer systems, as determined by a dynamometer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 12 shows the temperature and driving torque for wheels based on different prepolymer systems as the load increased over time. The wheel temperature increased over time as the load increased, as shown in Figure 12(a). However, the speed of the temperature rise depended on the prepolymer systems. Hyperlast T840/95A exhibited a slower heat buildup, followed by Hyperlast T140/95A, sample D, and sample E. The driving torque of the wheels increased as the load increased over time. The driving torque for the wheels based on Hyperlast T840/95A and T140/95A exhibited very similar trends, whereas those for the wheels based on samples D and E showed more rapid increases as the load increased.

Figure 13 shows the maximum load of the wheels based on different prepolymer systems. Hyperlast T840/95A demonstrated some improvements over Diprane T940/95A and a 95A low free TDI-PTMEG system. However, the advantage of Hyperlast T840/95A was not significant compared to Hyperlast T140/95A and Diprane T950/95A. Nevertheless, all of the wheels made from the previous prepolymer systems had significantly better performance compared to wheels made from prepolymers D and E. The result here agreed well with what was observed in the compression fatigue testing, as shown in Figure 8. With regard to the results shown in Figure 3 and 4, it appeared that the most desired viscoelastic properties for a PU wheel compound were those demonstrated by Hyperlast T840/95A and T140/95A, such as a flat G' over a wide temperature window and a low $\tan \delta$ value, especially at the softening temperature.

CONCLUSIONS

In this article, the heat buildup and fatigue resistance of various urethane elastomers were studied by a stress-controlled flexometer, and the load-bearing

capabilities of wheels based on a variety of urethane elastomers were investigated with a dynamometer. It was observed that the heat buildup in urethane elastomers depended on the building blocks, such as the molecular structure of the soft segments and the composition and molecular weight of the soft segments. The load-bearing capabilities of wheels made of urethane elastomers were found to be related to the heat buildup of the urethane elastomers. Wheels made of elastomers with lower heat buildup had higher load-bearing capabilities and lasted longer under the same testing conditions. These performance features were found to be correlated to the linear viscoelastic properties of the urethane elastomers measured by DMA. The heat buildup and internal temperature rise of the elastomers under cyclic constant stress deformation were found to be proportional to J'' of the elastomers, as predicted by a model represented as a spring and a dashpot. This simple correlation was of great practical importance, as it could be used to direct efforts for developing elastomers with improved dynamic fatigue resistance.

It has been shown that the heat buildup in elastomers was a linear response to the compression load. However, the slope increased when the internal temperature went beyond 100°C. Above 100°C, the rise in internal temperature in all of the elastomers followed a similar trend; this suggested that the temperature rise in the elastomers above 100°C might have been following the same mechanism. The sudden change in the speed of the temperature rise around 100°C and the reason behind the same speed of the temperature rise above 100°C in these elastomers remain to be studied.

By applying knowledge of material viscoelastic behavior and employing a stress-controlled flexometer and a dynamometer, we successfully developed urethane elastomers with improved dynamic fatigue

resistance. Our findings suggest that in general, PTMEG-based compounds perform the best in dynamic applications, followed by caprolactone- and polyester-based compounds. This was in good agreement with what was reported previously. However, the dynamic performance of PU elastomers also depends on the molecular weight and functionality of a given composition. For example, caprolactone- and polyester-based compounds could be formulated to outperform some PTMEG-based compounds, such as samples D and E, that may not be optimized for dynamic applications.

The authors thank Jack O'Donnell for his assistance with the DMA of the samples.

References

1. Reed, T. F. *Elastomerics* 1989, 121(12), 28.
2. Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed. Wiley: New York, 1980.
3. Medalia, A. I. *Rubber Chem Technol* 1991, 64, 481.
4. Browne, A. L.; Wickliffe, L. E. *Tire Sci Technol* 1976, 8, 37.
5. Clark, S. K. *Tire Sci Technol* 1976, 4, 181.
6. Singh, A.; Weissbein, L.; Molica, J. C. *Rubber Age* 1966, June, 77.
7. Shkol'nik, S. I.; Shimanskii, V. M. *Mater Sci* 1966, 2, 538.
8. Ong, C. J.; Saxon, R. *J Appl Polym Sci* 1976, 20, 1695.
9. Storey, E. B. *Rubber Chem Technol* 1950, 23, 910.
10. Gianatasio, P. A.; Ferrari, R. J. *Rubber Age* 1966, December, 83.
11. Mouri, H. *Rubber World* 1996, September, 24.
12. Mead, J. L.; Roylance, D. K.; Singh, S.; Patt, J. *Polym Prepr* 1985, 26, 162.
13. Flanagan, K.; Lakrout, H.; Xie, R. Presented at the Annual Meeting of Polyurethane Manufacturer Association, Orlando, May 2006.
14. Futamura, S. *Rubber Chem Technol* 1990, 63, 315.
15. Sumner, A. J. M.; Kelbch, S. A.; Eisele, V. Presented at the 146th ACS Rubber Division Meeting, October 1994; Paper No. 18.
16. Mouri, H. Presented at the 146th ACS Rubber Division Meeting, October 1994; Paper No. 56.