NOVEL HIGH PERFORMANCE POLYETHER BASED POLYURETHANE ELASTOMERS FOR DYNAMIC APPLICATIONS

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ABSTRACT

High performance polyurethane elastomers are widely used in dynamic applications, such as wheels, rollers, and tires. These applications account for more than 50% of the high performance engineering elastomer market. The majority of dynamic elastomers are based on polytetramethylene ether glycol (PTMEG). PTMEG elastomers have excellent dynamic performance but are often found to be over engineered for less demanding applications. In this study, a new modified polyether polyol from The Dow Chemical Company is evaluated for replacing PTMEG in less demanding dynamic applications while providing an improvement in viscosity and processing. The elastomers based on the new polyol showed significant improvement over the standard polypropylene glycol (PPG) elastomers and approached the dynamic performance of PTMEG elastomers. As a result of the work, Dow Polyurethanes is commercializing HYPERLAST[TM] 301 Prepolymer series.

INTRODUCTION

Polyurethane (PU) elastomers are suitable candidates for making elastomers used in dynamic applications, such as Industrial wheels (forklift wheels, material cart wheels, escalator wheels), industrial rollers (printing rolls, paper mill rolls, metal handling rolls), automotive bushings, suspension pads, and industrial belts (drive belts, conveyor belts, and timing belts). These applications account for more than 50% of the high performance engineering elastomer market. In these applications, PU elastomers are subjected to cyclic deformations of large magnitude and high frequency. This leads to the internal heat buildup due to the internal molecular friction during the deformation cycles.[1-3] Heat generation depends on the many factors such as; load applied to the elastomer, size and shape of the elastomer and urethane viscoelastic characteristics.[4-5] Similarly heat dissipation is very important and highly dependent on the thermal conductivity of the urethane compound. Because, common urethane elastomers are poor thermal conductors, the heat dissipation is poor which leads to increased temperature of elastomer. Such high temperature is the principal cause of urethane thermal degradation which leads to the failure of PU elastomer in the dynamic applications.[6] So, the desired elastomer should have certain characteristics such as; retention of modulus at elevated temperature, low heat buildup under load and repeat deformations, and chemical/moisture resistance at elevated temperature.

Polytetramethylene ether glycol (PTMEG) polyol is widely used for dynamic applications because of an excellent dynamic performance of the PTMEG based PU elastomers.[7] PTMEG is also suitable for the PU applications where hydrolytic resistance is required. However, in many applications, PTMEG elastomers are often found to be over-engineered for less demanding applications (low speed under limited load) which translate into an unfavorable cost/performance ratio. Also, PTMEG is solid at ambient temperature and has to be melted before using it in a PU formulation. So, it requires special processing

equipment due to high viscosity of polyol and the prepolymer made out of it. In this study, a new modified polyether polyol from the The Dow Chemical Company, which has significantly lower viscosity compared to PTMEG, is evaluated as an alternative to PTMEG in less demanding dynamic applications at an improved cost/performance ratio and also compared against a typical polypropylene glycol (PPG) system showing improved performance.

Table 1. Prepolymer used in the study

Sample	System	Application method	Chemistry	Prepolymer	Curative
A	HYPERLAST™	General Casting	Reaction product of MDI and high performance polyether polyol	HYPERLAST™ 301	HYPERLAST™ C301
B	HYPERLAST™	General Casting	Reaction product of MDI and PTMEG	HYPERLAST™ 101	HYPERLAST™ C101
C	HYPERLAST™	General Casting	Reaction product of MDI and regular polyether polyols	HYPERLAST™ 201	HYPERLAST™ C201

Table 2. Processing parameters for the components

	Temperature (°C)	Viscosity (poise)
HYPERLAST™ 301 Prepolymer	40	0.5 -0.8 at 40°C
HYPERLAST™ 301 Polyol Curatives	40	0.1 -0.3 at 40°C
HYPERLAST™ 101 Prepolymer	40	0.5 -1.0 at 40°C
HYPERLAST™ 101 Polyol Curatives	40	0.2 – 0.3 at 40°C
HYPERLAST™ 201 Prepolymer	40	0.1 -0.2 at 25°C
HYPERLAST™ 201 Polyol Curatives	40	1.0 -2.5 at 25°C

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EXPERIMENTAL

Preparation of the PU prepolymer

Various polyols were reacted with methylene diisocyanate (MDI) to get the required prepolymers. The reaction was conducted in a reactor under nitrogen pad at 80°C with continuous stirring. The extent of the reaction was determined by an isocyanate equivalent method to achieve required isocyanate value. After the reaction was finished, the prepolymers were degassed at 70°C under vacuum.

Percent Isocyanate Determination

The percent isocyanate of the prepolymer was measured by ASTM method D5155-96, test method C. Herein, the urethane prepolymer was reacted with an excess of di-n-butylamine to form the corresponding urea. The remaining dibutylamine was determined by back titration, and the amount of NCO was then calculated from the amount of reacted dibutylamine.

Viscosity

The prepolymer viscosity was analyzed using an AR2000 rheometer. The viscosity was measured by heating samples from 20 to 80 °C at a rate of 3°C/min,and at a constant shear rate of 1 Hz.

Plaque Preparation

A mold was assembled and preheated to 80 °C. The mold consisted of 2 outer metal plates (8" or 14"), two thin inner Teflon coated metal pieces, a 3 mm U-shaped metal spacer, and a piece of polypropylene tubing. The parts were held together with C-clamps.

Both components, the prepolymer and curative side (table 1), were weighed into separate FlacTek cups and were degassed at room temperature in a vacuum chamber for 1 hour. After degassing, both sides were heated to 40 °C. Next, the polyol side was added to the prepolymer side, and mixed in a FlacTek mixer for 5 seconds at 800 rpm and 50 seconds at 2350 rpm. The mixture was then poured into the 80 °C open mold, and placed in an 80 °C oven for 1 hour. The plaque was then demolded, and post-cured at 80 °C overnight. The hardness of the elastomer was measured using durometer on Shore A scale.

Gel Time Determination

The gel time was determined at 40 °C by hand mixing 100 grams of formulation in a Flack Tec cup for 1 minute. The cup was then placed in a piece of polyurethane foam to maintain temperature. The gel time was recorded as the time required for the solution to solidify.

Dynamic Mechanical Analysis

Samples (47.5 mm x 7 mm) were stamped out from the elastomer plaques on the Indusco Hydraulic Swing Arm Cutting Machine. The sample was cut down to 35 mm length with a pair of scissors. The sample was tested on TA instrument ARES rheometer in the torsion fixtures. The linear viscoelastic response (4% strain with auto adjustment) of the sample was measured with oscillatory test (1Hz) along a temperature ramp (3°C/min).

Initial properties

The tensile properties of the elastomers were obtained on tensile bar samples that were punched out from the plaques as per BS 903 Pt A2 method. The dogbone shaped specimens were stamped from plaque using Die C. The tensile properties were measured using a Monsanto Tensometer from Alpha technologies. The dogbones were clamped pneumatically and pulled at a test speed of 20"/min.

Resilience (Lupke Pendulum)

Resilience is recorded using a Lupke type Rebound Pendulum and is based on ISO4662 (Rubber, vulcanized or thermoplastic -- Determination of rebound resilience; 2009). Duplicate samples, (typically 12.5mm thick and 29mm diameter, although other thicknesses may be used with suitable adjustment) were placed on the holder and the pendulum released. The resilience (%) was recorded and repeated until three consecutive impacts gave resilience values of +/- 1% point of resilience. Report the mean value of these three determinations.

Abrasion Resistance

The abrasion resistance was determined using the DIN abrasion method (DIN 53516), using small pucks of 16 mm diameter and 6 mm thickness.

Compression Set

The compression set of 0.5" pucks was determined by ASTM D395, in which a sample was compressed 25%, and held at 70 °C for 22 hours. The decrease in thickness was measured 30 minutes after release from the compression.

Hydrolytic Ageing

Tensile bars were weighed individually before the ageing study was started. Bars were submerged in a bottle filled with deionized water and screwed with a cap. All of the bottles were put at the specific temperature in an oven for given period of time with a secondary container to avoid spillage. Samples at varying time intervals were removed and dabbed with paper towel to get rid of as much as water from the surface before measurement was performed. Samples were weighed to measure the water uptake as a function of ageing time. Samples were further dried at 70 °C in an oven overnight before the tensile measurements were carried out.

RESULTS AND DISCUSSION

Initial properties

Table 3 shows typical physical performance of the HYPERLAST^{TM} 301 system at 90, 85, and 70 shore A. The elastomers demonstrate good stress strain properties, excellent tear strength, and outstanding abrasion resistance. These performance enhancements, in addition to the processing advantages, such as low viscosity, low temperature casting and cure, and convenience of achieving a wide hardness range (70A to 90A) with a single system, make HYPERLAST^{TM} 301 the ideal choice for general castings of a variety of applications. These applications include wheels, rollers, mining screens, mechanical parts, agricultural parts, and replacement of other materials, such as rubber in industrial applications.

Table 3. Typical Physical Properties of HYPERLAST^{TM} 301

Hardness (A)		90	85	70
T.S.(MPa)	BS 903/A	29	22	22
% Elong. at Break	BS 903/A	483	678	691
100% Modulus (MPa)	BS 903/A	7.7	5.7	3.3
Resilience	Lupke Pendulum	32%	44%	49%
C-Tear Strength (N/mm)	Angle, BS903,Pt A3	92	77	56
Gel Time	100 g, 40 ^{o}C	4 min	4.25 min	4.5 min
DIN Abrasion (mm^3)	DIN 53516	59	79	67

Table 4 shows performance comparison of HYPERLAST^{TM} 301 to HYPERLAST^{TM} 101, a PTMEG based system, and HYPERLAST^{TM} 201, a conventional PPG based system at 85 shore A hardness. Comparing to HYPERLAST 201^{TM}, HYPERLAST^{TM} 301 demonstrates improved stress-strain properties, superior tear strength, abrasion resistance, and resilience. While its tensile strength, resilience, and abrasion resistance are lower than HYPERLAST^{TM} 101, the difference is relatively small. Tear strength of the system is similar to HYPERLAST^{TM} 101, and compression set is better than HYPERLAST^{TM} 101. Clearly, from mechanical property point of view, HYPERLAST^{TM} 301 represents a significant improvement over conventional PPG based systems, such as HYPERLAST^{TM} 201, and a closer match to the performance of PTMEG based systems.

Table 4. Comparison of Typical Physical Properties of HYPERLAST[TM] 301, 201 and 101 at 85 Shore A Hardness

		HYPERLAST 101/85	HYPERLAST 201/85	HYPERLAST 301/85
Hardness (A)		85	85	87
Polyol Type		PTMEG	Regular PPG	High performance Polyether polyol
T.S.(MPa)	BS 903/A	34	13	22
% Elong. at Break	BS 903/A	450	325	678
100% Modulus (MPa)	BS 903/A	6.2	5	5.7
Resilience	Lupke Pendulum	50%		44%
Tear Strength (N/mm)	C-Angle, BS903,Pt A3	80	50*	77
Gel Time	100 g, 40 ^{o}C	4.5 to 6 min	7 to 9 min	3.5 to 5 min
Abrasion (mm^3)	DIN 53516	45	155	79
Compresison set (%) 22h @ 70 °C	ASTM D395	40	-	27
* ASTM D624, Nicked Crescent				

Dynamic Mechanical Analysis

Figure 1 shows Dynamic Mechanical Analysis (DMA) profile of HYPERLAST[TM] 301 based elastomers at different hardnesses. To better understand dynamic performance of HYPERLAST[TM] 301, the DMA profile of a 95 Shore A elastomer based on HYPERLAST [TM] 101 is included as a benchmark. PTMEG based elastomers have been the gold standard in dynamic elastomer applications, primarily due to their ability to retain modulus at elevated temperature and low tan δ value over a wide service temperature window. A wider service temperature window, defined by the glass transition temperature of the elastomers and the temperature where the modulus drops significantly, is preferred as it allows the elastomers to perform in both low temperature and high temperature environments. The elastomers based on HYPERLAST[TM] 301 exhibit similar glass transition temperature comparing to the PTMEG based elastomer, as evident by the peak of the tan δ at about -30˚C. The elastic modulus of the HYPERLAST [TM] 301 based elastomers, G', remains flat with rising temperature until 120˚C to 130˚C, similar or better than the 95 Shore A PTMEG elastomer based on HYPERLAST [TM] 101. As a result, one can expect that the service temperature for the HYPERLAST [TM] 301 based elastomers would be similar to that of PTMEG based elastomers. In addition, tan δ profiles of the elastomers based on HYPERLAST [TM] 301 match that of the PTMEG elastomer, showing low tan δ value across the service temperature window. The data implies that heat buildup in the HYPERLAST [TM] 301 systems is similar to that in the PTMEG based systems.

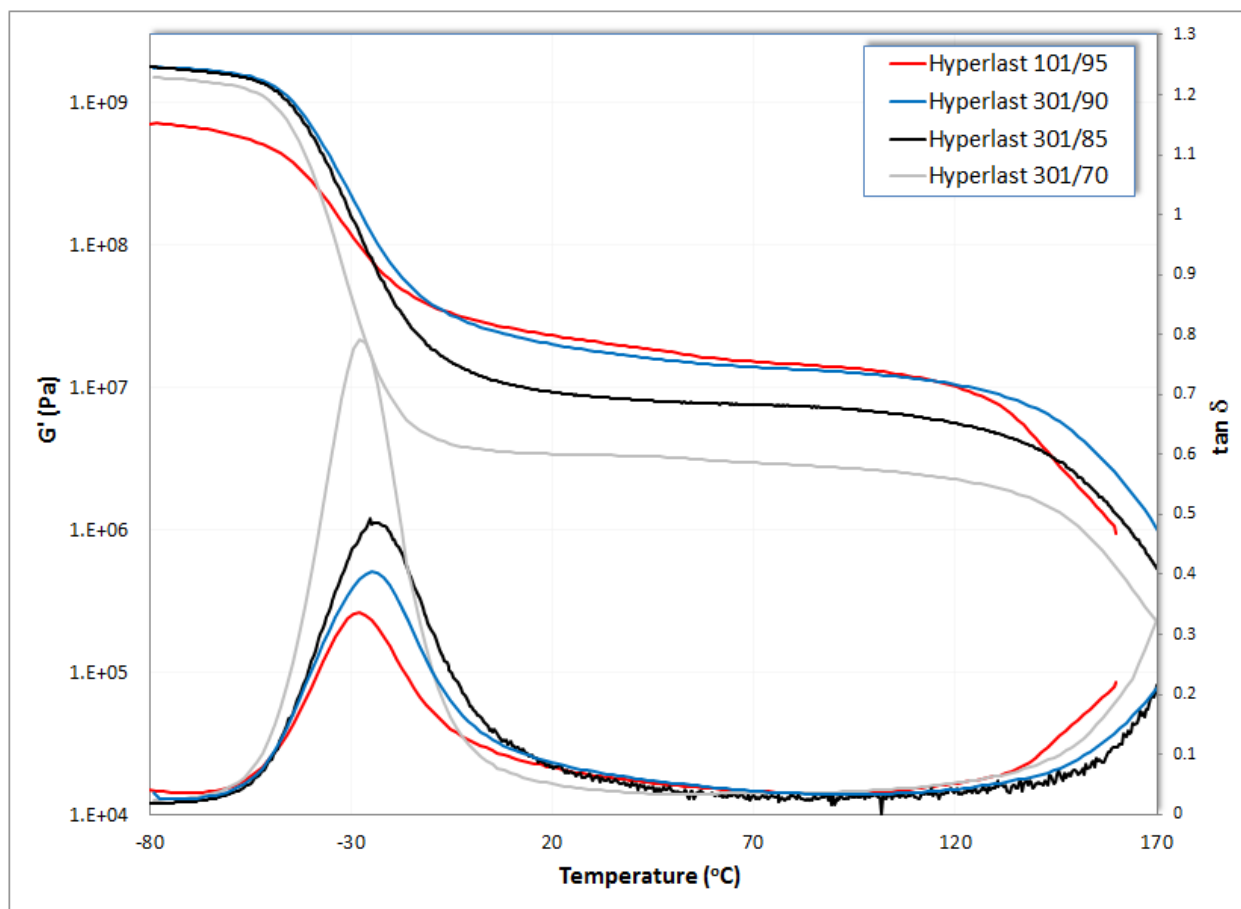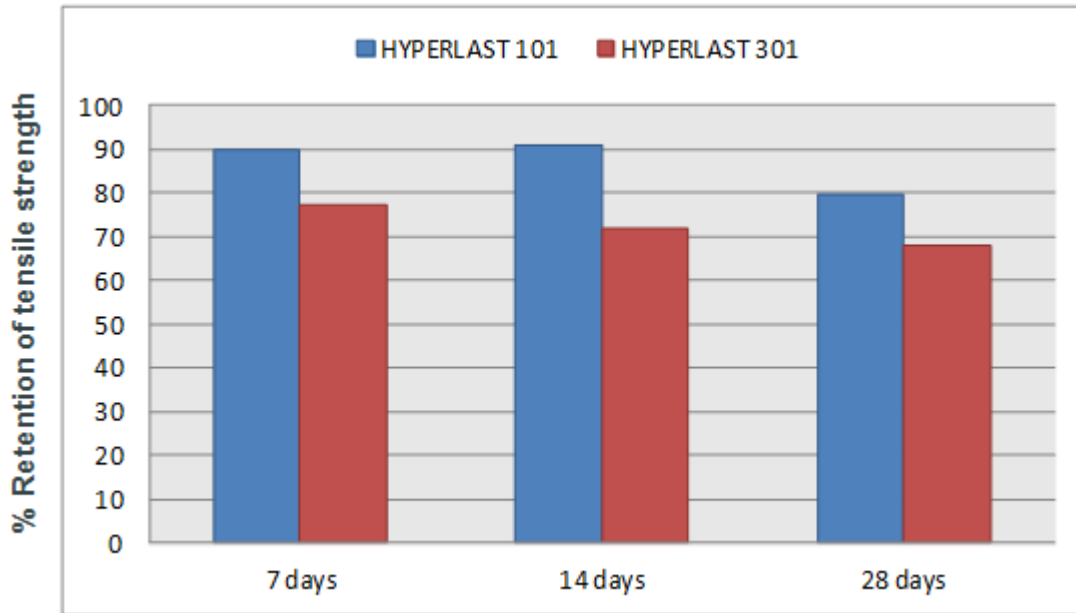™ Trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow.

Figure 1. Dynamic Mechanical Analysis (DMA) profile of HYPERLAST™ 101 at 95 shore A and HYPERLAST™ 301 at 90, 85, and 70 Shore A.
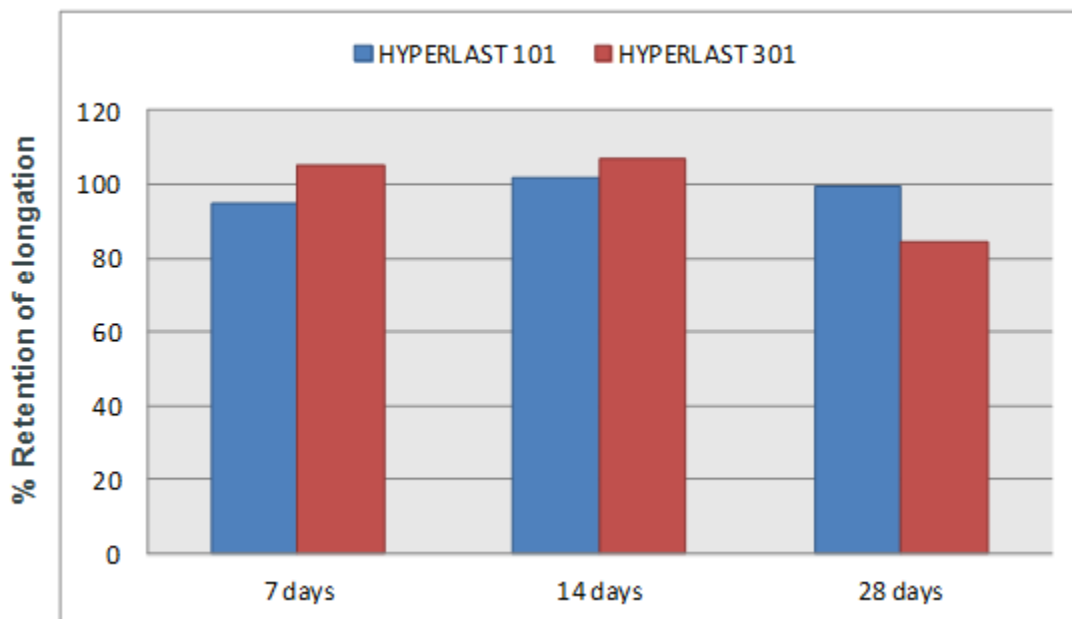

Hydrolytic Ageing

Figure 2 shows the hydrolytic stability of elastomers based on HYPERLAST™ 101 and HYPERLAST™ 301. Specimens of both elastomers were aged in water at 70⁰C for a given period of time and dried overnight before their stress-strain properties were measured. HYPERLAST™ 101 demonstrates better hydrolytic stability than HYPERLAST™ 301, as evident by retention of the tensile properties after ageing. However, the difference is not big, and it can be attributed to the lower hardness of the HYPERLAST™ 301 specimen. Hardness of the HYPERLAST™ 101 elastomer was at 95 shore A, and that of the HYPERLAST™ 301 elastomer was at 80 shore A. Properties of a softer elastomer are more prone to hydrolysis comparing to a harder elastomer based on the same backbones, as widely reported by others.[8]

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(a) Remaining Tensile Strength

(b) Remaining Elongation

Figure 2. Remaining tensile strength and elongation of HYPERLAST[TM] 301 and HYPERLAST[TM] 101 after ageing in water at 70˚C for extended period of time. Hardness of the HYPERLAST[TM] 101 elastomer was at 95 Shore A, and hardness of the HYPERLAST[TM] 301 elastomer was at 80 Shore A.

We further performed long term ageing studies. Figure 3 shows the hydrolytic stability of 90 Shore A elastomer based on HYPERLAST[TM] 301 system. Specimens of 90 Shore A elastomer were aged in water at 23, 50 and 70 °C for a given period of time before their stress-strain properties were measured. HYPERLAST[TM] 301 based 90 Shore A elastomer demonstrated a very good hydrolytic stability, as evident by retention of the tensile properties, elongation and hardness after accelerated ageing.
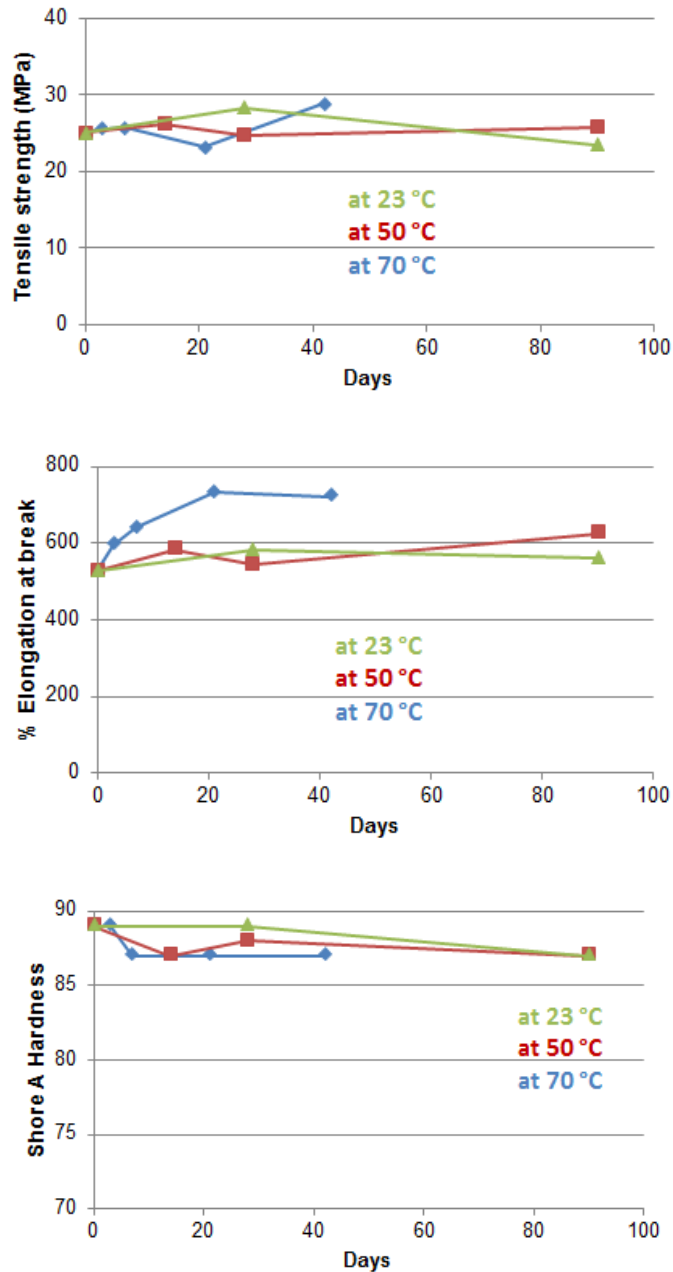
Figure 3. Dynamic Mechanical Analysis (DMA) profile of HYPERLAST [TM] 301 at 90 Shore A.

CONCLUSION

HYPERLAST™ 301 series delivers improved mechanical properties and dynamic performance compared to regular PPG based elastomers while achieving processing characteristics superior to PTMEG based elastomers. The system shows good promises to replace PTMEG in some dynamic applications at a significantly improved cost/performance ratio. HYPERLAST™ 301 system is commercial and available for sampling.

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