

# Unique viscoelastic properties of new family of thermoplastic polyurethanes

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## ABSTRACT

Huntsman has developed a new family of novel thermoplastic polyurethanes that show unique melt viscosity behavior. This behavior is derived from a new chemical approach, and allows the material to display lower viscosity than conventional thermoplastic polyurethanes at conventional melt temperatures. This work describes the detailed rheological behavior of these products. These novel products exhibit a sharp melt transition at a particular temperature. Room temperature properties of these products are not compromised by this high flow behavior. These new materials have potential for applications in many areas such as coatings, adhesives and injection molding etc. Some typical adhesive data will also be presented.

## INTRODUCTION

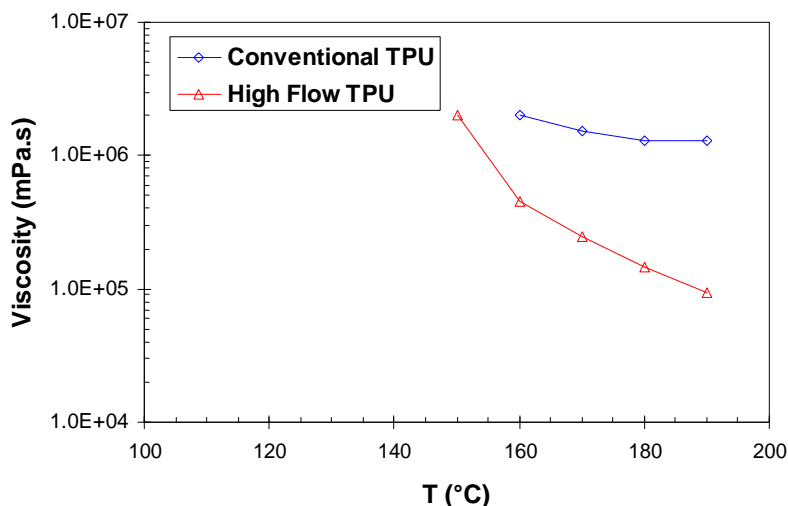
Thermoplastic polyurethanes (TPUs) are a unique group of products in the polyurethane family [1]. Unlike other polyurethane systems which are supplied as reactive liquids, TPU is typically supplied as fully-reacted granules or pellets, and then processed into the final form by conventional thermoplastic equipments such as extrusion, injection and thermoforming. Similar to most thermoplastic materials, TPU materials have linear chain structure in order to flow at elevated temperatures. Moreover, TPUs are linear block copolymers composed of both hard and soft blocks. At application temperatures, hard blocks phase separate from the soft block matrix, behaving as physical crosslinks, while hard domains can melt at processing temperatures, resulting in the thermoplastic behavior. This unique molecular structure leads to a combination of many physical properties, including high elongation and tensile strength, excellent abrasion and tear resistance, high resilience and good compression set. Therefore, TPU bridges the gap between rubbers and plastics, making it a very versatile material spanning from hard rubber to soft thermoplastic material. TPUs are utilized in a variety of applications including footwear, wire and cable sheathing, hoses, tubing, film and sheet, coatings and adhesives.

In addition, TPUs can also be processed by solvent casting for some coating and adhesive applications, which require low viscosity. However, solvent casting procedure faces more and more challenge in stricter regulation on the VOC and high energy cost upon drying. To attack this problem, Huntsman has developed a new family of novel TPUs, which show much lower viscosity than conventional TPUs at processing temperatures, as illustrated in Figure 1. On the other hand, the end use properties of these TPUs are not compromised by this unique flow behavior. Table 1 demonstrates that typical physical properties of the high flow TPU are comparable with its conventional counterpart. To further understand the thermal properties of these novel products, we investigated rheological properties for four TPU samples listed in Table 1. In this paper, some fundamentals of rheology will be first introduced. Then both heating and cooling behaviors will be presented, followed by some adhesion results.

## RHEOLOGY MEASUREMENT

The rheology study was conducted on a stress-controlled AR-2000 rheometer (TA Instruments). Dynamic testing was used to characterize rheological properties for four TPU materials, HG-conv, HG-hf, SG-conv and SG-hf, listed in Table

1. **HG** and **SG** denote hard grade and soft grade, respectively; **conv** and **hf** stand for conventional and high flow, respectively.



**Figure 1.** Viscosity as a function of temperature for a hard grade conventional TPU (HG-conv) and its high flow version (HG-hf). Viscosity was measured using a Brookfield viscometer.

*Table 1. Physical properties of conventional and high flow TPU samples.*

Samples <sup>a</sup>	HG-conv	HG-hf	SG-conv	SG-hf
Melt Index <sup>b</sup>	20	100	40	too high to read
Shore A Hardness	90	90	78	78
Tensile Strength (psi)	3000	2530	2750	2010
Ultimate Elongation (%)	640	570	800	580
100% Modulus (psi)	820	890	290	320
300% Modulus (psi)	790	960	730	690
Tear Resistance (pli)	540	560	300	262
Specific Gravity	1.15	1.15	1.15	1.15
TMA Softening Peak (°C)	102	120	75	99

<sup>a</sup> **HG** and **SG** denote hard grade and soft grade, respectively; **conv** and **hf** stand for conventional and high flow, respectively.

<sup>b</sup> Melt index was measured at 190 °C/5.0 kg for hard grade materials, and at 177 °C/2.2 kg for soft grade materials.

Under dynamic mode, sinusoidal stress with a certain frequency was applied on a specimen by a motor, while the response strain was monitored by a displacement sensor. How a material responds to a dynamic stress depends on its own viscoelasticity [2,3]. An elastic material shows a sinusoidal strain response without any phase lag compared to the applied stress curve, while a viscous material yields a strain response with 90° phase lag. For a typical viscoelastic material such as TPU, the strain response has a phase lag between 0 and 90°. This phase lag is referred to as phase angle ( $\delta$ ). The response can be resolved into two components: one is elastic component with 0 phase angle, the other is viscous component with 90° phase angle. As a result, viscoelastic properties can be characterized by three variables: storage or elastic modulus ( $G'$ ), loss or viscous modulus ( $G''$ ), and phase angle ( $\delta$ ). In general,  $\tan(\delta)$  is more commonly used due to the relationship of  $\tan(\delta) = G''/G'$ .

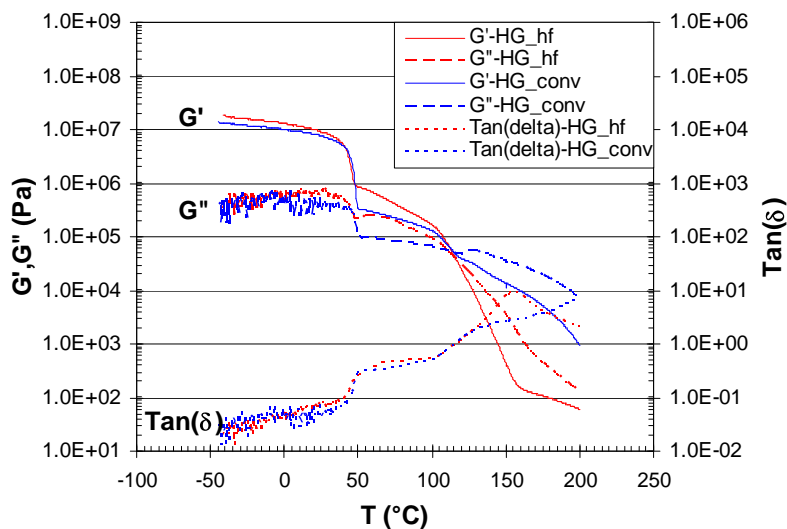
Three types of dynamic tests were carried out for these TPU samples. One is temperature ramp test, which is also called dynamic mechanical thermal analysis (DMTA). Some thermal transitions including glass transition can be detected by DMTA. Relaxation behavior was characterized using dynamic frequency sweep test at certain temperatures. Master curves over a large frequency range can be built based on time-temperature superposition [2-4]. In addition, dynamic time sweep test was used to monitor the isochronal change of modulus and phase angle at a certain temperature. Time sweep test is usually used to study kinetics of a chemical or physical process, such as curing kinetics and phase transition kinetics. All

rheological measurements were conducted with the fixture of 25 mm parallel plates. Some details will be discussed in the following section.

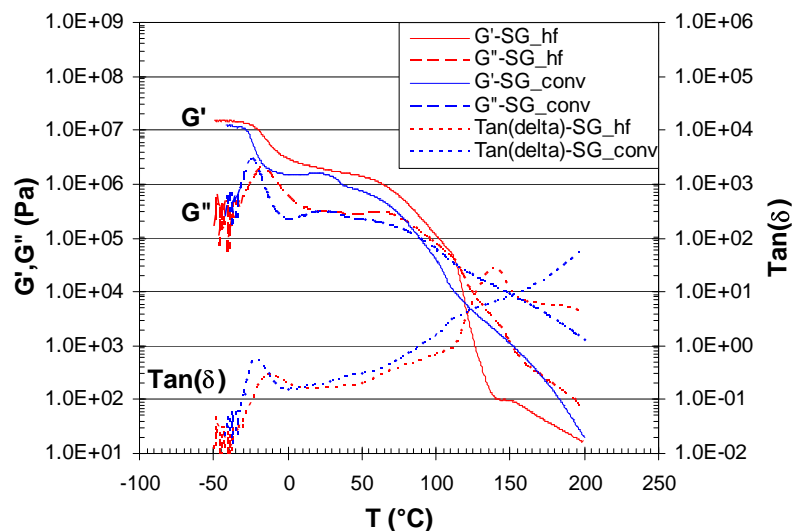
## RESULTS AND DISCUSSION

### Heating Behavior

Figure 2 compares DMTA heating curves between HG-conv and HG-hf. Both materials showed similar behavior below 100 °C. The precipitous drop in both  $G'$  and  $G''$  at 50 °C is associated with the melting of crystalline soft blocks. In contrast to the conventional TPU,  $G'$  and  $G''$  dropped much more quickly for the high flow material above 100 °C and then slowed down above 160 °C. This high temperature behavior is consistent with the viscosity data shown in Figure 1. Since samples became more liquid-like above the crossover temperature (about 115 °C) of  $G'$  and  $G''$ , the viscosity is approximately proportional to the  $G''$ . The fact that  $G''$  and viscosity showed similar temperature dependence at high temperatures results from their linear correlation above the crossover temperature. As illustrated in Figure 3, SG-hf showed similar rheological transition compared to SG-conv;  $G''$  (or viscosity) dropped to about ten times lower than SG-conv at 150 °C. Because strong intermolecular interaction is introduced via a novel chemistry for high flow TPUs, the melt transition can be attributed to the competition between molecular association and thermal energy. The molecular association is broken down at high temperatures, leading to significant modulus (or viscosity) drop. The low viscosity of high flow materials indicates a great advantage in various applications. For instance, it makes the high flow materials penetrate the substrate more quickly and easily than conventional materials for hot melt adhesive applications, thereby generating stronger bonding between substrates.

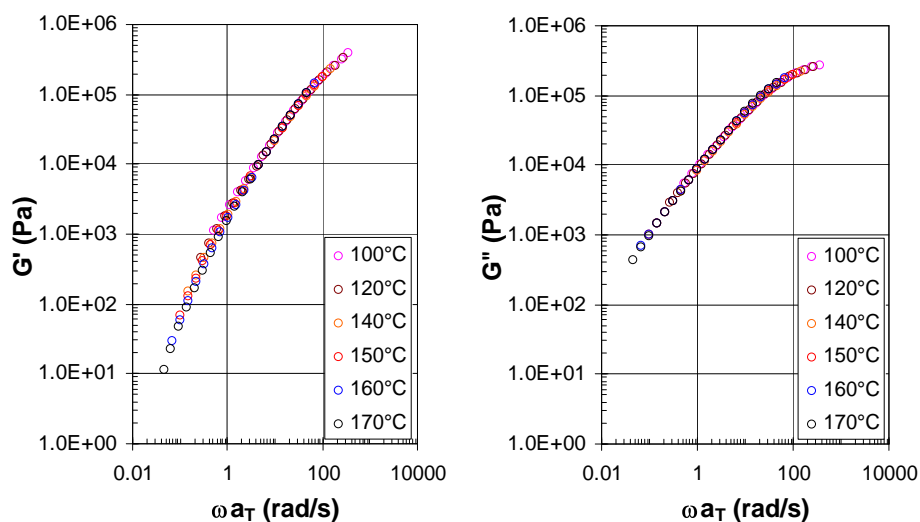


**Figure 2.** DMTA of HG-conv and HG-hf. Blue and red curves denote conventional and high flow TPUs, respectively.



**Figure 3.** DMTA of SG-conv and SG-hf. Blue and red curves denote conventional and high flow TPUs, respectively.

High flow TPUs also display interesting relaxation behavior near the transition. Figures 4 and 5 illustrates master curves of dynamic moduli versus frequency for HG-conv and HG-hf, respectively, at a reference temperature of 150 °C. Master curves were built by horizontally shifting frequency sweep data collected at various temperatures based on time-temperature equivalency [2-4]. For HG-conv, time-temperature superposition works very well such that data measured at different temperatures can overlap smoothly (Figure 4). In contrast, time-temperature equivalency breaks down for HG-hf, as illustrated in Figure 5. Although the high frequency data of  $G''$  can overlap well, both  $G'$  and  $G''$  show distinct relaxation patterns at low frequencies with increasing temperatures. In particular, the relaxation behavior transitioned rapidly from solid-like response at 130 °C to liquid-like response at 140 °C. It is this dramatic change of low frequency relaxation that results in the sharp drop in both  $G'$  and  $G''$  between 120 and 150 °C observed for HG-hf (Figure 2). SG-conv (Figure 6) and SG-hf (Figure 7) show similar relaxation behaviors to HG-conv and HG-hf, respectively. Interestingly, similar rheological phenomena were reported for polyolefin diblock and multiblock copolymers near the order-disorder transition [5,6]; the chain relaxation changes dramatically when ordered microdomains disappear for those block copolymer melts. Based on the molecular structure of high flow TPUs, their unique viscoelastic properties can be attributed to the dissociation of molecules at high temperatures, leading to the rheological transition from solid-like response to liquid-like response. Note that the melt transition temperature can be further tuned chemically for this family of TPUs based on application requirements.



**Figure 4.** Master Curves of  $G'$  and  $G''$  versus frequency for HG-conv at a reference temperature of 150 °C.

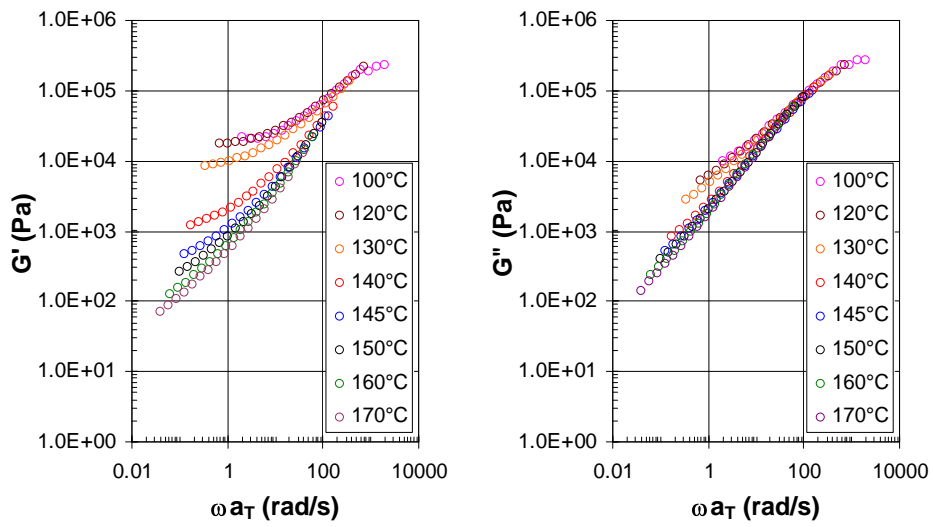


Figure 5. Master Curves of  $G'$  and  $G''$  versus frequency for HG-hf at a reference temperature of 150 °C.

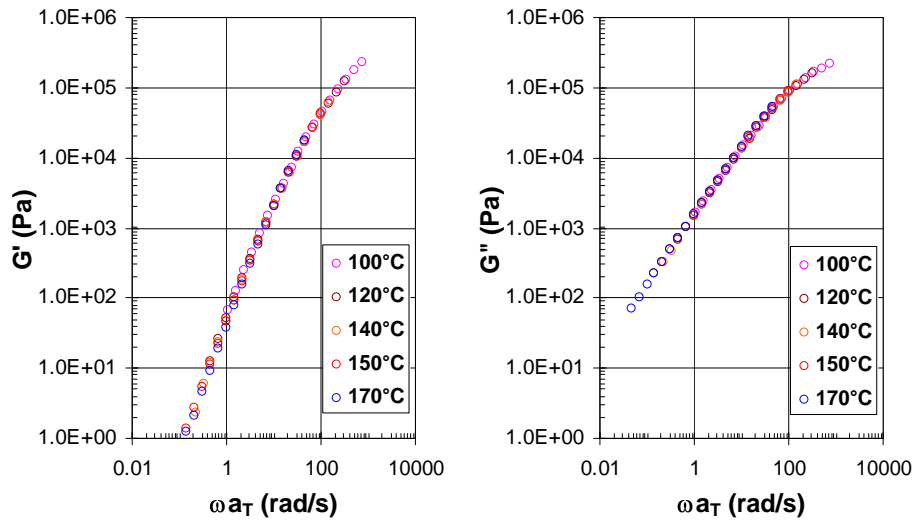
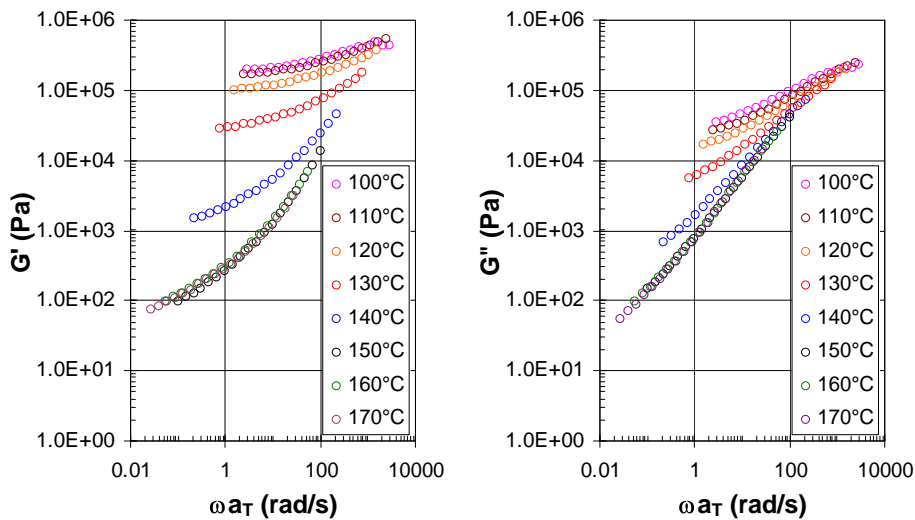


Figure 6. Master Curves of  $G'$  and  $G''$  versus frequency for SG-conv at a reference temperature of 150 °C.

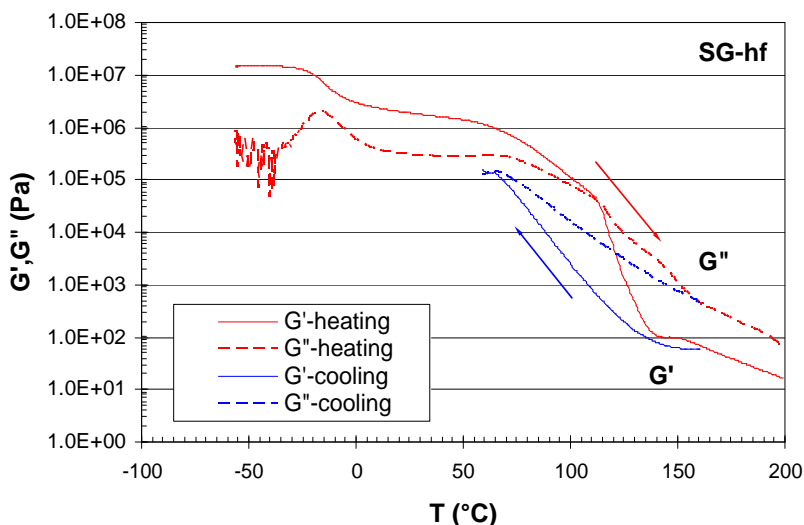


**Figure 7.** Master Curves of  $G'$  and  $G''$  versus frequency for SG-hf at a reference temperature of 150 °C.

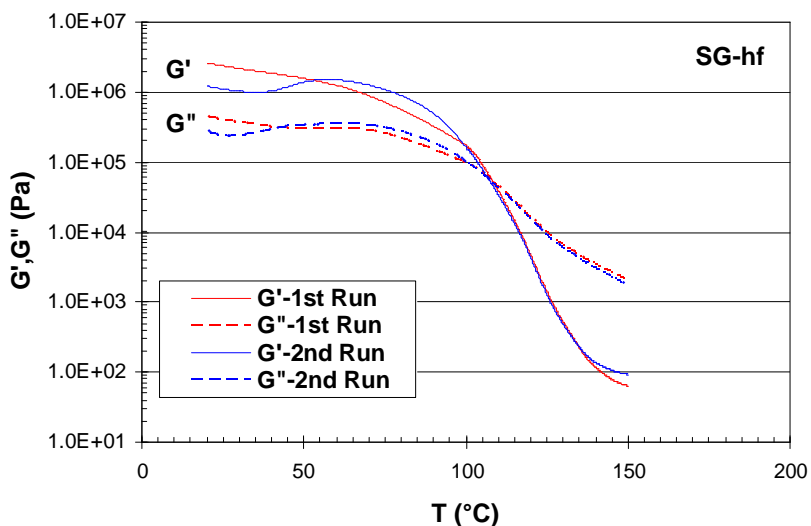
### Cooling Behavior

Figure 8 illustrates DMTA data of SG-hf upon cooling from 160 °C. The cooling curves showed a significant hysteresis compared to the heating curves. If we can use the crossover temperature of  $G'$  and  $G''$  as a demarcation between solid response and liquid response, SG-hf showed a 55 °C lag in crossover temperature upon cooling. On the other hand, cooling DMTA of conventional TPUs typically have 10 – 30 °C lag compared to heating DMTA (data not shown here). This indicates that SG-hf exhibits slow “hardening” upon cooling. To further examine this behavior, a second run of heating DMTA was carried out after the first cycle of heating and cooling. Sample was equilibrated at 20 °C for five minutes before the second run. SG-hf displayed interesting DMTA curves for the second run (Figure 9):  $G'$  and  $G''$  initially increased upon heating up to 60 °C, and then decreased with increasing temperature. As a result, both  $G'$  and  $G''$  showed maxima at 60 °C; the maxima of  $G'$  and  $G''$  are even higher than modulus data of first run at the same temperature. In addition, the sharp melt transition occurred at the same temperature region as the first run.

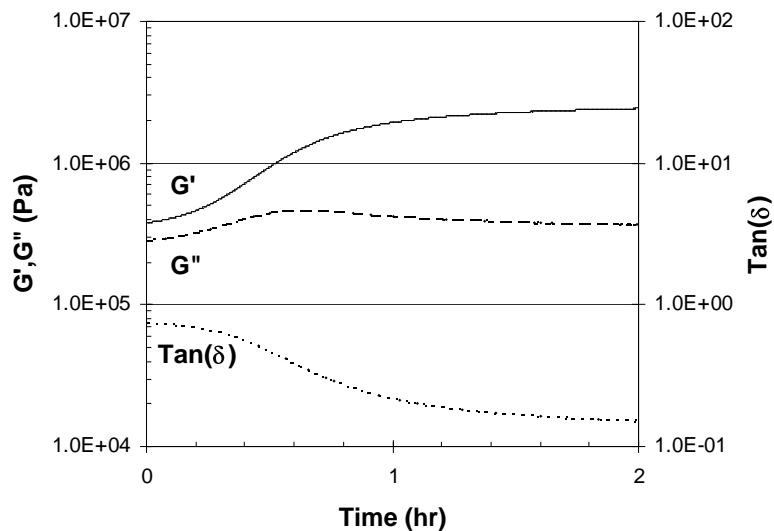
It is of interest to understand the initial modulus build-up below 60 °C for this high flow TPU. Figure 10 illustrates dynamic time sweep data at 60 °C for SG-hf upon cooling from 150 °C.  $G'$  data initially increased with annealing time and then leveled off after one hour.  $G''$  data showed a maximum at about 40 minutes.  $\tan(\delta)$  initially dropped with annealing time and then leveled off after one hour. The time evolution of rheological response can be attributed to the molecular association due to intermolecular interaction. Figure 11 further illustrates the buildup of  $G'$  at various annealing temperatures



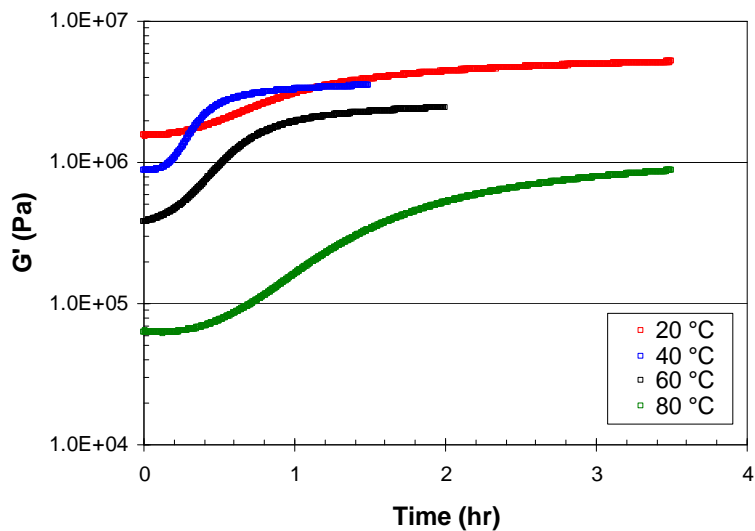
**Figure 8.** Heating (red) and cooling (blue) DMTA curves for SG-hf. Solid and dash lines denote  $G'$  and  $G''$ , respectively.



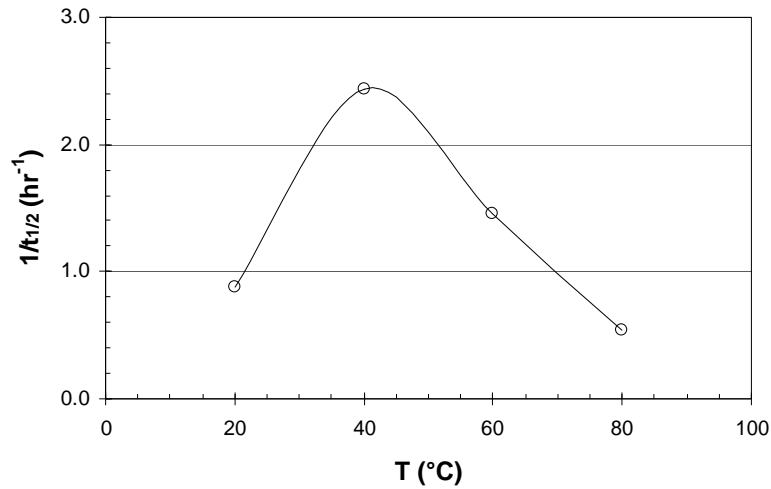
**Figure 9.** First (red) and second (blue) runs of DMTA curves for the same SG-hf sample. Solid and dash lines denote  $G'$  and  $G''$ , respectively.



**Figure 10.** Dynamic time sweep test at 60 °C for SG-hf upon cooling from 150 °C. Solid, dash and dot lines denote  $G'$ ,  $G''$  and  $Tan(\delta)$ , respectively.



**Figure 11.** Dynamic time sweeps at various annealing temperatures for SG-hf upon cooling from 150 °C.



**Figure 12.** Chain association rate versus annealing temperature for SG-hf upon cooling from 150 °C.

between 20 and 80 °C. Interestingly,  $G'$  grew more quickly at 40 °C than other temperatures, and then saturated in less than one hour. To better compare growth rate between varied temperatures, chain association rate can be defined as  $1/t_{1/2}$ , where  $t_{1/2}$  is the annealing time when

$$\frac{G'(t) - G'(0)}{G'(\infty) - G'(0)} = \frac{1}{2}. \quad (1)$$

$G'(0)$  and  $G'(\infty)$  denote initial value and steady state value of  $G'$ , respectively. Figure 12 shows the chain association rate as a function of annealing temperature. As temperature increased from 20 °C, the rate increased and reached the maximum around 40 °C. Above 40 °C, the increase of temperature reduced the chain association rate. For instance, the rate at 40 °C is about 3 times and 4 times higher than that at 20 °C and 80 °C, respectively. This temperature effect on chain association exhibits the same feature as observed in polymer crystallization [4,7]. Similarly, it can also be understood in terms of competition between thermodynamic driving force and dynamic diffusion rate at different temperatures. The driving force to form the molecular association is small at 80 °C. The driving force increases with decreasing temperature, leading to higher association rate right below 80 °C. On the other hand, the diffusion rate dominates at low temperature; molecules move and bond together very slowly at 20 °C. Chain diffusion becomes faster at elevated temperature and therefore raises the chain extension rate right above 20 °C. As a result, an optimum molecular association rate appears at a certain temperature between 20 °C and 80 °C. The strength buildup is relatively slow for SG-hf compared to its conventional equivalent. It takes up to several hours for the high flow material to achieve its optimum physical properties.

### Adhesion Evaluation

TPUs are very versatile adhesives in a wide range of applications including transportation, furniture, footwear and textile. TPU can bond to various substrates such as metal, plastics, rubber, ceramic and wood, due to their polar groups of molecular structure. Both HG-conv and SG-conv can be applied as hot melt and film adhesives. Figure 13 compares shear test results for different adhesives to bond hard wood. Both HG-conv and HG-hf show much better bonding strength than typical polyamide and polyester adhesives. In particular, HG-hf has 10% higher bonding strength than HG-conv, probably associated with better penetration of HG-hf into the substrates due to its high flow feature. In addition, both TPU adhesives can build up significant bonding strength within an hour.

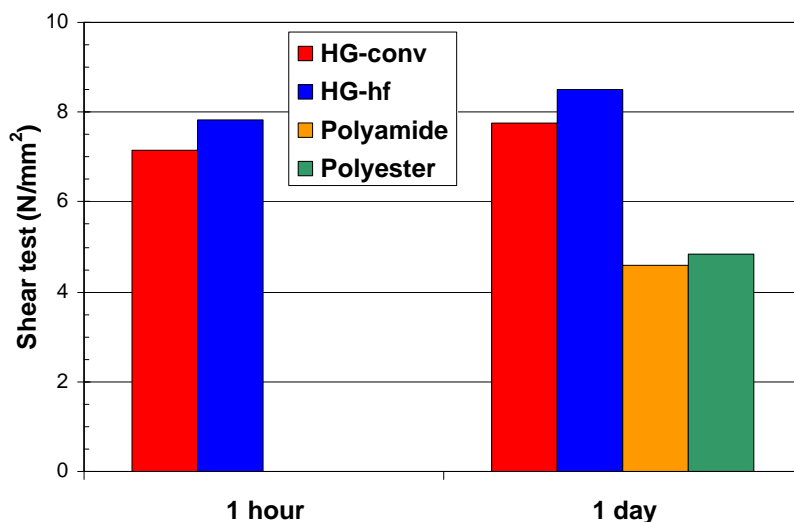


Figure 13. Shear test results for HG-conv, HG-hf, polyamide and polyester adhesives with hard wood substrate.

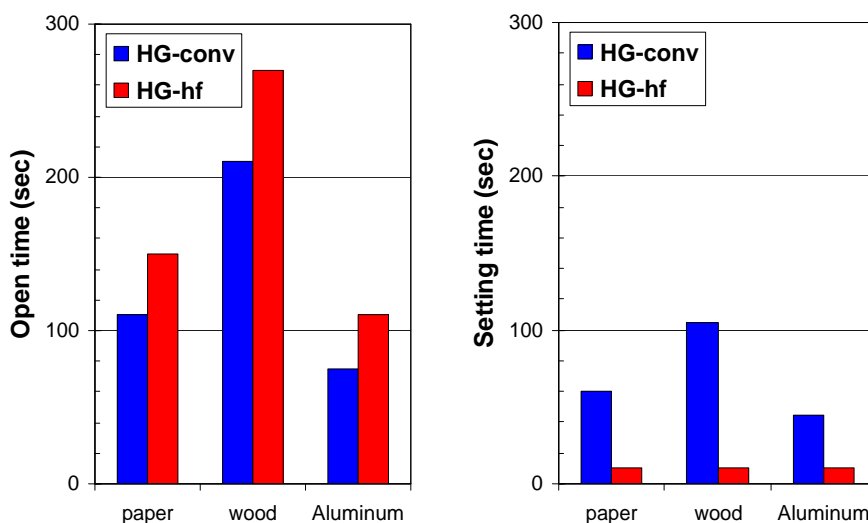


Figure 14. Open time and setting time for HG-conv and HG-hf adhesives with paper, wood and aluminum substrates.

Open time and setting times are important parameters to apply an adhesive in a production line. Figure 14 compares open time and setting time between HG-conv and HG-hf for paper, wood and aluminum substrates. For all substrates tested, the high flow material showed longer open time than its conventional equivalent. This is consistent with the slow-hardening behavior observed upon cooling. For both high flow and conventional materials, the open time is shortest for aluminum substrate and longest for wood substrate. This can be attributed to different thermal conductivity of substrates. For instance, aluminum has much higher thermal conductivity and more effective cooling of adhesive layer, and therefore leads to shorter open time than wood substrate. Interestingly, HG-hf exhibited much shorter setting time than HG-conv for all three substrates. This seems contrary to the open time results because setting time and open time usually increase or decrease together. This short setting time can be associated with fast crystallization of HG-hf upon cooling. As discussed in the previous section, there is a relatively slow molecular re-association process for the high flow material. We speculate that dissociated molecules of HG-hf can diffuse quickly and enhance crystallization rate upon cooling compared to HG-conv. This suggests a nice synergy for high flow crystalline TPUs for hot melt adhesive applications. In practice, open time and setting time can be correlated to the operating speed of production lines. The above results indicate that HG-hf has a much wider operating window than HG-conv.

## CONCLUSION

Unique viscoelastic properties were discovered for a new family of high flow TPUs developed by Huntsman. Dynamic moduli and viscosity display a precipitous drop around 150 °C during heating. Slow hardening was observed for the high flow TPU upon cooling. Both heating and cooling behaviors can be attributed to molecular association introduced via a novel chemistry. Moreover, high flow feature does not deteriorate mechanical properties. Adhesion evaluation further demonstrates stronger bonding strength of the high flow crystalline TPU and a synergy for hot melt processing. These important advantages of high flow TPUs will benefit various applications in the market.

## ACKNOWLEDGMENTS

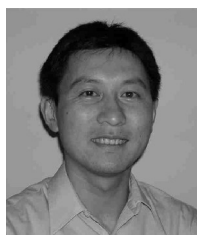
The authors would like to acknowledge the contributions to the development of these products and to the material presented here by our global team in Huntsman.

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## BIOGRAPHIES

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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.

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Steve A. Wouters is currently an experimental chemist in the Advanced Polymer Team within the Core Science Group of the Huntsman Polyurethanes Business at Everberg, Belgium. He has been working on the development and application of novel thermoplastic polyurethane-chemistries and has 7 years of experience in this field. Mr. Wouters obtained his BSc in chemistry from the Katholieke Hogeschool of Ghent, Belgium in 2000.