

# Role of Hard Segment Induced Nanosized Domain on Concentrated Solutions and Bulk Properties of Ether Based Thermoplastic Polyurethanes

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## ABSTRACT

A systematic study was conducted to investigate the effect of hard segment molecular weight on concentrated solution and bulk properties of thermoplastic ether based polyurethanes (TPUs). The molar feed was used to determine the molecular weight of the hard segment, and the weight fraction of the hard segment was then calculated as the ratio of the molecular weight of the hard segment to the number average molecular weight of the TPU determined by GPC. Similar to the study of dilution solution properties [1], it was found that rheological properties in concentration solutions, thermal properties and mechanical properties in the bulk were significantly affected at low weight fraction of the hard segment. Also, a limiting weight fraction of the hard segment was found at about 0.4 at above which the increase in weight fraction of the hard segment has a diminishing effect on the rheological properties in concentrated solution, thermal properties and dynamical mechanical properties in bulk.

**Keywords:** thermoplastic polyurethanes (TPUs), a limiting weight fraction of the hard segment, concentration solution properties, bulk properties, Han Plot.

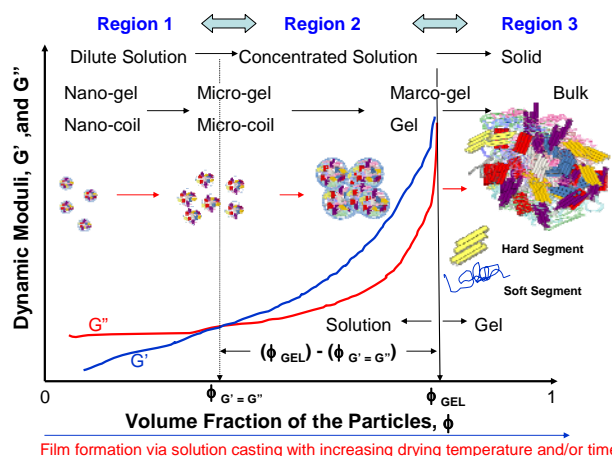
## 1. APPROACH OF THE STUDY

A roadmap of the study in Fig. 1 illustrates a bottom-up approach to the study of the effect of hard segment length (i.e., molecular weight) on properties of a polyurethane material from a very dilute solution to bulk. In Fig. 1, we have used  $\phi(G''=G')$  and  $\phi(\text{GEL})$  as boundary markers to distinguish the shape of hard segment controlled polyurethane molecules in the size range of nanogels/nanocoils, microgels/microgels, or hard and soft segmented domains in the bulk:

1. Region 1 ( $\phi < \phi(G''=G')$ ) – The domain size and the shape of polyurethane molecules are extremely small. They may exist in the form of nano-coils or nano-gel particles. The morphology and the structure of these nano-scaled polyurethane particles are determined primarily by the chemical composition and the nature of the hard and soft segments illustrated in Fig. 1. In this region, the

polymer fluid (in the form of solution, suspension, and emulsion) is often transparent because the wavelength of the scattered light is longer than the diameter of the polyurethane particles in this region. As the polymer concentration increases, the solution becomes more structural and the size of the polymer becomes bigger and approaches Region 2.

Figure 1 - A Roadmap to Study the Effect of Hard Segment



2. Region 2 ( $\phi(G''=G') < \phi(\text{GEL})$ ) – With the increasing polymer concentration and solution becoming increasing “structurally complex”, the size and shape of the polyurethane particles become larger by coalescing of several nanosized polyurethane particles. The size may be no longer in the nano-scale but is instead in the range of the micro-scale. Morphology and structure of these micro-scaled polyurethane particles are determined primarily by the size and nature of the nano-scaled particles from Region 1.

3. Region 3 ( $\phi > \phi(G''=G')$ ) – At the solid state, the shape of the polyurethane molecules now exist in hard and soft segmented domains of a two-phase morphology on the micro-scale in the bulk. The size and nature of the micro-scaled particles from Regions 1 and 2 greatly impact the structure-property of these hard and soft segmented micro-

domains in the bulk, which in term impact the end-use properties of the polyurethanes.

Previously, we reported the findings of the effects of hard segment molecular weight on properties of dilute solution of TPUs in N, N-dimethyl formamide (DMF) [1]. We found that the weight fraction of the hard segment affects the weight average molecular weight and molecular weight distribution, intrinsic viscosities, critical concentration, hydrodynamic diameter, polymer-solvent interaction parameter and second virial coefficient for low hard segment weight fractions. However these properties stabilize above 0.4 weight fraction. It is noted further that weight fraction has little impact on number average molecular weight, and the expansion parameter in Flory-Huggins analysis.

## 2. MATERIAL CHARACTERIZATION

A di-block thermoplastic polyurethane (TPU) has been synthesized in this study, following the procedure and the analysis described by Lem et al [1], the molecular weights results are given in Table 1.

Table 1: Molecular Weights of the TPUs and Weight Fraction of Hard Segment [1]

Sample Code	Molecular Weights			Total Hard Segment Mw	Weight Fraction of Hard Segment*
	M <sub>n</sub>	M <sub>w</sub>	MWD		
TPU <sub>HS1</sub>	8,400	38,600	4.60	590	0.070
TPU <sub>HS2</sub>	7,700	43,400	5.64	930	0.121
TPU <sub>HS3</sub>	7,700	54,000	7.01	1610	0.209
TPU <sub>HS4</sub>	6,600	56,400	8.55	2970	0.450
TPU <sub>HS5</sub>	7,100	54,200	7.63	5690	0.801

\* Weight Fraction of Hard Segment = Mw Hard Segment /Mn Polyurethane

Rheological properties of 50 wt% TPU in DMF solutions were studied using a cone-plate rheometer (R-21, TA Instrument) at 25 °C. For characterization of the bulk properties of TPUs, samples were obtained by casting TPU solutions in a silicone mold and drying them at 50 °C. Thermal properties were studied using a differential scanning calorimeter (DSC 910 from DuPont Instruments equipped with TA 2000). In order to control the thermal history of the samples, all the samples were heated up to 230 °C, maintained for 3 min, and then cooled down at -10 °C/min in the DSC. The samples were quenched to -120 °C to complete the crystallization of the TPUs and then reheated from -100 to 230 °C with a heating rate of 10 °C/min.

Dynamic mechanical properties were measured by a dynamic mechanical analyzer (DMA, DMA 983 equipped with TA2000). Temperature sweeps for the samples were done by employing the DMA from -100 °C to about 180 °C at 1 Hz under nitrogen gas flow. Tensile properties were

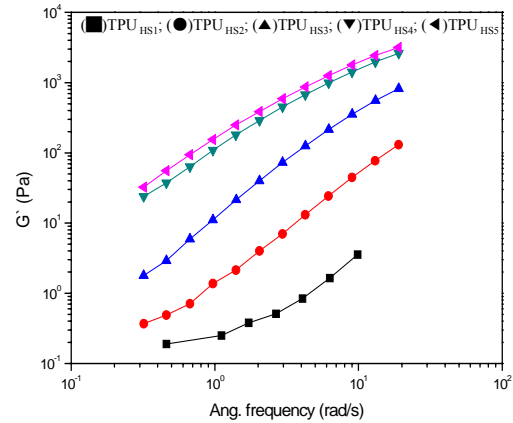
measured by using a Universal Testing Machine at room temperature with a cross head speed of 500 mm/min.

## 3. RESULTS AND DISCUSSION

### 3.1 Rheological Properties

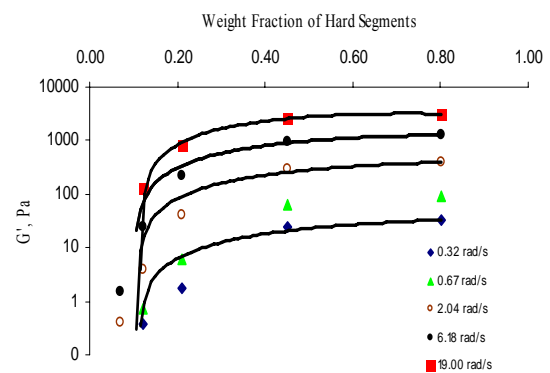
As expected,  $\log G'$ , and  $\log G''$  increase with increasing frequency ( $\omega$ ) at a fixed weight fraction of hard segment.

Figure 1 – Log  $G'$  vs Log  $\omega$  at 25 °C.



At a constant frequency,  $G'$  (and  $G''$ ) increase with increasing hard segment weight fraction. This increase is more pronounced at low weight fraction than at high weight fraction. In fact, the increase seems to peak at a constant value as seen in Fig. 2 for  $G'$  (and similar for  $G''$ ) at a weight fraction of hard segment higher than 0.4 for several frequencies.

Figure 2 – Log  $G'$  vs. Weight Fraction of Hard Segment

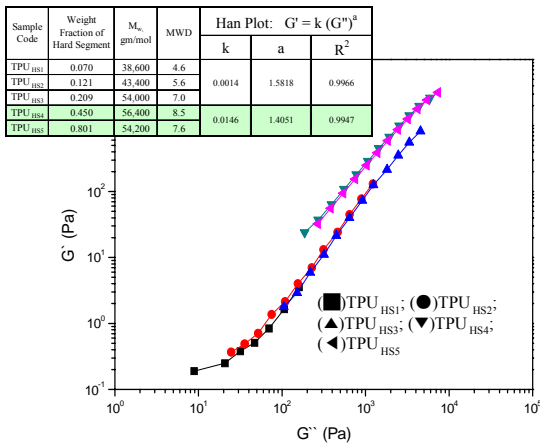


These findings suggest that when weight fraction of hard segment is above 0.4, the TPUs in 50 wt% DMF solution exhibits a very different structure compared to that for low weight fractions. This structure is induced by increasing intermolecular interactions driven by chemical composition and hydrogen bonding with increasing hard segment molecular weight. In other word, the solution is

now experiencing increased “structural” or “supramolecular ordering” due to the secondary bonding .

This finding of a “more structural” nature in the TPU solutions appears to be supported by a Han Plot [2], as seen in Fig. 3. A Han Plot is a plot of  $\log(G')$  vs.  $\log(G'')$  that showed virtually independence of temperature for a number linear and flexible homopolymers. The slope of the correlation in a Han Plot is 2 at the terminal region in the viscoelastic spectrum and it is independent of temperature and molecular weight. When the slope is smaller than 2, the fluid is becoming “more structural” and has deviated from its random coil state using a reptation model. The more structural ordering which occurs and the higher MWD, the smaller the value of the slope in a Han Plot. A more comprehensive discussion of the use of Han Plot for other polymer systems can be found in the two monographs recently published by Han [2].

Figure 3 – Han Plot (Log  $G''$  vs. Log  $G'$ ) for TPUs



### 3.2 Thermal Properties

The DSC cooling curves and the heating curves after crystallizations by cooling at 10 °C/min for TPUs are shown in Fig. 4a, and Fig. 4b, respectively [3]. In Fig. 4a,  $\Delta H_c$  is the heat of crystallization of the hard segment. It is the area under the exotherm peak. The on-set crystallization temperature is defined as  $(T_{cc})_i$ , the peak temperature is  $(T_{cc})_p$ , and the temperature where the transition concludes is  $(T_{cc})_f$ . In Fig. 4b, the on-set glass transition temperature of the soft segment is defined as  $(T_{gs})_i$ , and the off-set glass transition temperature is  $(T_{gs})_f$ . Also, the first melt endotherm peak temperature for the hard segment is defined as  $(T_{mhp})_i$  and the final endotherm peak temperature is  $(T_{mhp})_f$ . The heat of crystallization of the hard segment dramatically decreases and levels off with increasing weight fraction of hard segment as shown in Fig. 5. According to Kim and Lee [3], the decrease of  $\Delta H_c$  with increasing the hard segment length is attributable to the

decrease of MDI portion in the hard segment even though the overall composition of TPUs is fixed.

Figure 4 – DSC Thermograms of TPUs [3]

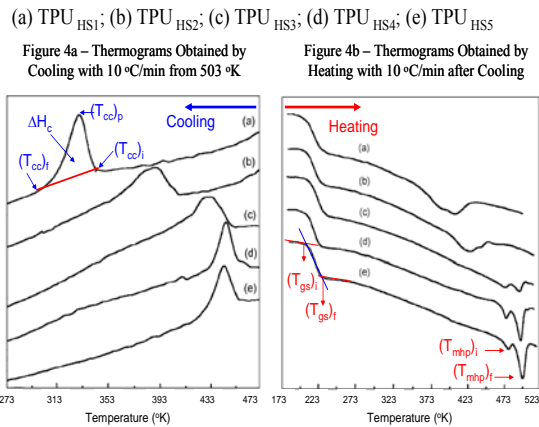
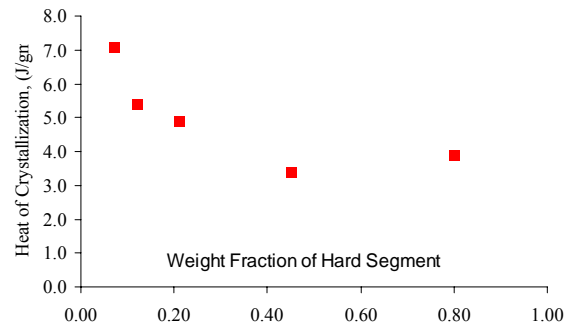
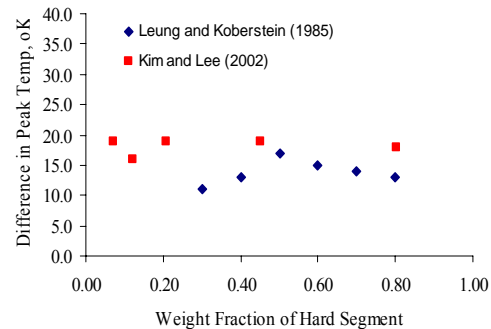


Figure 5. Heat of Crystallization of Hard Segment



There are two melting peaks in the melting temperature of the hard segment ( $T_{mh}$ ) in Figs. 4b and 6.

Figure 6: Difference in Peak Temperature

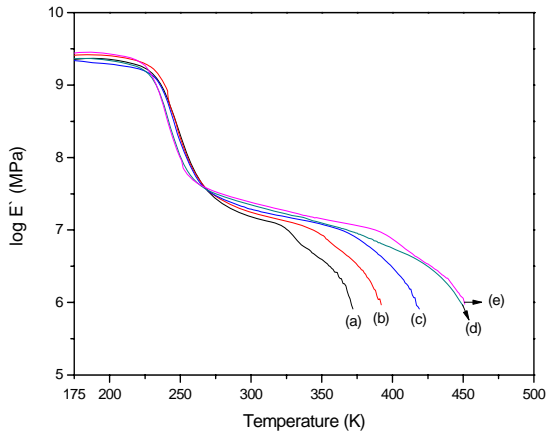


With increasing hard segment molecular weight; the resolution becomes shaper with very little overlap It is worth noting (see Fig. 6), the results obtained by Kim and Lee [3], and by Leung and Koberstein [4] are of the same order of magnitude even though the TPU systems were different in their studies.

### 3.3 Dynamic Mechanical Properties

Fig. 7 presents the changes of storage moduli and loss moduli with temperature for the TPUs investigated. The storage modulus of TPU showed a decrease of the glass-rubbery transition of soft segments around  $-30\text{ }^{\circ}\text{C}$  and another decrease after the rubbery plateau region due to melting of hard segment crystallites. We observed that the rubbery plateau modulus increased with increasing hard segment molecular weight [3].

Figure 7: Storage Modulus

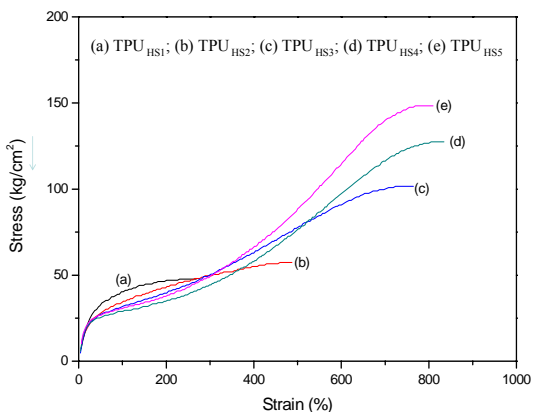


The glass transition temperatures of the soft segment ( $T_g$ s) of TPUs, using the peak value of  $E''$ , decreased slightly and became almost constant with an increase in hard segment molecular weight at about 0.4 weight fraction of hard segment. The same trend is observed with the  $T_g$ s obtained from DSC[5].

### 3.4 Mechanical Properties

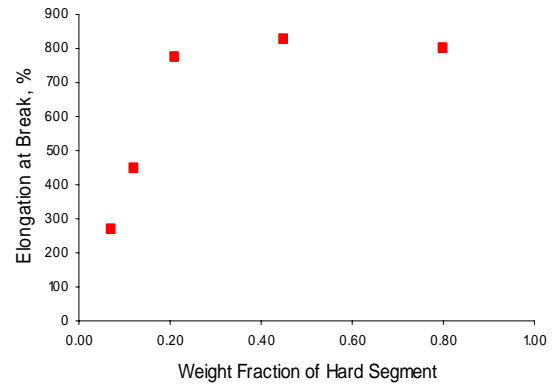
The stress and strain curves for TPUs are shown in Fig. 8 [3]. An upturn in the stress-strain curves is observed for increasing the hard segment molecular weight.

Figure 8: Stress and Strain of TPUs [3]



Very similar to the findings of other bulk properties reported so far, the elongation at breaking shows a rapid increase with the hard segment molecular weight at low fraction of hard segment molecule weight. However, at high hard segment weight fraction ( $\geq 0.4$ ) this increase appears to approach a constant as shown in Fig. 9.

Figure 9: Elongation at Breaking



### 3.5 Conclusions

The ultimate purpose for this type of study is to provide a roadmap to deliver the desired end-use performance of a thermoplastic polyurethane product based on the optimal design of the starting materials. Using a bottom-up approach, we found the limiting weight fraction of hard segment. This helps us to understand the role of the size and shape of hard segment controlled polyurethane molecules, during the formation of nano-domains in very dilute solution, micro-domains in concentrated solutions, and hard and soft segmented domains in the bulk via intermolecular interactions, on the polymer performance [5]. We will study the effect of molecular weight of soft segment on the properties of thermoplastic polyurethane in the future.

### 3.6 References

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