Effect of Hard Segment Molecular Weight on Concentrated Solution 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. Then the weight fraction of the hard segment is determined by calculating 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 dilute solution properties, it was found that thermal and mechanical properties in the bulk were significantly affected at low weight fractions of the hard segment. The critical weight fraction of the hard segment was found at about 0.4. Above critical weight fraction of hard segment there is a diminishing effect on the thermal properties and dynamical/ mechanical properties in bulk.

Keywords Thermoplastic Polyurethanes (TPUs), A Critical Weight Fraction of the Hard Segment, Bulk Properties

1. Introduction

Many useful polyurethane devices are made from liquids, via solution, dispersion, emulsion, or suspension. When a polyurethane film forms from solution, its end-use properties depend strongly on its solution properties. We have conducted a systematic study to investigate the effect of hard segment molecular weight on the properties of thermoplastic ether based polyurethanes (TPUs). The purpose of this study is to provide a roadmap to deliver the desired end-use performance of a polyurethane product based on the optimal design of the starting materials. Such a roadmap shown in Figure 1, illustrates a bottom-up approach to study the effect of hard segment length (i.e., molecular weight) on properties of a polyurethane material from a very dilute solution to bulk [1-3].

Figure 1. A Roadmap of the Study for the Effect of Hard Segment (After Lem et al., 2011) [1-3]

Table 1. Molecular Weights of the TPUs and Weight Fraction of Hard Segment Prepared by Different Polymerization Procedures [1-3]

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

* Weight Fraction of Hard Segment = Mw Hard Segment / Mn Polyurethane (GPC data)

Separately, we reported the findings of the effects of hard segment molecular weight on the properties of dilute solutions of TPUs in N, N-dimethyl formamide (DMF) in Region 1. Similar to the onset of micellization at critical micelle concentration (CMC) observed by sudden change in measured properties of solution at characteristic surfactant concentration[2], our experimental results suggest that there is a critical or limiting weight fraction (*at about 0.4*) of hard segment on measured properties. We found that the weight fraction of the hard segment strongly affects the weight average molecular weight, molecular weight distribution, intrinsic viscosities, critical concentration, hydrodynamic diameter, polymer-solvent interaction parameter and second virial coefficient. Once the weight fraction reaches approximately 0.4, the influence of the hard segment molecular weight on these properties becomes minimal. Above approximately 0.4 hard segment molecular weight has little impact on number average molecular weight or the expansion parameter in Flory-Huggins analysis, at all concentrations [1-3].

In this paper, we report the highlights of our study on the effect of hard segment molecular weight on concentrated solutions and bulk properties such as rheological, thermal, and mechanical properties in Regions 2 and 3.

2. Experimental

We have used the following procedure to prepare materials and measurement to characterize their properties in concentrated solution and in bulk.

2.1. Material Preparation

A segmented di-block thermoplastic polyurethane (TPU) has been synthesized in this study, following the procedure

and the analysis described by Kim and Lee [4] and Nguyen et al. [5]. The details of the synthesis of TPU and the sample preparation were discussed in our previous papers [1-5]. The molecular weight of the hard segment was determined from the molar feed. The weight fraction of the hard segment is the ratio of the molecular weight of the hard segment to the number average molecular weight of the TPU determined by GPC [1-5]. Table 1 summarized the polyurethane compositions used in this study .

2.2. Rheological Measurement

Rheological properties of the TPU solutions were studied employing a cone-plate rheometer (Weissenberg Rheogoniometer R-21, TA Instrument) at 25 °C. The dynamic rheological properties of the 50wt % concentration of TPU in DMF solution were performed at 25 °C. The rheological properties of the melts were characterized at 190 and 200°C by standard shearing measurement.

2.3. Thermal Properties Measurement

For characterization of the bulk properties of TPUs, samples were obtained by casting TPU solutions in a silicone mold and drying at 50 °C. Thermal properties of the TPUs were studied by 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 to 230 °C, maintained for 3 min, and then cooled down at -10 °C/min in DSC. Then the samples were quenched to -120 °C. After exotherms due to crystallization of the TPUs were completed the samples were reheated from -100 to 230 °C with a heating rate of 10 °C/min.

2.4. Dynamic Mechanical Properties Measurement

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

2.5. Mechanical Testing Measurement

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

3. Results and Discussion

The dynamic rheological properties of the concentrated solutions at 50 wt% solids were characterized at room temperature. To characterize the bulk properties of TPUs in Region 3 ($\phi \geq \phi_{\text{GEL}}$) in Figure 1, samples were prepared by casting TPU solutions in a silicone mold and drying at 50 °C. We expect differences in bulk properties of TPUs investigated will not be driven by average molecular weights alone. This is because the average molecular weights of these TPU were not dramatically different than reported earlier [1-5]. The difference is attributed primarily to the nano/micro-domain structure in TPUs induced by the hard segment.

In the bulk, the polyurethane molecules reside in hard and soft segment domains with a two-phase morphology on the micro-scale. The size and nature of the nano/micro-scaled domains with a supramolecular structure from Regions 1 and 2 significantly impacts the structure-property relationship of these hard and soft segmented domains in the bulk, which in turn affects the end-use properties of the polyurethanes. Several models have been reported in the literature to account for the hard segment induced morphological structure found in segmented thermoplastic polyurethane [6-9].

The highlights of our experimental findings on the effect of hard segment molecular weight on the rheological, thermal, dynamic, and mechanical properties are described in the following sections. Our results are in agreement those reported in the literature.

3.1. Dynamic Rheological Properties of Concentrated Solutions

Figure 2 gives a plot dynamic complex viscosity ($\log \eta^*$) vs. frequency ($\log \omega$) at different hard segment weight fractions.

Several observations can be made from Figure 2.

The dynamic complex viscosity remains insensitive to frequency at low hard segment weight fraction as seen in Figure 2. We did however, observe shear thinning behavior with increasing high hard segment.

Figure 2. Log η^* vs. log ω for different TPU solutions at 25°C
 (■)TPU HS1; (●)TPU HS2; (▲)TPU HS3; (▼)TPU HS4; (◆)TPU HS5

The dynamic complex viscosity increases with increasing hard segment weight fraction at a constant angular frequency. This behavior is primarily attributed to the morphology rather than the molecular weight since the average molecular weights of these TPUs were not significantly different as seen in Table 1.

At a very low frequency, the complex viscosity approaches to zero (simple) shear viscosity. The zero shear viscosity (extrapolated dynamic viscosity at zero angular frequency) of the TPUs in DMF solution increases with increasing weight fraction of hard segment, and then levels off at about 0.4 weight fraction of the hard segment as seen in Figure 3.

The increase in zero shear viscosity is primarily due to the increase in the domain size from nano scale to micro scale due to intermolecular interactions.

Similarly in Figures 3 and 4, the increase in the dynamic complex viscosity appears to reach a constant value at a weight fraction of hard segment higher than 0.4 for several frequencies.

Figure 3. Zero Shear Viscosity vs. Weight Fraction of Hard Segment

Figure 4. $\log \eta^*$ vs. Weight fraction of Hard Segment at 25°C

Figures 5 and 6 show a plot of storage modulus ($\log G'$), loss modulus ($\log G''$) vs. frequency ($\log \omega$), respectively, at different hard segment weight fraction.

Figure 5. $\log G'$ vs. $\log \omega$ for different TPU solutions at 25°C.

(■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◄)TPU_{HS5}

Figure 6. $\log G''$ vs. $\log \omega$ for different TPU solutions at 25°C.

(■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◄)TPU_{HS5}

Figure 7. Log G' vs. Weight Fraction of Hard Segment at 25°C.

Figure 8. Log G'' vs. Weight Fraction of Hard Segment at 25°C.

Several interesting findings are illustrated in these figures.

As expected, $\log G'$, and $\log G''$ increase with increasing frequency at a fixed weight fraction of hard segment. However, the shape of the curves for $\log G''$ vs. $\log(\omega)$ appears to be more linear than $\log G'$ vs. $\log(\omega)$, particularly at a low weight fraction of hard segment. With increasing weight fraction of the hard segment, $\log G'$ vs. $\log(\omega)$ becomes more linear.

At a constant frequency, both 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 reach a constant value for G' (Figure 7) and for G'' (Figure 8) at weight fraction of hard segment higher than 0.4 for several frequencies.

These findings suggest that when weight fraction of hard segment is above 0.4, the TPUs in 50 wt% DMF solution exhibit very different structures 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. Ultimately, the solution is now experiencing increased “structural” or “supramolecular ordering” due to the secondary bonding as depicted in Figure 1.

This finding of a “more structural” nature in the TPU solutions appears to be supported by a Han Plot [10], as shown in Figure 9 and in Table 2.

A Han Plot is a plot of $\log(G')$ vs. $\log(G'')$ that shows 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 usually 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. The more structured ordering occurs at a higher MWD, which results in a smaller value of the slope in a Han Plot [10, 12].

In recent decades, Han and his coworkers have demonstrated, both experimentally and theoretically, the usefulness of this type of plot to determine the structural state of a great number of polymeric fluids, especially for block copolymers and liquid crystalline polymers. A more comprehensive discussion of the use of Han Plots for other

polymer systems can be found in the two monographs recently published by Han [10].

We observe that the curves in Figure 9, instead of collapsing into one graph, have split into two sets and each set of curves has a different slope in the plots of $\log G'$ vs. $\log G''$.

The first set of curves, which is collapsed together as one single graph in the Han Plot, is from the data for weight fraction of hard segment from 0.07 to 0.209.

Figure 9. Han Plot ($\log G'$ vs. $\log G''$) for TPUs
 (■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◆)TPU_{HS5}

Table 2. Estimated Parameters for Han Plot by Regression in Figure 9

Sample Code	Weight Fraction of Hard Segment	M_w , gm/mol	MWD	Han Plot: $G' = k (G'')^a$		
				k	a	R^2
TPU _{HS1}	0.070	38,600	4.6	0.0014	1.5818	0.9966
TPU _{HS2}	0.121	43,400	5.6			
TPU _{HS3}	0.209	54,000	7.0			
TPU _{HS4}	0.450	56,400	8.5	0.0146	1.4051	0.9947
TPU _{HS5}	0.801	54,200	7.6			

The slope of the Han Plot is found to be 1.5818, suggesting the structure of the fluids has been ordered on a nanoscale. Similar observations were found in the study by Yoon and Han [11] where they observed that the microstructure in TPUs depends very much on the thermal history.

The second set of data, also collapsed into one curve from weight fraction 0.450 to 0.801. The slope is 1.4051, suggesting the structure of the fluid is even more ordered. Ultimately the Han Plot is sensitive in determining the effect of hard segment on the supramolecular structure in TPU solutions. Table 2 gives estimates of the parameters for the Han Plot by regression.

Our findings are in agreement of those reported by Han and Kim [12]. With more structural ordering and higher MWD, one expects smaller values of the slope in the Han Plot. Thus, as the weight fraction of the hard segment increases, the structure of TPU molecules become more and more ordered due to the hydrogen bonding from the urethane groups. Similar findings can be seen in Figure 10 for triblock and multiblock polyamide copolymers reported by Arun and Gaymans [13].

Figure 10. Han Plot for Multiblock and Triblock Polyamides (Data taken from Fig. 14 of Arun and Gaymans, 2008) [13]

Figure 11. Shear Viscosity vs. Shear Rate at 190 °C
 (■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◄)TPU_{HS5}

Note that even at 50 wt% polymer in DMF, the polyurethane polymer solutions still remain in Region 1 because the $\tan(\delta)$ is never less than one (i.e., $G'' > G'$) as seen in Figures 5, 6, and 9. Because of the formation of nano-domain supramolecular structures in higher weight fraction of hard segment at above 0.4, the polymer solutions exhibit shear thinning behavior as seen in Figure 2.

3.2. Rheological Properties of Melts

3.2.1. Melt Viscosity of the TPUs at 190 and 200 °C

Figures 11 and 12 give plots of simple shearing viscosity, ($\log \eta$) vs. shear rate ($\log \dot{\gamma}$), at different hard segment weight fraction, measured at 190 °C and 200 °C, respectively. Several effects are illustrated in Figures 11 and 12.

Unlike the dynamic viscosity of the concentrated solution and of the melts (see next section), the shear viscosity of the

melts is very sensitive to shear rate for both temperatures, except at 190 °C at 0.07 weight fraction of the hard segment. We observed that the melts exhibit higher shear thinning with increasing high hard segment and the effect is more profound at 190 °C than at 200 °C. Since the rheological behavior is affected primarily by the morphology rather than the molecular weight, we expected the temperature will play a critical role in the determination of the flow behavior of the TPUs.

Similar to the dynamic viscosity of 50 wt% TPU in solution, the rise in shear viscosity with increasing weight fraction of the hard segment at 190 °C and 200 °C. At 200 °C, the results in Figure 13 are very similar to those found in dynamic complex viscosity of 50% TPU in DMF.

Unlike the flow behavior at 200 °C, we observed different results for the TPU melts at 190 °C. The shear viscosity continues to climb after 0.4 weight fraction of the hard segment.

Figure 12. Shear Viscosity vs. Shear Rate at 190 °C
 (■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◆)TPU_{HS5}

Figure 13. Log η vs. Weight Fraction of Hard Segment at 200 °C

Figure 14. Log η vs. Weight Fraction of Hard Segment at 190°C.

Figure 15. Log η^* vs. log ω for different TPU solutions at 190°C

(■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◄)TPU_{HS5}

Figure 16. Log η^* vs. log ω for different TPU solutions at 200°C

(■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◄)TPU_{HS5}

3.2.1. Dynamic Complex Viscosity of the TPU Melts

Figures 15 and 16 give plots of dynamic complex viscosity (log η^*) vs. frequency (log ω) at different hard segment weight fraction at 190 and 200 °C, respectively.

As seen from Figures 11 and 15 at 190 °C, and Figures 12 and 16 at 200 °C, the flow behavior of the TPU melts are similar in the shear viscosity measurement and the dynamic viscosity measurement. Similar to the shear viscosity of the TPU melts, the increase in the dynamic complex viscosity

seems to reach to a constant value at a weight fraction of hard segment of 0.4 for several frequencies.

3.2.2 Han Plots of the TPU Melts

Han Plots of Log (G') vs. Log (G'') for the TPU melts at 190 °C and 200 °C are given in Figure 17. Note that the curves in Figure 17, instead of collapsing into one graph, have split into two sets and each set of curves has a different slope.

The first set of curves collapsed together as a single curve in the Han Plot for both temperatures is from the data for weight fraction of hard segment from 0.07 to 0.209. The second set of data which also collapses to one curve is from the weight fraction 0.450 and 0.801 for both temperatures. Therefore, the Han Plot is useful for determining the effect of hard segment on the supramolecular structure in TPU solutions and in the melts. Lem et al.[14-15] have found the Han Plots are extremely useful in the development of self cracking asphalts materials.

3.3. Thermal Properties

The thermal treatment approach above is used to generate similar micro-domain structure, with a controlled thermal history without any annealing [6-9; 16-18]. The DSC cooling curves and heating curves after crystallization created by cooling with 10 °C/min for TPUs are shown in Figure 18a, and Figure 18b, respectively [4, 5].

Figure 17. Han Plot ($\text{Log } G'$ vs. $\text{Log } G''$) for TPU Melts (Open Symbol = 200 °C; Closed Symbol = 190 °C)
 (■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◆)TPU_{HS5}

Figure 18a – Thermograms Obtained by Cooling with 10 °C/min from 503 °K

Figure 18b – Thermograms Obtained by Heating with 10 °C/min after Cooling

Figure 18. DSC Thermograms of TPUs (After Kim and Lee, 2002)³
 (a) TPU_{HS1}; (b) TPU_{HS2}; (c) TPU_{HS3}; (d) TPU_{HS4}; (e) TPU_{HS5}

Also, in Figure 18a, and Figure 18b, the nomenclature of the transition temperatures observed during cooling and heating of these samples was defined as follows:

In Figure 18a, ΔH_c is the heat of crystallization of the hard segment and 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 Figure 18b, 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

$(T_{mhp})_f$.

Several interesting features are apparent in Figure 18.

Cooling induced crystallization behavior of the hard segment in a thermoplastic polyurethane depends on chemical composition and nature of the hard and soft segments as seen in Figure 18a. As with the dilute solution measurement, the change of the crystallization behavior is very profound at low weight fraction of the hard segment. The increase of T_{cc} of TPU implies that the crystallization of hard segments results in a crystalline order that melts at higher temperatures. This suggests greater crystalline perfection but further study is needed to substantiate this assertion.

Figure 19. Hard Segment Crystallization Temperatures vs. Weight Fraction of Hard Segment

At high hard segment weight fraction (≥ 0.4) this change appears to approach a constant value as seen in Figure 19. However, the heat of crystallization of the hard segment dramatically decreases and levels off with increasing weight fraction of hard segment as seen in Figure 20. According to Kim and Lee [4], the decrease of ΔH_c with increasing hard segment length is attributable to the decrease of the MDI portion of the hard segment even though the overall composition of TPUs is fixed [2-5].

Figure 20. Heat of Crystallization of Hard Segment vs. Weight Fraction of Hard Segment

DSC thermograms were obtained by heating the samples after crystallization by cooling at 10 °C/min as illustrated the process in Figures 18b. The glass transition temperatures of the soft segment (T_{gs}) of TPUs in Figure 21 decreased slightly and becomes almost constant with increasing hard segment molecular weight.

Figure 21. Glass Transition Temperatures of Soft Segment vs. Weight Fraction of Hard Segment

The same trend is observed with the Tgs obtained from DMA measurement using the peak value of E'' (in Figure 25 and Table 4), even though their values are higher than those obtained by DSC. The slight decrease of Tgs is attributable to the lower degree of hard-soft segment micro domain mixing [4, 18].

There are several findings that are worth noting in the melt temperature of the hard segment (T_{mh}) in Figures 18b and Figure 22:

Figure 22. Melting Temperatures of Hard Segment vs. Weight Fraction of Hard Segment

There are two melting peaks, with increasing hard segment molecular weight; the resolution becomes sharper with very little overlap (see Figure 18b). As seen in Table 3 and Figure 23, it can be pointed out that the results obtained by Kim and Lee [4], and by Leung and Koberstein [18] are of the same order of magnitude even though the TPU systems were different in their studies.

The increase in the melting temperature of the hard segment crystallites is more dramatic at low weight fraction. The increase of T_{mh} resulted from the increase in the hard segment molecular weight. However, at about 0.2 weight fraction or greater, the melting temperature stabilizes.

According to Koberstein et al. [9, 16-21], there is a tendency in hard segments based on MDI and BD for intermediate

length sequences to crystallize preferentially. It is speculated that increasing hard segment molecular weight of TPU resulted in both extended and folded hard segment conformations which give rise to the increase in T_{mh} at lower weight fraction and then T_{mh} levels off at high weight fraction of hard segment where the intermediate length sequences are readily available.

Table 3. Melting Temperatures of Hard Segment vs. Weight Fraction of Hard Segment

Kim and Lee (2002)					Leung and Koberstein (1985)				
Sample Code	Weight Fraction of Hard Segment	(T_{mhp}) _i °K	(T_{mhp}) _f °K	Δ , °K	Sample Code	Weight Fraction of Hard Segment	(T_{mhp}) _i °K	(T_{mhp}) _f °K	Δ , °K
TPU _{HS1}	0.070	389	408	19					
TPU _{HS2}	0.121	427	443	16					
TPU _{HS3}	0.209	476	495	19					
					PU-30	0.300	437	448	11
TPU _{HS4}	0.450	477	496	19	PU-40	0.400	441	454	13
					PU-50	0.500	461	478	17
					PU-60	0.600	468	483	15
					PU-70	0.700	468	482	14
TPU _{HS5}	0.801	480	498	18	PU-80	0.800	471	484	13

Figure 23. Difference in Peak Temperature for Hard Segment Melting

Figure 24. E' vs. Temperature of TPUs (After Kim and Lee, 2002)³
 (■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◄)TPU_{HS5}

Figure 25. E'' vs. Temperature of TPUs (After Kim and Lee, 2002)³
 (■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◄)TPU_{HS5}

3.3. Dynamic Mechanical Properties

Figures 24 and 25 present 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 temperature of soft segments around -30 °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, 4].

The glass transition temperatures of the soft segment (T_{gs}) of TPUs, using the peak value of E'' in Figure 25, decreased slightly and became almost constant with an increase in hard segment molecular weight of about 0.4 weight fraction

of hard segment. The same trend is observed with the T_{gs} obtained from DSC in Table 4.

The slight decrease in T_{gs} was attributed to the lower degree of hard-soft segment micro domain mixing⁹. The peak temperatures of loss moduli, which can be considered as T_{gs} of soft segment, showed a minor decrease with increasing hard segment molecular weight. T_{gs} of TPUs are generally affected by phase mixing of soft segments and hard segments, that is, dissolution of hard segments into soft segments results in the increase of T_{gs} . The observed decrease of T_{gs} implies that the soft segment domain contains less hard segments and has a more phase separated morphology.

Table 4. Glass Transition Temperatures of Soft Segment from DSC & DMA Measurement

Weight Fraction of Hard Segment	DSC		DMA
	$(T_{gs})_i$, °K	$(T_{gs})_f$, °K	$(T_{gs})_p$, °K
0.070	205.0	228.0	240.6
0.121	205.0	227.0	240.6
0.209	207.0	230.0	241.0
0.450	205.0	224.0	234.4
0.801	204.0	223.0	231.3

Figure 26. Stress and Strain of TPUs (After Kim and Lee, 2002)³
 (■)TPU_{HS1}; (●)TPU_{HS2}; (▲)TPU_{HS3}; (▼)TPU_{HS4}; (◆)TPU_{HS5}

The increase of the rubbery plateau moduli of TPUs indicates that the higher molecular weight of the hard segments resulted in efficient physical crosslinking as indicated in Figure 24. It is of interest to note that the rubbery plateau region becomes broader with increasing hard segment molecular weight due to the increase of T_{mh} , as shown in Figure 18b and Table 4. As with our other observations there is a very strong relationship at lower weight fractions, but the effect stabilizes at approximately 0.4 weight fraction hard segment.

3.4. Mechanical Properties

The mechanical properties that have been extrapolated from the stress and strain curves for TPUs and are shown in Figure 26 and are given in Table 5.

An upturn in the stress-strain curves is observed for increasing hard segment molecular weight. During the mechanical extension testing, TPU specimens exhibited

exotherms due to crystallization since extension of elastomers frequently results in crystallization and strain hardening.

TPUs with higher weight fraction of hard segment also have a longer soft segment as seen in the segment structure of Figure 1. The longer soft segment linked by urethane enables stronger secondary bonding during extension because it favors strain induced crystallizations. It is postulated that strain induced crystallization of soft segment is responsible for the upturn in stress-strain curves with increase of the hard segment molecular weight as shown in Figure 26.

Very similar to the findings of other bulk properties reported so far, the elongation at breaking shows rapid increase with the hard segment molecular weight at low fraction of hard segment molecule weight. However, at high hard segment weight fraction (≥ 0.4) this increase appears to approach a constant as shown in Figure 27.

Table 5. Mechanical Properties of TPUs

Sample Code	Weight Fraction of Hard Segment	Molecular Weights			Mechanical Properties of TPUs					
		M_n	M_w	MWD	Young's Modulus MPa	100% Modulus MPa	200% Modulus MPa	300% Modulus MPa	Tensile stress MPa	Elongation at break (%)
TPU _{HS1}	0.070	8,400	38,600	4.6	0.13	3.95	4.59	-	4.71	268.20
TPU _{HS2}	0.121	7,700	43,400	5.6	0.13	3.39	4.24	4.86	5.46	445.20
TPU _{HS3}	0.209	7,700	54,000	7.0	0.13	3.23	4.04	5.08	10.22	773.90
TPU _{HS4}	0.450	6,600	56,400	8.5	0.15	2.83	3.43	4.34	12.42	827.70
TPU _{HS5}	0.801	7,100	54,200	7.6	0.16	3.13	3.86	5.07	16.75	797.40

Figure 27. Elongation at Breaking vs. Weight Fraction of Hard Segment

Figure 28. Breaking Tensile Strength vs. Weight Fraction of Hard Segment

Figure 29. Summary of Experimental Findings

The break strength of these TPU elastomers increases with weight fraction of hard segment as shown in Figure 28. The rate of increase was higher at low weight fraction of hard segment and it was decreased at about 0.4 weight fraction of the hard segment. With the exception of Young's modulus, the high % extension moduli decreases with weight fraction of hard segment and reaches a constant value at about 0.4 weight fraction of hard segment as shown in Table 5.

4. Concluding Remarks

The ultimate purpose of 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 to study the effect of hard segment length (i.e., molecular weight) on properties of a polyurethane material from a very dilute solution to bulk [1-5, 21], we found that the critical weight fraction of hard segment, in our study, is about 0.4 for the purposes of tuning the physical properties.

As seen in Figure 29, with exception of very few properties, most properties transition from solution to bulk and reach a constant value. This critical value may help us understand the nature and tunability of TPUs: For example;

- (1) the role of the size and shape of hard segment controlled polyurethane molecules
- (2) the formation of nano-domains in very dilute solution
- (3) the micro-domains in concentrated solutions
- (4) the hard and soft segmented domains in the bulk via intermolecular interactions
- (5) the polymer end-use performance

It is suggested that with the findings of this study, the

properties of a TPU can be tuned using the nature of molecular dynamics in mixing of the hard and soft segments in nano-size domains [1-5].

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