Role of Hard Segment Induced Nanosized Domain on Dilute Solution Properties of Ether Based Thermoplastic Polyurethanes

K. W. Lem[1a], D.S. Lee[2], J.R. Haw[1], G. S. Song[2], S. Curran[3], S. Sund[4], Z. Iqbal[5], and C. Brumlik[6]

[1] Department of Materials Chemistry and Engineering, Konkuk University, Seoul, Korea
(a) (O) 02-450-3497; (FAX) 02-444-3490; (email) kwlem@konkuk.ac.kr
[2] Department of Chemical Engineering, Chonbuk National University, Chonju 561-756, Korea
[3] Boston Scientific, MA, USA
[4] Nygard Consulting, LLC, NJ, USA
[5] Department of Chemistry and Environmental Science, New Jersey Institute of Technology, NJ, USA.
[6] Nanobiz, LLC, NJ, USA

ABSTRACT

A systematic study was conducted on the effect of hard segment molecular weight on solution and bulk properties of ether based thermoplastic 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 using a bottom-up approach [1]. We found the role of nanosized domains induced by hard segment molecular weight significantly impacts the solution, rheological and bulk properties of TPU. Also, at a limiting weight fraction of the hard segment, the increase in weight fraction of the hard segment has a diminishing effect for both solution and bulk properties. Highlights of the experimental findings in the TPU synthesis and characterization of solution properties are discussed.

Keywords: thermoplastic polyurethanes (TPUs), synthesis, Flory-Huggins , and dilute solution properties.

1. INTRODUCTION

In this paper, we report our findings on the effects of hard segment molecular weight on properties of a dilute solution of TPUs in N, N-dimethyl formamide (DMF). The molar feed was used to determine the molecular weight of the hard segment, and the weight fraction of the hard segment is then the ratio of the molecular weight of the hard segment to the number average molecular weight of the TPU determined by GPC.

We found that at low segment weight fraction there is a significant impact on the weight average molecular weight and molecular weight distribution, intrinsic viscosity, critical concentration, hydrodynamic diameter, polymer-solvent interaction parameter and second virial coefficient. However, at high weight fraction, the impact is minimal. Furthermore, weight fraction has a minimal impact on number average molecular weight, and the expansion parameter in a Flory-Huggins analysis.

2. APPROACH OF THE STUDY

Many useful components in polyurethane devices are made from solution, in the form of dispersion, emulsion, or suspension. A film is cast from solution, the volume fraction of polymer in the film increases with increasing drying temperature and/or time. The viscoelastic behavior of the polymer solution is transformed from more viscous (where $G'' > G'$) in dilution solution to more elastic (where $G' > G''$) as the volume fraction of the polymer (ϕ) increases and final solidification or gelation occurs when the film is formed [2]. We have used ϕ ($G''=G'$) and at ϕ(GEL) as a dividing point to distinguish hard segment controlled polyurethane molecules in the size of nanogels/nanocoils, microgels/microgels, or hard and soft segmented domains in the bulk in Fig.1.

Figure 1. Effect of Volume Fraction of Polymer in Solution (ϕ) on Dynamic Moduli (G', G") [2]
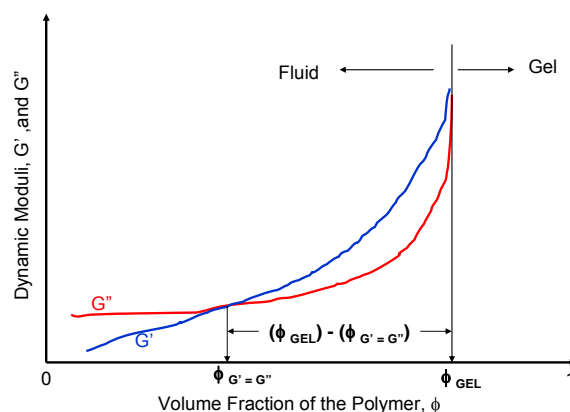
A continuing effort has been made to study the effect of size on properties of nano-structured polymers during a transition from nanoscaling to macroscaling [3]. We have conducted a systematic study to investigate the role of hard segment molecular weight induced nanosized domain on solution and bulk properties of thermoplastic ether based polyurethanes (TPUs).

3. SYNTHESIS

TPU was prepared by a solution polymerization technique in N,N-dimethylformamide. Poly(tetramethylene ether glycol) was reacted with various amounts of 4,4'-diphenylmethane at 60 °C for 90 min to prepare prepolymer with terminal NCO groups. The prepolymer was chain-extended in DMF by adding 1,4-butanediol and additional MDI at 60°C for 120 minutes. Both reactions were carried out under dry nitrogen atmosphere. For various TPUs, we have calculated the hard segment molecular weight based on the segment structure and molar feed. The molecular weight of the hard segment increases systematically by changing polymerization procedures.

4. MATERIAL CHARACTERIZATION

TPU molecular weights were measured by a GPC, gel permeation chromatoraphgy (Spectra-Physics SP8800). Intrinsic viscosities of the TPUs were determined with an Ubbelodh viscometer at 25 °C to investigate interactions between TPUs and DMF.

5. RESULTS AND DISCUSSION
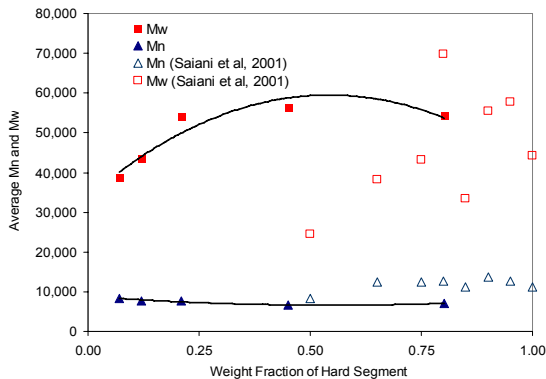
5.1 Molecular Weights

The average molecular weights of TPUs determined by GPC and the weight fraction of the hard segment in the TPU are given in Table 1, and the effect of wt% of hard segment on molecular weight is given in Fig. 2.

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

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

Figure 2. Effect of wt% Hard Segment on MW

Interestingly, the effect of increasing hard segment content has minimal influence on the number average molecular weight as also reported by Saiani et al [4], but it has a significant impact on the weight average molecular weight to a certain degree. This impact levels off at about 0.4 weight fraction of the hard segment in the TPU.

5.2 Dilute Solution Properties

We have employed the experimental methods reported by Kok and Rudin[5-7], Qian et al.[8], and Shmakov [9] to determine the parameters of the solution properties such as intrinsic viscosities, critical concentration, interaction parameters, and the size of TPU molecules in region where $\phi < \phi_{G''=G'}$.

Qian et al.[8], and Shmakov[9] have suggested that the intrinsic viscosity at θ-condition can be estimated as follows:

$$[\eta]_\theta = \frac{[\eta]\left[1 - \exp\left(-\dfrac{c}{c^*}\right)\right]}{\dfrac{0.77^3\rho}{c^*} - \exp\left(-\dfrac{c}{c^*}\right)} \qquad (1)$$

where ρ and c* are respectively the coil density and the critical concentration at which the polymer coils begin to overlap and are defined by

$$\rho = \frac{c}{\eta_{sp}}\left(1.25 + 0.5\sqrt{56.4\eta_{sp} + 6.25}\right) \qquad (2)$$

and

$$c^* = \frac{3\phi'}{4\pi N_A [\eta]} \qquad (3)$$

In Eqs (2) and (3), η_{sp} is specific viscosity, ϕ' is the Flory universal constant, which equals 3.1×10^{24} when $[\eta]$ is expressed in ml/gm, and N_A is Avogadro's number. Using the intrinsic viscosities and the number average molecular weights of TPUs determined by GPC, we can estimate osmotic pressure of the TPU solutions using the following methods suggested by Kok and Rudin [5-7] as follows

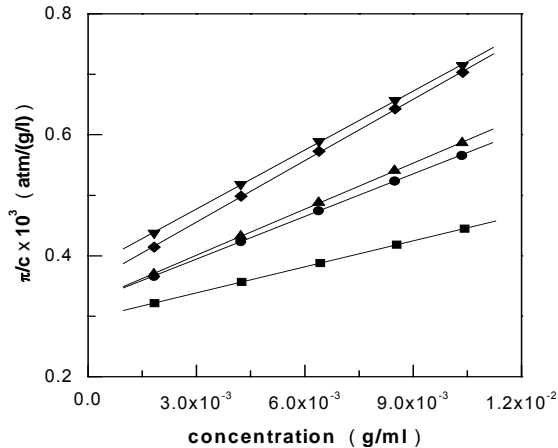$$\frac{\pi}{c} = \frac{RT}{M_n}\left(1 + A_2^* \frac{M_n c}{2}\right)^2 \qquad (4)$$

where A_2^* is given by

$$A_2^* = \frac{16\pi N_A [\eta]}{M_n\left(9.3 \times 10^{24} + 4\pi N_A c([\eta] - [\eta]_\theta)\right)}\left(1 - \frac{[\eta]_\theta}{[\eta]}\right) \qquad (5)$$

Then, we can get the second virial coefficient, A_2, from the following definition and the plots shown in Fig. 3.

$$\frac{\pi}{c} = RT\left(\frac{1}{M_n} + A_2c + A_3c^2 + \cdots\right) \quad (6)$$

Figure 3. Reduced Osmotic Pressure

The interaction parameter, χ, can be obtained finally from the following;

$$A_2 = \frac{\frac{1}{2} - \chi}{\rho_p^2 V_s} \quad (7)$$

By assuming the TPU molecules are spherical in solution, the hydrodynamic radius (R_H) was estimated using Eq. 8 by Flickinger et al [10]. and the hydrodynamic diameter is $2R_H$.
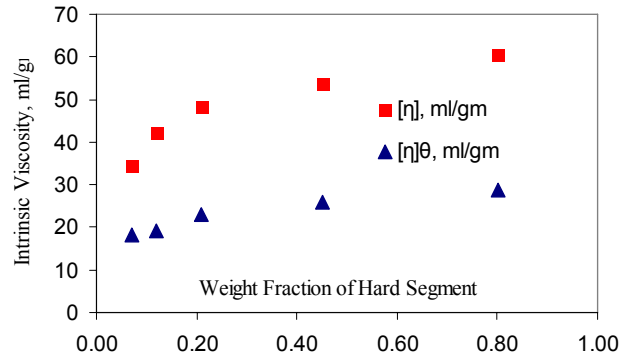
$$R_H = \left(0.3\frac{M_w[\eta]}{\pi N_A}\right)^{1/3} \quad (8)$$

5.3   Intrinsic Viscosities

Fig. 4 gives the plots of $[\eta]$ and $[\eta]_\theta$ as a function of weight fraction of hard segment. Both intrinsic viscosities increase with fraction of hard segment molecular weight. The relation of $[\eta]$ and $[\eta]_\theta$ can be further developed using the definition of intrinsic viscosity of dilute linear polyurethane solutions in a theta solvent and a non-theta solvent as expressed by Eq (9) [11].

$$\alpha = ([\eta]/[\eta]_\theta)^{1/3} \quad (9)$$

Figure 4. Intrinsic Viscosities

According to Beachell and Peterson [11], the factor α defined in Eq. 9 is the intrinsic viscosities expansion parameter, that is a direct a measured of long–range interaction due to perturbation of the polymer coil relative to the unperturbed dimensions of the thermoplastic polyurethane molecules.

5.4   Critical Concentration and Hydro-dynamic Diameter

Fig. 5 shows a plot of critical concentration, and Fig. 6 gives a plot of hydrodynamic diameter, as a function of weight fraction of hard segment, respectively. The critical concentration is defined as the concentration of polymer at which the polymer coils begin to overlap each other [8]. The critical concentration decreases with the expected increase in size of hydro-dynamic diameter. The weight fraction of the hard segment increases at low weight fraction of hard segment until it reaches a constant value at about 0.4 weight fraction of the hard segment.
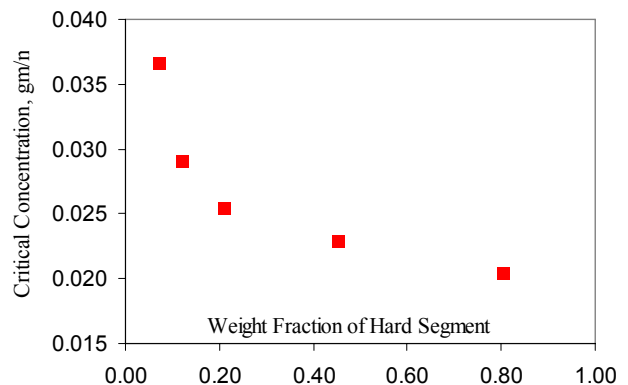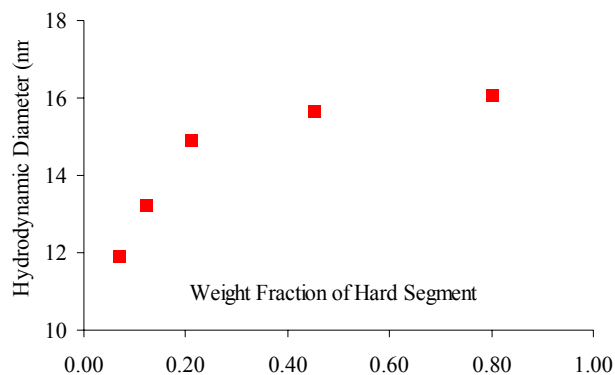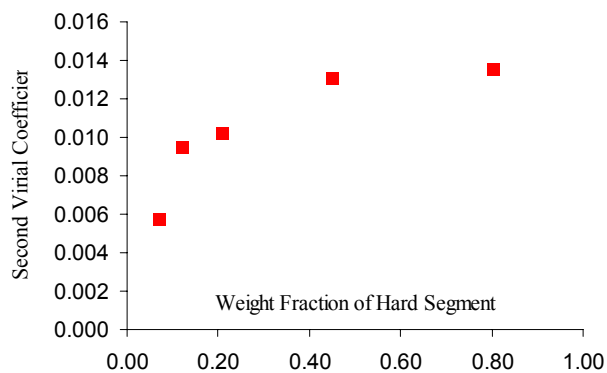
Figure 5 – Critical Concentration

Figure 6 – Hydrodynamic Diameter

5.5 Interaction Parameter and Second Virial Coefficients

The polymer-solvent interaction parameter (χ), based on the Flory-Huggins analysis, is an important parameter to characterize the stability of a polymer solution. A value of $\chi \leq 0.5$ is a general criterion for polymer solubility for infinitely dilute solutions of very high molecular weight polymers [7]. A negative χ implies ΔG_{mix} becomes more negative which in term suggests a favorable interaction. With increasing hard segment molecular weight, there are more intermolecular interactions and entanglements due to hydrogen bonding from the urethane groups. Therefore, there it is an unsurprising observation that the hard segment molecular weight impacts the value of χ more significantly than any other solution properties.

Figure 7 – Second Virial Coefficient

When the interaction parameter (χ) is large and negative, the second virial coefficient is large and positive, as in this case shown in Fig. 7. Similar to the results for critical concentration and hydrodynamic diameter, they change rapidly with increasing weight fraction of hard segment until about 0.4.

Furthermore, as illustrated in Fig. 3, the slope of osmotic pressure (π/c) vs. c is increasing and positive with increasing weight fraction of hard segment. This in turn implies that DMF is a good solvent for this TPUs system; i.e. the higher the slope, the better the solvent.

5.6 Conclusions

In this paper, we report the highlights of our study on the effects of hard segment molecular weight on the properties of a dilute solution of TPUs in N, N-dimethyl formamide (DMF). We found that the weight fraction of the hard segment more strongly affects the weight average molecular weight and 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. However, hard segment molecular weight has little impact on number average molecular weight or the expansion parameter in Flory-Huggins analysis, at all concentrations.

In subsequent papers, we will report the highlights of our study on the effects of hard segment molecular weight on concentration solution and bulk properties.

5.7 References

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