

# Effect of Degradation During Processing on the Melt Viscosity of a Thermoplastic Polyurethane

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## ABSTRACT

The rheological properties of a thermoplastic polyurethane (TPU) were studied at small and large deformation via three different types of rheometry: dynamic shear, capillary, and torque (an instrumented batch mixer). The effect of degradation during TPU processing on the melt viscosity was investigated and several factors, such as temperature, time, shear stress, and flow type that may affect the degradation were studied. A simple model is used to describe the relationship of molecular weight and thermal dissociation of urethane linkages.

## 1. INTRODUCTION

Thermoplastic polyurethanes (TPUs) are extensively used as high performance elastomers and tough thermo-plastics in a wide variety of applications requiring high impact strength, abrasion resistance, solvent and oil resistance, good adhesion, paintability, etc. TPUs are linear segmented copolymers, composed of micro-phase separated hard and soft segments. The hard segments are held together by hydrogen bonds, which form physical crosslinks. These physical crosslinks are thermally labile at melt temperatures and enable TPUs to be processed like other thermoplastics via extrusion, injection molding, etc. However, the covalent urethane bonds in the TPU backbone are also prone to dissociate at elevated temperatures.

The thermal degradation of polyurethanes in the melt state is inevitable because melting usually occurs around or beyond the stability temperature of the urethane linkages [1]. Thermal degradation mechanisms have been widely investigated and are well understood. Under 'mild' conditions (temperature below 250 °C), equilibrium is quickly established between urethane linkages and free isocyanate and hydroxyl end-groups. However, during thermal processing of TPUs, one must be careful since this equilibrium even starts at a temperature 50 °C below the stability point and several degradation mechanisms play a significant role [2-4]. The thermal degradation of TPU exerts a significant effect on rheological behavior, and thus processing conditions, and eventually material properties [5]. However, it has been reported that, during injection molding, TPU showed a sharp increase in flow, which was greater than expected due to thermal effects only [6]. To explain this

unusual processing behavior, it is important to understand and predict the rheological properties of TPU under processing conditions. Care must be taken when working with traditional rheological models that deal with temperature and molecular weight separately. Since the degree of thermal degradation is changing with temperature, molecular weight also becomes temperature-dependent.

In this work, a model TPU of 100 % hard segment content was selected to avoid any effect from soft segment degradation. Measurements were started only after the system reached steady state, i.e. only viscosities at equilibrium are our focus. The effect of thermal degradation on the melt viscosity is investigated simultaneously with the effect of temperature. Several factors, such as temperature, time, shear stress, and flow type that may affect the degradation were studied. The melt viscosity of TPU is obtained at small and large deformation via different types of rheometry: dynamic shear, capillary, and torque (an instrumented batch mixer). A simple model [7] is used to describe the relationship of molecular weight and thermal dissociation of urethane linkages, as well as the correlation of the overall activation energy of the apparent viscosity and the enthalpy change of TPU degradation reaction.

## 2. EXPERIMENTAL

The polyurethane used in this study is Isoplast 101, a commercial resin from Dow Chemicals. It is made of 4,4' - methylenebis(phenyl isocyanate) (MDI) and hexanediol. This polyurethane resembles the hard segment units of commercial polyurethanes; it will be referred to as TPU. The molecular weight was reported to be 20,000 g/mol based on size exclusion

chromatography (SEC) with a calibration of oligomeric polyurethane standards [8]. The glass transition temperature and melting point of the resin are 89 °C and 192 °C, respectively, determined by differential scanning calorimetry (DSC7, Perkins – Elmer). In order to prevent interferences by moisture adsorption, TPU pellets were dried overnight in a vacuum oven at 100 °C prior to all the measurements. This temperature is just above its glass transition temperature so that the moisture could be eliminated without promoting degradation.

Dynamic viscosity of TPU and time sweeps were obtained in a parallel plate fixture subjected to small amplitude oscillatory shear (RMS-800, Rheometric Scientific). The temperature was controlled by forced convection of nitrogen to avoid oxidative degradation. Steady shear viscosity of TPU was obtained in capillary die geometry (Visco-tester 1500, Gottfert). No corrections were applied to the data and only apparent viscosities are reported. Torque data was obtained in an instrumented batch mixer (HBI System 90, Haake) with a mixing chamber capacity of 80 cm<sup>3</sup> and roller blade rotors. By approximating the mixer blades as a pair of coaxial cylinders, viscosity values from torque readings were calculated as described elsewhere [7].

### 3. RESULTS AND DISCUSSION

Newtonian viscosities of TPU obtained from three different rheometers: dynamic mechanical analyzer (DMA), capillary, and torque instrumented batch mixer, are presented in Table 1. Temperatures at which dynamic and capillary viscosities were measured are 210, 220, 230 and 240 °C. The actual temperatures where the torques of batch mixing were recorded correspond these set temperature points: 220, 230, and 240 °C.

Table 1. Newtonian melt viscosity of TPU.

Viscosity (Pa.s)	Temperature (°C)		
	220	230	240
Dynamic	5000	1600	300
Capillary	4000	1500	350
Torque	N/A	1000	250

Viscosities were evaluated both for DMA and capillary rheometers at a constant frequency or single rate for sustained for 30 min and found to remain constant at the three working temperatures. Therefore, any degradation of molecular weight must happen during the loading and melting period and already reach equilibrium prior to the

measurements.

Good agreement between dynamic, steady and melt viscosities is observed in Table. 1. Agreement between dynamic and steady measurements is expected for homogeneous polymeric liquids [9]. This agreement also suggests that the polymer underwent the same degradation regardless of shear strain or stress imposed. For reactive extrusion of a cross-linking urethane, Charbonneau [10] reported a critical value of shear stress at which the polymerization reaction seemed to stop and possibly some bond opening reaction began to play a dominant role. He found that the value of critical shear stress depended on the type of formulation used, however, it is in the order of magnitude of 10<sup>3</sup> Pa. The shear stress levels in present viscosity measurements of TPU are about ten times the critical one reported by Charbonneau. The fact that the steady shear viscosity of TPU agrees with the dynamic data suggests that degradation is independent of the shear stress. This is important because it means most of the degradation happens during the melting step and no more mechanical degradation occurs during the shearing at the experimental conditions.

The zero shear rate viscosities ( $\eta_0$ ) obtained from DMA and capillary data [11] are listed in Table 2. The onset for shear thinning is evaluated as the intersection of the Newtonian region to the power law region, where the viscosity drops as a function of frequency or shear rate. The point where the two lines intercept is defined as the onset frequency ( $\omega_{\text{onset}}$ ).

Table 2. Rheological constants for TPU.

T (°C)	$\eta_0$ (Pa.s)	$\omega_{\text{onset}}$ (s <sup>-1</sup> )
210	42,6 x 10 <sup>4</sup>	6
220	7,20 x 10 <sup>4</sup>	37
230	1,54 x 10 <sup>4</sup>	70
240	3,55 x 10 <sup>4</sup>	160

The value of  $\omega_{\text{onset}}$  is proportional to the inverse of the relaxation time characteristic for the process [12]. This characteristic time is of the same order of magnitude as the longest relaxation time in the terminal zone. Hence, the onset of non-Newtonian behavior is related to the time required to complete configurational rearrangements of an entangled molecule. This implies that onset for shear thinning appears at smaller values of  $\omega$  with increasing molecular weight because larger molecules are more entangled and need more time to disentangle

[13]. The fact that  $\omega_{\text{onset}}$  increases with temperature for TPU (cf. Table 2) indicates that molecular weight of the TPU melt decreases at higher temperature as a consequence of degradation. Values for the rheological constants [7]  $K\eta$  and  $n$  for several temperatures are also listed in Table 2.

Normalization of the melt viscosity with respect to temperature showed that the ratio of apparent viscosity to the initial Newtonian viscosity becomes a temperature-independent function of the shear stress  $\tau$ . Furthermore, as shown by Malkin and Vinogradov [14], these scaling results in a molecular weight independent function for the viscosity as well, if molecular weight distribution is constant.

Since the urethane bond opening reactions are reversible and at equilibrium the molecular weight distribution tends to be the most probable in the polycondensation system, the molecular weight distribution of TPU should exhibit little change. This was confirmed by GPC [15]. Therefore, the dependence of viscosity on molecular weight will be similar for both thermal and flow effects, in fact, as shown by Lu and coworkers [7], contributions of flow and chemical reaction of degradation to overall activation energy are additive. The discrepancy of the Arrhenius temperature dependence from the instrumented batch mixer might be due to the extensional stresses inherent to the mixer. These stresses were higher at low temperatures, which could cause a greater reduction in molecular weight. The effect of extensional stress may become less significant with the temperature increase. An extensional rheometer may help to confirm the hypothesis of the extensional stress effect and further find out which factor is dominantly responsible for much lower flow activation energy in the instrumented batch mixer.

#### 4. CONCLUSIONS

When TPU is melted and processed, reversible molecular weight change is imminent.

One way to estimate melt viscosity considering temperature, shear rate and changes in molecular weight is to use a temperature independent master curve by plotting the ratio of the viscosity to the Newtonian viscosity vs. the product of the shear rate and the Newtonian viscosity [7]. The steady shear viscosity of TPU agrees with the dynamic one, which suggests that its behavior is insensitive to the way the shear flow is imposed and also indicates that the thermal degradation is not affected by the level of

shear stress. The flow of melt TPU can be considered an activated process, in which both flow and degradation reaction contribute to the total activation energy. This works well for simple shear flows. However, for complex flows in an instrumented batch mixer where elongational components are present, extensional stresses might facilitate the degradation and reduce the molecular weight of TPU.

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