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Explaining the abnormally high flow activation energy of thermoplastic polyurethanes

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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. Apparent activation energy of flow (E_a) was determined to be 328 kJ/mol, much larger than expected. A simple model was derived to describe the relationship of molecular weight and thermal dissociation of urethane linkages. Contributions of flow and the degradation reaction of TPU to overall activation energy were found to be additive: $E_a = E_\eta + 1.7\Delta H_{deg}$. True activation energy of flow (E_η) was estimated to be 144 kJ/mol. While the high apparent flow activation energies in dynamic shear and capillary rheometry can be explained by simple thermal degradation, melt viscosities interpreted from the instrumented batch mixer showed a much lower apparent activation energy (186 kJ/mol). This low value may be due to a combination of effects: errors in the relation between viscosity and mixer torque for TPU, side reactions resulting from air exposure, high stress level during the melting, and extensional stresses.

Keywords: Thermoplastic polyurethane; Thermal degradation; Viscosity

1. Introduction

Thermoplastic polyurethanes (TPUs) are extensively used as high performance elastomers and tough thermoplastics 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 TPU 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. This equilibrium even starts at a temperature 50 °C below the stability point and has been confirmed by Fourier-transform infrared (FT-IR) spectroscopy [2–5].

The thermal degradation of TPU exerts a significant effect on rheological behavior, and thus processing conditions, and eventually material properties. It was reported that, during injection molding, TPU showed a sharp increase in flow, which was greater than expected due to thermal effects only [4,6]. To understand this unusual processing behavior, it is important to understand and predict the rheological properties of TPU under processing conditions. However, traditional rheological models deal with temperature and molecular weight separately. Since the degree of thermal degradation is changing with temperature, molecular weight also becomes temperature dependent. Hentschel and Münstedt [7] used on-line dynamic viscosity measurement to monitor the molecular

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weight reduction of a TPU. A kinetic model was applied to fit the time and temperature dependence of the zero shear rate viscosity. They reported a true flow activation energy of 131 kJ/mol and an enthalpy change of 58 kJ/mol of the reversible urethane linkage dissociation. The enthalpy change is much lower and time to equilibrium is longer compared with the data monitored by infrared [2,3,5,8].

In this paper, 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 was derived 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. Viscosity models

The viscosity of a polymer melt depends on several variables including shear rate, molecular weight, and temperature:

$$\eta = f(\dot{\gamma}, M_w, T) \tag{1}$$

In some instances, it is possible to study the effects of one of these variables, keeping everything else constant. Shear rate can be separated as an independent variable:

$$\eta = \eta_0(M_w, T)g(\dot{\gamma}) \tag{2}$$

The dependence of viscosity on shear rate can be described by the Cross model that exhibits Newtonian viscosity at low, η_0, and high, η_∞, shear rates:

$$\frac{\eta(\dot{\gamma}) - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\dot{\gamma})^{1-n}} \tag{3}$$

where K is a constant and n is power law index. This equation can be adapted to describe the power law region [9],

$$\eta(\dot{\gamma}) \cong \frac{\eta_0}{K^{1-n}} \dot{\gamma}^{n-1} \tag{4}$$

Molecular weight is one of the most important variables affecting the viscosity of a polymer melt [10]. The following correlation is quite reliable for high molecular weight linear polymers:

$$\eta \propto M_w^{3.4} \tag{5}$$

For lower molecular weight, the dependence in molecular weight is less severe, with a power of 1 instead of 3.4, transition between this two regimes happens at a critical value of molecular weight (M_{cr}) where entanglements begin to play an important role. M_{cr} for the TPU was calculated using the group contribution method described by van Krevelen [10] to be 3670 g/mol, significantly lower than the value of the model TPU ($M_n \cong 20,000$ g/mol) used in this study.

For temperatures high above the glass transition temperature (T_g), e.g. $T > T_g + 100$ °C, the effect of the temperature can be modeled by an Arrhenius type of empirical equation as proposed by Andrade [11] and by Eyring [12]:

$$\eta(T) = A_\eta \exp\left(\frac{E_\eta}{RT}\right) \tag{6}$$

where E_η is the activation energy for flow and A_η is a constant.

However, in case of the melt viscosities measurements of TPU, flow and reversible molecular weight change occur simultaneously. Therefore, E_η cannot be measured directly and has to be estimated according to other methods, such as group contributions. Since a decrease in molecular weight caused by thermal degradation can reduce melt viscosity, molecular weight and temperature in Eq. (2) cannot be separated. The zero shear rate viscosities can be expressed as a product of the two effects:

$$\eta_0(M_w, T) \propto \exp\left(\frac{E_\eta}{RT}\right) M_w^{3.4} \tag{7}$$

3. Experimental

The polyurethane used in this work is Isoplast 101, a commercial resin from Dow Chemicals. It is made of 4,4′-methylenebis(phenyl isocyanate) 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 gel permeation chromatography (GPC) with a calibration of oligomeric polyurethane standards [8,13]. The glass transition temperature and melting point of the resin are 89 and 192 °C, respectively, determined by differential scanning calorimetry (DSC7, Perkins–Elmer; 10 °C/min). In order to prevent interferences by moisture adsorption, TPU pellets were dried overnight in a vacuum oven (~500 mTorr) 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 shear viscosity of TPU was obtained in a parallel plate fixture subjected to small amplitude oscillatory shear (RMS-800, Rheometric Scientific) at 5% strain over a frequency range of 1 to 250 rad s^{-1}. The temperature was controlled by forced convection of nitrogen to avoid oxidative degradation. The parallel plates diameter was 25 mm and the gap was set to about 1.0 mm in all the runs. 20 min was required to load, melt the pellets, and set the gap. Meanwhile, dynamic time sweep test was performed at 210 °C. The frequency was set to 0.628 rad s^{-1} and strain was controlled within the linear viscoelastic region. Data acquisitions began 2 min after sample mounting. It should be noted that the samples in the dynamic time sweep test were prepared by compression molding (Wabash, 200 °C, 0.55 MPa) to round disks (25 mm × 1 mm).

Steady shear viscosity of TPU was obtained in a capillary die geometry (Visco-tester 1500, Göttfert) with a capillary die of $L/D = 30$ and 180° entrance angle. Typically 10 min was required for loading and melting the pellets and a programmed test lasted for about 5 min. No corrections were applied to the data and only apparent viscosities were reported. The lowest test temperature was 220 °C. At lower temperatures, 210 °C for example, the pressure output was noisy and lacked reproducibility and the extrudate contained an excessive amount of bubbles [13].

Torque data was obtained in an instrumented batch mixer (HBI System 90, Haake) with a mixing chamber capacity of 80 cm^3 and roller blade rotors. 50 g of TPU was run with a rotor speed of 50 rpm at 220, 230, and 240 °C, respectively. At 220 °C, TPU was also run at 75 and 100 rpm.

In order to convert experimental data (rotor speed and torque) to the shear rate and viscosity, the following expressions were used:

$$\dot{\gamma} = \frac{0.075N}{n(1 - 0.924^{2/n})} \tag{8}$$

$$\eta = \frac{800Mn(1 - 0.924^{2/n})}{N} \tag{9}$$

where M is the torque (mgf) and N, shaft speed (rpm). Their derivations and values of the constants are given in Appendix A.

4. Results and discussion

The dynamic melt viscosity of TPU in oscillatory shear vs. frequency at four temperatures is plotted in Fig. 1. Viscosities were evaluated at a constant frequency for 30 min and found to remain unchanged. Fig. 1 also shows the apparent steady viscosity of TPU in capillary flow. Viscosity was evaluated at a single shear rate (10 s^{-1}) 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 and steady melt viscosities was observed in Fig. 1. Agreement between dynamic and steady measurements is expected for homogeneous polymeric liquids [14–16]. 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, Charbonneaux [17–19] 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 10^3 Pa. The shear stress levels in present viscosity measurements of TPU are above the critical one reported by Charbonneaux [17]. If we consider the region where dynamic and steady viscosities overlap, the range of shear stress in the capillary measurements is 10^4–10^6 Pa and for the dynamic measurements is about 10^3–10^4 Pa depending on strain level. 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.

To observe how fast the thermal dissociation of the urethane linkages can reach equilibrium, the zero shear rate viscosity is plotted as a function of residence time in Fig. 2. Small changes in molecular weight are expected to have a significant effect on viscosity through Eq. (5). The results clearly demonstrate that molecular weight reduction due to the thermal association of the urethane linkages occurs rapidly; equilibrium is established within 5 min. Shorter equilibrium time is expected at higher temperatures. The equilibrium time in this work is smaller than that reported by Hentschel and Münstedt [7]. It can be attributed to differences in the two TPU raw materials: the initial concentration of urethane linkages is much higher in our material (6.5 mol/l) than the one Hentschel and Münstedt [7] used (~2.5 mol/l), a result of the large difference in hard segment content of the materials used: 100% here vs. 34% in their work. Therefore, TPU during our rheological tests is essentially at steady state. Meanwhile, it is noticed that the Newtonian viscosity level from the dynamic time sweep test is lower than that from the dynamic frequency one. It is most likely due to a different batch of commercial raw material used in the dynamic time test from the experiments in Fig. 1. In addition, compression molding may contribute to the degradation. Hentschel and Münstedt observed 8% degradation after compression molding [7], which may account for ~25% decrease in melt viscosity.

The zero shear rate viscosities (η_0) were obtained by plotting $\log(1/\eta)$ vs. stress [20] and are listed in Table 1. The onset for shear thinning is evaluated as the intersection of the Newtonian region to the power law region, shown in Fig. 1. The point where the two lines intercept is defined as the onset frequency (ω_{onset}). The value of ω_{onset} is proportional to the inverse of the relaxation time characteristic for the process [15]. This characteristic time is of the same order of magnitude as the longest relaxation time in the terminal

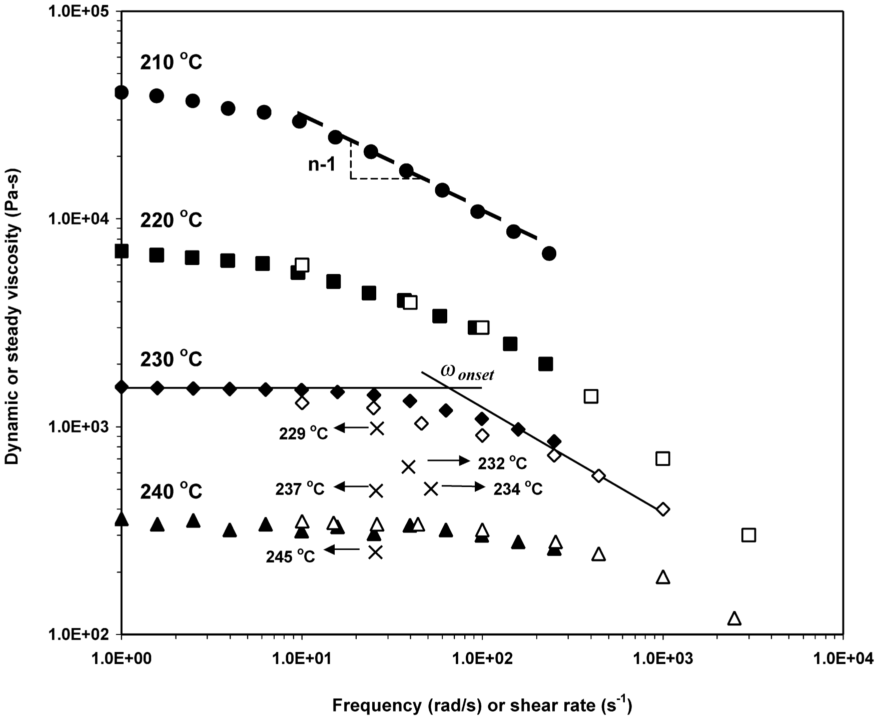

Fig. 1. Dynamic viscosity (closed symbols), steady shear viscosity from capillary (open symbols), and viscosity from the instrumented batch mixer (×) of TPU as a function of frequency or shear rate. The temperatures at which dynamic and shear viscosities were measured: 210 °C (●); 220 °C (■, □); 230 °C (◆, ◇); 240 °C (▲, △). The arrows are directing to the actual temperatures where the torques of batch mixing were recorded. The five data points of batch mixing correspond to three set temperature points (220, 230, and 240 °C) and three rotor speeds (50, 75, and 100 rpm). The intersection of two straight lines defines onset frequency, ω_{onset}.

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 ω with increasing molecular weight because larger molecules are more entangled and need more time to disentangle. Khanna [21] showed several examples of this dependence of the onset on molecular weight for polymer melts. The fact that ω_{onset} increases with temperature for TPU (cf. Table 1) indicates that molecular weight of the TPU melt decreases at higher temperature as a consequence of degradation. The shear rate dependence can be modeled with the power law model applied to an intermediate region of shear rate represented in Eq. (4) where the term η_0/K^{1-n} will be

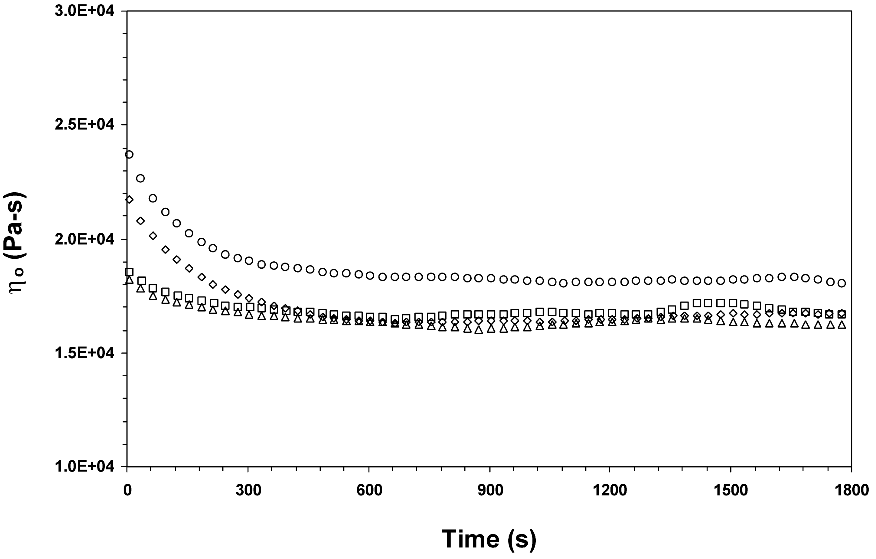

Fig. 2. Dynamic zero shear rate viscosity (η_0) of TPU as a function of residence time at 210 °C. Symbols represent four different runs to demonstrate reproducibility.

Table 1
Rheological constants for TPU from dynamic and shear rheometry

T (°C)	η_0 (Pa s)	ω_{onset} (s^{-1})	K_η (Pa s^{2-n})	n
210	42,600	6	92,316	0.54
220	7200	37	12,025	0.7
230	1540	70	2507	0.82
240	355	160	354	0.97

referred to K_η in this work. Values for the rheological constants K_η and n for several temperatures are also listed in Table 1.

Normalization of the melt viscosity with respect to temperature allows us to investigate the dependence of the viscosity on shear alone. It can be performed through normalizing the data with respect to the Newtonian value of the viscosity η_0. The ratio of apparent viscosity to the initial Newtonian viscosity becomes a temperature-independent function of the product of the shear rate by the Newtonian viscosity, i.e. function of the shear stress τ [20,22]. Furthermore, as shown by Malkin and Vinogradov [23], this scaling results in a molecular weight independent function for the viscosity as well, if molecular weight distribution is constant. Fig. 3 shows what can be considered a master curve for melt viscosity of TPU at several temperatures following Vinogradov and Malkin's approach. By plotting data in this way, viscosity dependence on both temperature and molecular weight are eliminated.

Torque and temperature vs. time in the instrumented batch mixer at three temperatures with a constant rotor speed of 50 rpm is shown in Fig. 4. The peaks observed for the torque response correspond to the melting of the pellets. The peak positions and levels of the torques depend on temperature. After the pellets melt, the temperature slowly recovers, reaching steady state after about 8 min [13]. It should be noted the actual temperatures of the TPU melt were higher than the set values due to shear heating. For example, at the set point of 220 °C, the real temperature is almost 229 °C and increased slightly with rotor speed (see Table 2). The torque rheometry results plotted in Fig. 1 show better agreement with 230 °C dynamic viscosity data.

Steady and dynamic viscosity values for a polystyrene sample (Styron 666, DOW Chemicals) obtained at 180 °C agree very well with the values of viscosity estimated from Eq. (9) in Fig. 5. The agreement confirms the validity of the models in Appendix A for typical thermoplastics. To estimate viscosity of TPU in the same way, it is necessary to obtain the instrumental constant (a) required in Eq. (A3). However, in order to obtain this constant for TPU, an instrumental calibration at several temperatures must be done. Since the molecular weight of TPU melt is temperature dependent and the instrumental constant depends strongly on the material and the run conditions [24], a proper instrumental calibrations cannot be done because it is uncertain how this constant will change with the molecular weight of the material. As an approximation, the viscosity of TPU was estimated with the instrumental constant reported for polystyrene, i.e. Eq. (9).

Fig. 6 shows Arrhenius temperature dependence of the zero shear rate viscosity and the viscosity from the instrumented batch mixer (only data at 50 rpm are included, see Table 2). The activation energies were calculated from the slopes to be 328 kJ/mol for η_0 and 186 kJ/mol for the batch mixer data. The discrepancy is discussed later. Nonetheless, the dynamic and steady shear rheometries are well-defined, 328 kJ/mol is real for the apparent flow activation energy of TPU.

The correlation between the molecular weight of TPU and the enthalpy change for the degradation process is derived in the Appendix B. Since the urethane bond opening

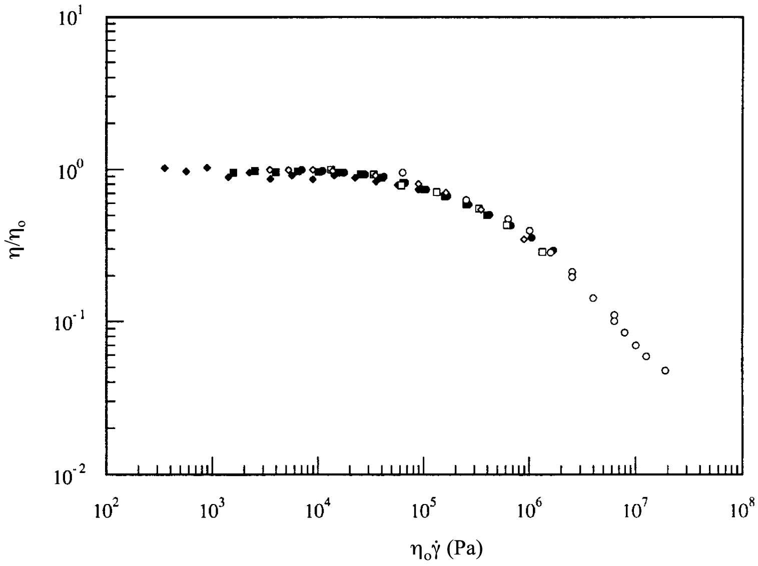

Fig. 3. Master curve for the viscosity of TPU. Open symbols represent steady viscosity data; closed symbols represent dynamic data. The temperatures at which dynamic and shear viscosities were measured: 220 °C (◆, ◇); 230 °C (■, □); 240 °C (●, ○).

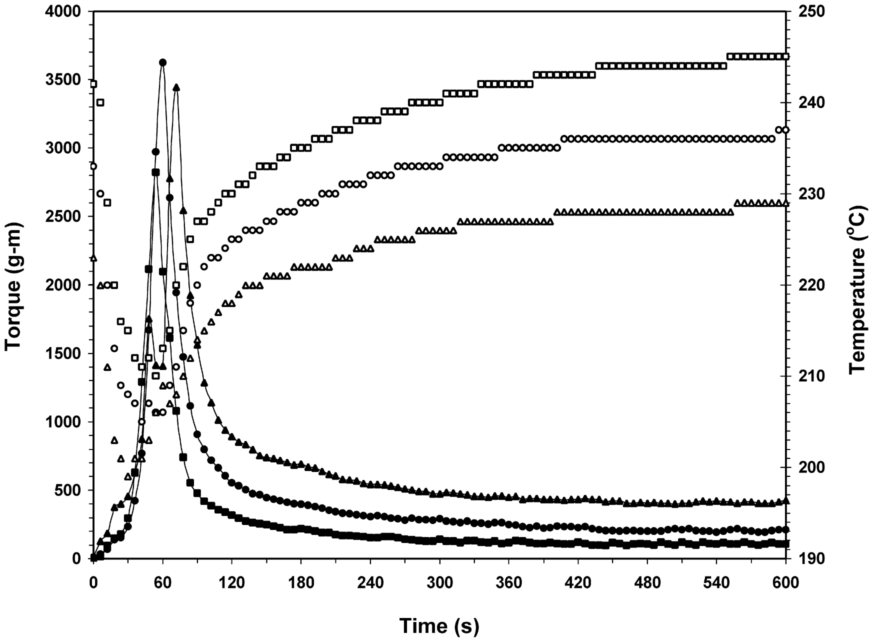

Fig. 4. Torque (closed symbols) and temperature (open symbols) data of TPU as a function of time. The set points of temperature were: 220 °C (■, □); 230 °C (●, ○); 240 °C (◆, ◇).

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 [7] and the master curve shown in Fig. 3. We can accordingly obtain:

$$\eta = K_w M_w^{3.4} \approx K_n M_n^{3.4} \tag{10}$$

where K_w and K_n are constants.

Combining Eqs. (7), (10) and (B13), we have:

$$\begin{aligned}\ln \eta_0 &= C_1 + \frac{E_\eta}{RT} + 3.4 \ln M_n \\ &= C_3 + \frac{E_\eta + 1.7\Delta H_{\text{deg}}}{RT}\end{aligned} \tag{11}$$

where C_1 and C_3 are constants.

It is clear that contributions of flow and chemical reaction of degradation to overall activation energy are additive:

$$E_a = E_\eta + 1.7\Delta H_{\text{deg}} \tag{12}$$

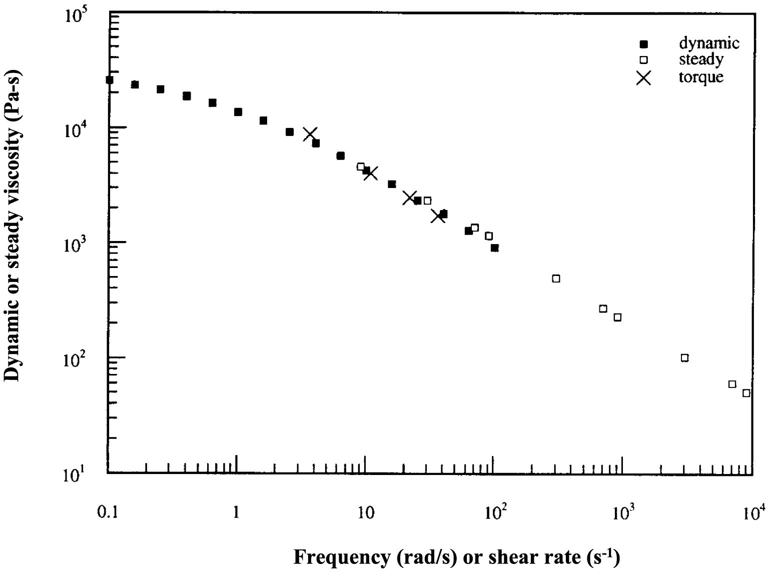

Fig. 5. Dynamic and steady viscosities of polystyrene (Styron 660) as a function of frequency or shear rate at 180 °C. Dynamic shear (■); steady shear (□); torque (×).

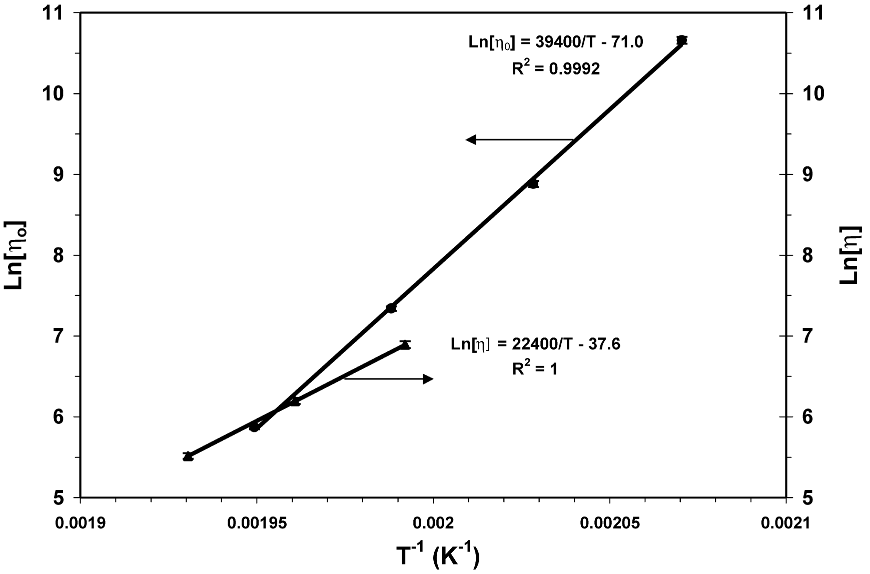

Fig. 6. Arrhenius plot of the zero shear rate viscosity (η_0, ●) and viscosity from torque rheometry (η, ▲) for TPU.

This relationship coincides with the kinetic derivation by Hentschel and Münstedt [7]. The enthalpy change for urethane linkage dissociation varies from 85 to 110 kJ/mol with different starting materials [2,3,8]. Hernandez-Hernandez and Macosko [8] reported 108 kJ/mol, based on FT-IR results, for the same material used in this work. The value of E_η for TPU is accordingly calculated to be 144 kJ/mol, which is in good agreement with that (131 kJ/mol) reported by Hentschel and Münstedt [7]. While our apparent activation energy of flow (328 kJ/mol determined from η_0) is much higher than their result (233 kJ/mol), they reported much lower enthalpy change of thermal degradation (58 kJ/mol). It can also be attributed to differences in the two TPU raw materials as discussed above.

Fig. 6 also compares the Arrhenius dependence of the melt viscosity for TPU as measured by dynamic/steady and by torque rheometry. One would expect that for the flow of molten TPU, E_a be the same regardless of the deformation imposed. However, in the case of torque rheometry, E_a is only 186 kJ/mol. This significant discrepancy may be explained in terms of several effects: (1) errors in the viscosity model for TPU; (2) mechanical degradation due to higher stress in the batch mixer; (3) the differences between the two deformation modes: the instrumented batch mixer vs. steady or dynamic shear.

The first factor is already discussed above and in Appendix A. It indicates the approximation that the viscosity of TPU was estimated with the instrumental constant reported for polystyrene may not be valid.

The stresses in the batch mixer are only 10^3–10^4 Pa at equilibrium and in the order of 10^5 Pa at peak torque. Whereas, the local stress exerted on a single chain during the melting can be much higher, causing the mechanical degradation. If a chain is dissociated at the urethane linkages, it can still be recovered. Otherwise, the molecular weight will be permanently reduced. Since the polystyrene shows a good agreement between the viscosities from torque rheometry and from dynamic/steady shear rheometry (cf. Fig. 5), the effect of stress causing mechanical degradation cannot be a significant one.

More importantly, this viscosity model is based on the assumption that mixer may be considered as two adjacent coaxial cylinder viscometers [25], where only the shear flow was considered. However, in the batch mixer there is extensional flow that is absent from dynamic or steady measurements. The authors hypothesize that this extensional component in the complex flow may help to further reduce the molecular weight during measurements. It may be argued that there also is a fraction of extensional flow in the capillary rheometry. However, the extensional effect only exists at the central part of die entrance and equilibrium may be restored in the following, relatively, long residence time.

Table 2
Rheological data for TPU from torque rheometry

T_{set} (°C)	T_{equil} (°C)	Torque at equil. (g m)	Stress by Eq. (A5) (Pa)	Rotor speed (rpm)	$\dot{\gamma}$ by Eq. (8) (s^{-1})	η by Eq. (9) (Pa s)
220	229	428	25,680	50	26.1	984
220	232	417	25,020	75	39.0	642
220	234	433	25,980	100	51.8	502
230	237	211	12,660	50	25.8	491
240	245	106	6360	50	25.6	249

Experimental evidences that support the idea that extensional flow may contribute to further degradation were reported by Moses and co-workers [4,6] on degradation of TPU in injection molded parts. They found a strong reduction in the molecular weight across the thickness of a molded TPU part: molecular weight of samples taken at the surface of the part was about 10 times lower than the molecular weight of samples taken at the center of the part. For practical purposes, we can assume that the degradation of the TPU near the surface was almost instantly stopped with these fast cooling rates, while molecules at the center recombined at relative high temperatures. However, the 10 times discrepancy between the molecular weights at the center of the part and at the surface, seems to be too large for the temperature effect only and contradicts the examinations by GPC [7]. It is known that, during the mold-filling step in injection molding, the advancing front presents a fountain effect that is extensional in nature [26]. The melt is then subjected to a strong elongational deformation from the center of the mold towards the wall. Therefore, the low molecular weight at the surface of the part may be due to the combined action of temperature and extensional flow on the TPU melt during the mold filling.

In our case, the extensional stresses in the instrumented batch mixer 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. According to the slope (apparent activation energy) in the Arrhenius plot of viscosity vs. T^{-1} (Fig. 6) was less steep than the one calculated from dynamic or steady shear rheometry. An extensional rheometer may help to confirm the hypothesis of extensional stress effect and further find out which factor is dominantly responsible for much lower flow activation energy in the instrumented batch mixer.

5. 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 (cf. Fig. 3). The molecular weight reduction due to the thermal association of the urethane linkages occurs rapidly and equilibrium is established within 5 min. 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 for the process as: $E_a = E_\eta + 1.7\Delta H_{\text{deg}}$. 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.

Acknowledgements

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Appendix A. Rheology data from the instrumented batch mixer

By approximating the mixer blades as a pair of coaxial cylinders, viscosity values from torque readings may be calculated with the conversion equations for the shear stress τ and shear rate $\dot{\gamma}$ as function of torque and shaft speed as described by Lee and Purdon [24]:

$$9.8\times 10^3 M = R_e\tau\text{Area} = 2\pi R_e^2 L(1+2/3)\tau \tag{A1}$$

$$\tau = \frac{935.8M}{R_e^2 L}\ (\text{Pa}) \tag{A2}$$

$$\dot{\gamma} = \frac{2\times 2\pi N}{n[1-(R_e/R_c)^{2/n}]}\left[\frac{\frac{1}{2}\left(1+\frac{2}{3}\right)a}{60}\right]$$

$$= \frac{0.1745aN}{n[1-(R_e/R_c)^{2/n}]}\ (\text{s}^{-1}) \tag{A3}$$

where M is the torque (m gf), τ, the average shear stress (Pa), R_e, the equivalent radius (cm), L, the equivalent length of the adjacent coaxial cylinders (cm), $\dot{\gamma}$, the shear rate (s^{-1}), N, the shaft speed (rpm), R_c, the radius of the two rotor compartments (cm), n, the power law index, and a is the instrumental constant.

The real situation is more complicated. For example, while the average shear rate at 50 rpm is accordingly calculated to be approximately 26 s^{-1} at 220–240 °C, the maximum shear rate ($\dot{\gamma}_{\max}$) in the chamber of the batch mixer can be estimated as [27]:

$$\dot{\gamma}_{\text{chamber}}(x,\theta) = \frac{\pi DN}{H(x,\theta)} \Rightarrow \dot{\gamma}_{\max} = 47\ \text{s}^{-1} \tag{A4}$$

where $D = 2R_e$, is the diameter of rotor blade and $H(x,\theta) =$ clearance between rotor blade and chamber wall. Moreover, the shear rate is about zero near the mid point between the two rotor blades.

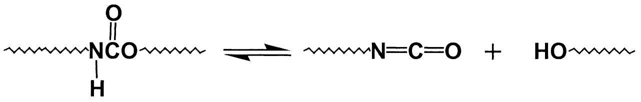
To obtain the total shear stress, the area of the imaginary cylinders is calculated from the blade dimensions as taken from the torque rheometer manual: radius = 1.825 cm, length = 4.73 cm. The R_e value used to calculate the area was considered to be equivalent to that of the maximum radius of the blades. As pointed out by Lee and Purdon [24], this approximation has negligible effect on the final result. With the area of the cylinders, Eq. (A2) becomes:

$$\tau = 60M \ \ (\mathrm{Pa}) \tag{A5}$$

The conversion equation for the shear rate (Eq. (A3)) was evaluated at $N = 50$ rpm and with the instrumental constant of polystyrene ($a = 0.43$) that was reported by Lee and Purdon [24]. Combining Eqs. (A3) and (A5), the values of viscosity as the ratio of shear stress to shear rate can be easily estimated.

Appendix B. Correlation of TPU molecular weight and temperature

The urethane bond opening reaction follows first order kinetics:



$$\sim\!\sim\mathrm{N(H)C(=O)O}\sim\!\sim \rightleftharpoons \sim\!\sim\mathrm{N{=}C{=}O} + \mathrm{HO}\sim\!\sim \tag{B1}$$

If the molecular weight for the repeating unit in a TPU is m_0 (368 g/mol for Isoplast 101) and the degree of polymerization is x, the initial molecular weight ($M_{n,0}$) is m_0x (20,000 g/mol for Isoplast 101 [13]). Assuming the TPU was synthesized under stoichiometric conditions,

$$[\mathrm{OH}]_0 = [\mathrm{NCO}]_0 = \frac{\rho}{M_{n,0}} = \frac{\rho}{m_0x} \tag{B2}$$

$$[\mathrm{U}]_0 = \frac{\rho}{M_{n,0}}2x = \frac{2\rho}{m_0} \tag{B3}$$

where ρ is the density of the TPU (1.19 g/cm^3 for Isoplast 101), $[\mathrm{OH}]_0$, $[\mathrm{NCO}]_0$, and $[\mathrm{U}]_0$ are the initial molar concentration of hydroxyl, isocyanate and urethane linkages (6.5 mol/l for Isoplast 101), respectively.

When the system reaches a steady state at an elevated temperature, the equilibrium constant in terms of molar concentration (K_c) will be equal to:

$$K_c = \frac{[\mathrm{OH}][\mathrm{NCO}]}{[\mathrm{U}]} = \frac{[\mathrm{OH}]^2}{[\mathrm{U}]} \tag{B4}$$

$$[\mathrm{OH}] - [\mathrm{OH}]_0 = [\mathrm{U}]_0 - [\mathrm{U}] \tag{B5}$$

where [OH], [NCO], and [U] are equilibrium concentration of hydroxyl, isocyanate and urethane linkage, respectively.

Therefore, it can be obtained:

$$[\mathrm{OH}]^2 + K_c[\mathrm{OH}] - K_c([\mathrm{U}]_0 + [\mathrm{OH}]_0) = 0 \tag{B6}$$

$$[\mathrm{OH}] = \frac{-K_c + \sqrt{K_c^2 + 4K_c([\mathrm{U}]_0 + [\mathrm{OH}]_0)}}{2} \tag{B7}$$

Since $[\mathrm{OH}]_0 \ll [\mathrm{U}]_0$,

$$[\mathrm{OH}] \approx \frac{-K_c + \sqrt{K_c^2 + 4K_c[\mathrm{U}]_0}}{2} \tag{B8}$$

The molecular weight after degradation (M_n) becomes,

$$\begin{aligned} M_n &= \frac{M_{n,0}[\mathrm{OH}]_0}{[\mathrm{OH}]} = \frac{2\rho}{-K_c + \sqrt{K_c^2 + 4K_c[\mathrm{U}]_0}} \\ &= \frac{\rho}{2[\mathrm{U}]_0}\left(\sqrt{\frac{4[\mathrm{U}]_0}{K_c} + 1} + 1\right) \\ &= \frac{m_0}{4}\left(\sqrt{\frac{8\rho}{m_0K_c} + 1} + 1\right) \end{aligned} \tag{B9}$$

If $K_c \ll 1$, which is reasonable for a small degree of degradation,

$$M_n \approx \frac{m_0}{4}\sqrt{\frac{8\rho}{m_0K_c}} = \sqrt{\frac{m_0\rho}{2K_c}} \propto K_c^{-1/2} \tag{B10}$$

and

$$\ln(M_n) = C_1 - \frac{1}{2}\ln(K_c) \tag{B11}$$

where C_1 is a constant.

For condensed liquids,

$$K^{\ominus} = K_c(c^{\ominus})^{-1} = K_c \tag{B12}$$

where $K^{\ominus}$ is the thermodynamic equilibrium constant at standard state and $c^{\ominus}$ is standard molar concentration that is by definition equal to 1 mol/l.

$$\text{Since, } K^{\ominus} = A\exp\left[-\frac{\Delta H_{\mathrm{deg}}}{RT}\right],$$

$$\ln(M_n) = C_1 - \frac{1}{2}\left[\ln(A) - \frac{\Delta H_{\mathrm{deg}}}{RT}\right] = C_2 + \frac{\Delta H_{\mathrm{deg}}}{2RT} \tag{B13}$$

where C_2 and A are constants and ΔH_{deg} is the enthalpy change of the degradation reaction.

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