Effects of the Incorporation of Low-Molecular-Weight Diurethanes on Thermal and Rheological Properties of Thermoplastic Polyurethane

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ABSTRACT: In this study, two low-molecular-weight diurethanes were synthesized and blended with thermoplastic polyurethane (TPU). The effects of the incorporation on the thermal and rheological properties of TPU were evaluated. The diurethanes were obtained from the reaction of 4,4′-diphenylmethane-diisocyanate (MDI) with 1-butanol (Additive 1) or 1-octanol (Additive 2). Blending of the additives with TPU was carried out in a torque rheometer, and the blends obtained were analyzed by differential scanning calorimetry (DSC), torque rheometry, and capillary rheometry. The torque rheometry showed that an increase in the amount of both additives displaced the charging peaks to longer times and reduced the torque values after melting. The DSC analysis showed that the incorporation of the additives did not affect the glass transition temperature (T_g) of the flexible phase of TPU. However, an increase in the amount of Additive 1 led to a reduction in the T_g of the rigid phase, while increasing the amount of Additive 2 caused an increase in the T_g of this phase. Capillary rheometry results showed that blends with up to 2 wt % of additive led to intrinsic viscosity and melt-flow stability values higher than those of processed TPU. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2896–2905, 2009

Key words: block copolymer; thermoplastic polyurethane; capillary rheometry; differential scanning calorimetry

INTRODUCTION

Polyurethanes (PUs) represent an important class of thermoplastic and thermoset polymers because their mechanical, thermal, and chemical properties can be tailored by reacting various polyols and polyisocyanates.[1] They can be found in products such as furniture, coatings, adhesives, constructional materials, fibers, paddings, paints, elastomers, and synthetic skins.[1–4]

Polyurethanes are a family of elastomeric materials whose chains are composed of alternating low glass transition temperature (soft) segments and more rigid, polar urethane (hard) segments, which soften at temperatures higher than room temperature. The soft segments are generally polyethers or polyesters, and the hard segments are formed from the extension of a diisocyanate (often aromatic) with a low-molecular-weight glycol. The unfavorable interactions between the hard and soft segments drive the system to form a microphase-separated structure, which typically imparts elastomeric properties to the polyurethane.[5–7]

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.[5]

TPUs are linear segmented copolymers, composed of microphase-separated hard and soft segments.[5,8–14] The properties of these polymers appear to result from a combination of chain segment flexibility, the rigidity of aromatic units, chain entanglement, orientation of segments, hydrogen bonding, and other intermolecular interactions.[14] TPUs can be processed by common techniques used for thermoplastic polymers, such as extrusion and injection molding.

Polyurethanes are generally characterized by their poor stability because of the thermally labile urethane group. Thermal decomposition starts in the range of 100–200°C,[15] where urethane bonds dissociate and reassociate simultaneously. This process affects the hard segment sequence length distribution, a phenomenon that is known as transurethanization. This mechanism, however, does not contribute to the change in molar mass since no free end groups are formed.[16]

The thermal degradation of polyurethanes in the melt state is inevitable because melting usually occurs around or above the stability temperature of the urethane linkages. Under mild conditions (temperature below 250°C), equilibrium is quickly established between urethane linkages and free isocyanate and hydroxyl end groups.[5] The dissociation of urethane bonds causes a considerable molar mass decrease because the equilibrium reaction is shifted toward the free end groups. As a consequence of transurethanization and a change in molar mass, any thermal treatment of TPU elastomers above a critical temperature, in particular measurements and processing in the molten liquid state, can significantly change the viscosity and crystallization behavior and even the mechanical properties.[16]

Urethane dissociation and recombination reactions occur above 170°C. Such reactions appear to decrease the molecular weight leading to reduced strength and elongation, particularly in harder TPU materials, since they need to be processed at higher temperatures.[17]

The thermal stability of urethane groups depends on the nature of the polyol backbone, the chain extender, and the type of isocyanate used. Attempts to increase the thermal stability of polyurethanes through the introduction of thermally stable groups and chain extenders have been reported, affecting, to some extent, the mechanical properties as well as the processability of the system. The low-temperature properties are also affected in some cases.[15]

Viscosity measurements have been obtained in many different ways. For shear viscosity, capillary rheometry is used.[18] In this type of analysis, the shear rates and flow geometry are similar to the conditions present during the extrusion and injection molding. The main disadvantage of the capillary viscometer is that the shear rate is not constant but varies across the capillary.[19]

Seymour and Cooper[6] analyzed differential scanning calorimetry (DSC) and infrared spectroscopy data for a series of polyurethane block polymers and observed that the DSC endothermic peaks resulted from ordering of the hard segments. Materials of low diisocyanate content (and thus short hard segments) are incapable of crystallization. Thus, in the case of TPU, a higher tendency toward crystallization is expected with increasing hard segment length.[20]

Crawford et al.[21] observed that DSC experiments on some model polymers revealed three prominent thermal transitions including a glass transition below 0°C and two broad endothermic transitions at higher temperatures. The lower temperature endothermic transition (60.4–72.0°C) is related to the disruption of soft segment/hard segment bonds or disruption of short-range order within the hard segment microdomains. The higher temperature endo-thermic transition (117.1–156.8°C) is related to the breakup of interurethane hydrogen bonds. According to these authors, this series of transitions is representative of the two phases that are present in the polymer and reflect the relative amounts of hard and soft segments present.

Lu et al.[5] studied the rheological properties of a TPU with small and large deformation via three different types of rheometry: dynamic shear, capillary, and torque (in an instrumented batch mixer). According to these authors, the apparent activation energy of the flow was much higher than expected. Melt viscosities obtained using the instrumented batch mixer showed a much lower apparent activation energy (186 kJ mol^{-1}) because of the combination of errors in the relationship between viscosity and mixer torque for TPU, side reactions resulting from air exposure, high stress levels during the melting, and extensional stresses.

Torró-Palau et al.[22] added different types of silica to a TPU and observed that the addition of silica increased the viscosity, the storage, and loss moduli of the PU/silica composites in solution but only the hydrophilic fumed silica imparted pseudoplasticity and thixotropy. Interactions between the hydrophilic-fumed silica, the polyurethane, and/or the solvent seemed to be responsible for the improved rheological properties of the composites. The addition of silica did not modify the glass transition temperature but increased the softening temperature of PU composites.

In this study, two additives of low molecular mass containing urethane groups were added to commercial TPU, and the effects of their addition on the thermal and rheological properties of TPU were studied.

EXPERIMENTAL

Materials

In the diurethane synthesis, 4,4′-diphenylmethane-diisocyanate (MDI-Isonate 125M, from Dow, USA), 1-butanol (Vetec, Brazil), 1-octanol (Merck, Germany), and dimethylformamide (DMF, Vetec) were used as received.

The TPU (Fortiprene TPU 5102/D43, FCC Fornecedora, Brazil), a polyester-based TPU, was dried at 90°C for 24 h in a vacuum oven (−650 mmHg) before use.

Diurethane synthesis

The diurethane additives were obtained by adding ~ 1.8 mol of 1-butanol to 0.8 mol of MDI [Additive 1: dibutyl 4,4′-methylenebis(phenyl carbamate)] or adding ~ 1.8 mol of 1-octanol to 0.8 mol of MDI [Additive 2: dioctyl 4,4′-methylenebis(phenyl

carbamate)]. Both additives have been previously used in similar studies.[23,24]

The isocyanate content of the MDI was analyzed according to ASTM D-5155B.[25] The value observed for the isocyanate was 32.9% (NCO); the expected value was 33.6%.

Diurethane synthesis was carried out in a DMF solution under vacuum, at 55°C ± 3°C and 600 rpm, in a 1-L three-way reaction flask. In these syntheses, MDI and 0.4 L of DMF were first added to the flask; temperature, vacuum, and mixer speed were controlled. The 1-butanol or 1-octanol was then slowly added. After total addition of the alcohol, the reaction was kept under controlled conditions for 1 h. The solutions obtained were maintained in closed flasks overnight. The solutions were then washed with distilled water, leading to crystallization of the additives. These were filtered and dried at 60°C for 48 h in a conventional oven, followed by 24 h in a vacuum oven at the same temperature. Diurethanes were characterized by DSC and Fourier transform infrared spectroscopy (FTIR).

Blends

Blends of 1, 2, 5, and 10 wt % of each additive with the TPU were obtained. The blending was carried out in a home-made torque rheometer (an instrumented batch mixer), using roller rotors, at 200°C and 60 rpm for 600 s. The mixture chamber had a free volume of ca. 75 cm^3; the total mass of each batch was 50 g. A sample containing 2 wt % of Additive 2 was also obtained using a commercial torque rheometer (Haake Rheomix 600, Thermo Electron Corporation) using the same processing conditions. After blending, the samples were grinded and dried at 90°C for 24 h in a vacuum oven.

Differential scanning calorimetry

Analysis of the diurethanes by DSC (Shimadzu DSC-50) was carried out as follows: the samples were first heated under N$_2$ at a flow of 50 mL min^{-1} and at a rate of 40°C min^{-1} up to 200°C and maintained at this temperature for 120 s. The additives were cooled at −20°C min^{-1} to a temperature of −100°C and heated again at 20°C min^{-1} up to 200°C. The samples analyzed had a mass of ca. 10 mg.

DSC analysis of TPU and its blends with additives were carried out at a heating rate of 20°C min^{-1}, in the range of −100 to 250°C. The atmosphere and mass were the same as those used for the additives.

Solubility parameters

Solubility parameters (δ) of rigid segments of TPU and the diurethanes were determined by group con-
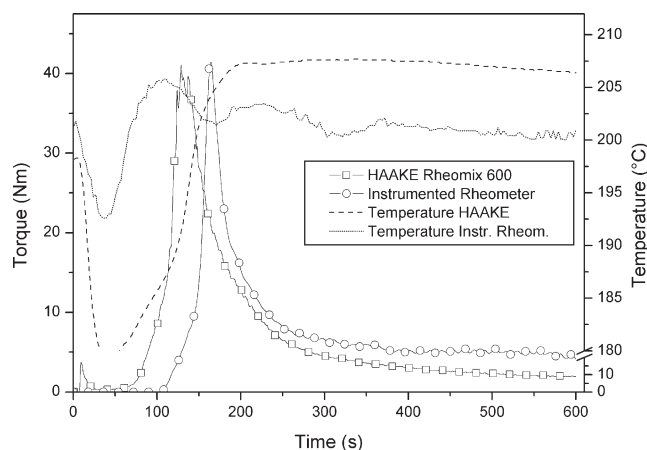
Figure 1 Torque and temperature versus processing time for the mixture containing 2 wt % of Additive 2 ($T = 200$°C, 60 rpm).

tributions theory.[26] The rigid segments of the TPU were assumed to be ideal (formed by two MDI units and one 1,4-butanediol unit).[27]

Capillary Rheometry

Capillary rheometry analysis (Galaxy III 9052, Kayeness) was carried out at 210°C, with a capillary L/D ratio of 20, according to ASTM D-3835.[28] The shear rates used were approximately 10, 20, 50, 100, 200, 500, and 1000 s^{-1}. Plunger/barrel friction and Rabinowitsch corrections were applied.

Intrinsic melt viscosity ([η]) and melt flow stability (κ) were determined through viscosity data at different residence times in the capillary rheometry, under identical conditions of shear rate and temperature.[28] For each sample, data were obtained at ca. 4, 7, and 10 min of residence time. Each sample was analyzed in triplicate.

RESULTS AND DISCUSSION

Blends

Figure 1 shows the torque and temperature versus processing time profiles for the blend containing 2 wt % of Additive 2, for the two different torque rheometers used. It was observed that the maximum torque peak, related to the melting of the TPU,[5] was higher for the sample mixed in the Haake rheometer than that blended in the instrumented rheometer. This is due to the higher chamber volume of the instrumented rheometer (∼ 75 cm^3) when compared with that of the Haake rheometer (69 cm^3), which reduced the shear during the TPU melting. Moreover, mixtures prepared in the Haake rheometer attained the maximum torque peak in a shorter time than the instrumented rheometer due to the higher
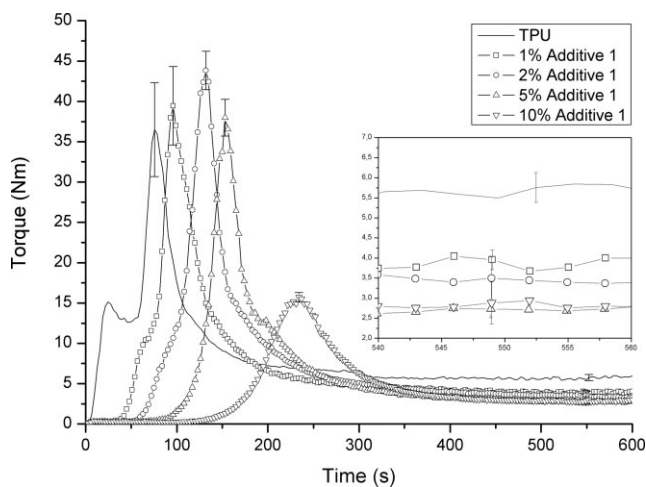
Figure 2 Torque versus time for TPU and blends containing Additive 1 (T = 200°C, 60 rpm).

shear, which caused a faster heating and consequent melting.

Figure 1 shows that after the melting peak, the "stabilized" torque for the Haake rheometer is lower than that found for the instrumented rheometer. This may be associated with the higher shear rates obtained in the Haake rheometer. This increased shear rate led to a higher temperature, and thus a reduction in viscosity and torque.

Figures 2 and 3 show the torque versus time profiles for the TPU and blends containing Additives 1 and 2, respectively. It was observed that the torque curve for the TPU had two peaks at different times. The first loading peak, of lower intensity, can be related to an initial packing of TPU granules in the solid state. The second torque peak is related to TPU melting.[5]

The torque versus time profiles for blends with 1 and 2% of either diurethane also had two loading peaks, but overlapping, relating to the packing and melting of TPU granules, respectively. For these samples, the first torque peak was lower than that observed for neat TPU probably because of the lubricant effect of the additives on the TPU granules, since the melting temperatures of the diurethanes are significantly lower than that used in the blending process. The first loading peak was not observed for samples with 5 and 10% of either additive due to a lubricant effect of the additive.

Addition of either additive up to a content of 5% did not lead to a significant change in the maximum torque values, considering the standard deviations. However, the samples with 10% of additive showed a significant reduction in maximum torque. This behavior is associated with both a reduction in the amount of TPU and its gradual melting due to a

greater residence time in the equipment, which can reduce torque since less effort is needed to promote flow. Also, it was observed that with an increase in the amount of additive, the maximum torque peak is reached after a longer time period because of the lubricant effect.

The insets in Figures 2 and 3 show the behavior of blends containing Additive 1 in the stabilized torque region. The standard deviation values were obtained from torque values in the range 500–600 s. It was observed that the neat TPU showed a stabilized torque value higher than that found for the blends with Additive 1. The mixtures with Additive 2 did not show a significant change in the amount of maximum torque with the incorporation of up to 2% of this additive; however, the incorporation and 5 and 10% of this additive promoted a gradual reduction in the amount of maximum torque. On increasing the amount of additive, the torque value tended to reduce because of the lubricating effect. This behavior may also be associated with the decoupling of the urethane groups of the additives.

On comparing blends containing the same amount of additive, one can observe that the maximum torque values for blends with Additive 1 were slightly higher than those for blends with Additive 2. Also, the maximum torque times for blends with Additive 2 were higher than those found for blends with Additive 1. This may be indicative that Additive 2 acted more efficiently as a lubricant between the TPU granules and equipment walls before TPU melting. The external lubrication promoted by Additive 2 reduced both the shear and the heating of the material related to the shear, which shifted the maximum torque peak to longer time periods and lowered the maximum torque values.
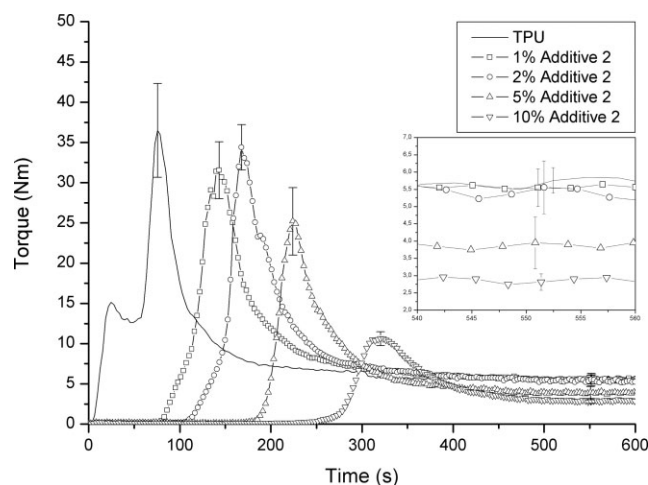
Figure 3 Torque versus time for TPU and blends containing Additive 2 (T = 200°C, 60 rpm).

Component	Solubility parameter ($cal^{1/2}\ cm^{-3/2}$)
TPU rigid segment	12.5
Additive 1	10.4
Additive 2	9.8

Figure 4 DSC thermograms of diurethane/TPU blends.

Solubility parameters

Solubility parameters (δ) calculated for TPU-rigid segments and additives, obtained from the group contribution theory,[26] are given in Table I. One can observe that the solubility parameter for Additive 1 is closer to that for the rigid segments than the value for Additive 2. This indicates that Additive 1 has a greater compatibility with the rigid segments of TPU than Additive 2.

Differential scanning calorimetry

DSC analysis of the diurethanes showed that both had crystalline structures. Additive 1 had a melting temperature (T_m) of 106.3°C and a melting enthalpy (ΔH) of 49.5 J g^{-1}. Additive 2 had a T_m of 117.2°C and a ΔH of 71.8 J g^{-1}. Previous studies have reported a T_m of 115–119°C for Additive 1 and a T_m of 117–119°C for Additive 2.[23,24] Differences in the melting temperatures reported in the literature to

those obtained in this study may be related to different thermomechanical histories of the samples.

Blends of the additives and TPU, as well as the processed and unprocessed TPU, showed four different events in the DSC thermograms (Fig. 4). These events are related to the glass transition temperature (T_g) of the flexible phase (ca. −20°C), the short-range interactions between the crystallites of the rigid phase and interactions between the rigid and flexible phases (2nd transition, 50–65°C), the rigid phase T_g (115–150°C), and the melting of TPU crystals (180–220°C).[6,7,13] Table II shows the values for the transitions obtained from the DSC analysis.

Figure 5 shows the DSC thermograms for the TPU blends and diurethanes. There were no significant changes in the T_g of the flexible phase with the incorporation of either additive. However, addition of 1% of Additive 1 shifted the T_g of the rigid phase to a temperature higher than that observed for processed TPU and for the other blends containing this additive. An increase in the amount of Additive 1 (from 2 to 10%) led to a reduction in the T_g value for the rigid phase. Addition of 1% of Additive 1 increased the T_g of the rigid phase when compared with that of the processed TPU, probably due to an

TABLE II
Transitions Observed from DSC Analysis

Sample	Flexible phase T_g (°C)	2nd Transition (°C)	Rigid phase T_g (°C)	T_m Peak (°C)	ΔH (J g^{-1})
Unprocessed TPU	−17.2	65.4	127.2	181.4	3.8
Processed TPU	−21.1	62.3	115.9	210.6	11.1
1% Additive 1	−22.9	53.5	136.5	208.2	10.5
2% Additive 1	−20.2	53.7	121.6	211.2	11.1
5% Additive 1	−22.0	54.2	118.2	217.1	10.6
10% Additive 1	−21.1	55.2	112.4	217.2	11.9
1% Additive 2	−23.1	58.8	118.4	207.3	11.9
2% Additive 2	−21.6	59.5	125.3	216.1	10.3
5% Additive 2	−21.9	56.2	145.1	214.2	10.3
10% Additive 2	−24.9	50.8	–	219.4	10.6
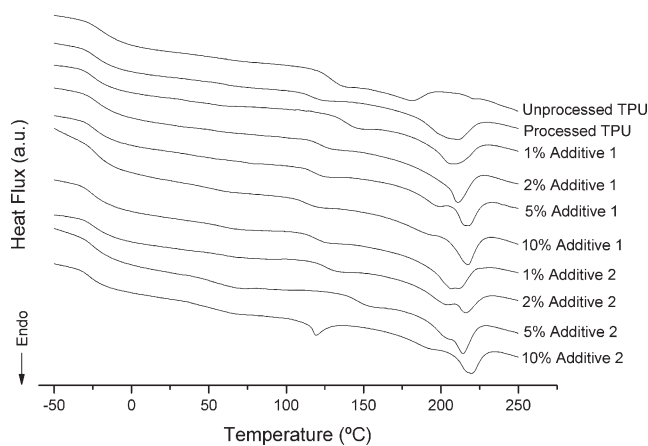
Figure 5 DSC thermograms for samples of TPU and TPU + additive.

increase in the chain mobility during the crystallization process, which led to an increase in the phase separation. With the incorporation of amounts of Additive 1 greater than 2%, there was a gradual decrease in the rigid phase T_g, probably due to a plasticizer effect. However, the addition of either diurethane increased the TPU chain mobility during crystallization, which increased the melting enthalpy and shifted the T_m to higher temperatures (Table II). Incorporation of either additive did not significantly modify the T_g of the flexible phase because of a greater interaction of the diurethanes with the rigid segments. We also observed that the T_g of the flexible phase is characteristic of a polyester-based TPU.[27]

Increasing the amount of Additive 2 to 5% by weight caused an increase in the T_g of the rigid phase. The blend with 10% of Additive 2 had two melting peaks at different temperatures (T_{m1} = 119.7°C, ΔH_1 = 2.6 J g^{-1}; T_{m2} = 219.4°C, ΔH_2 = 10.6 J g^{-1}), and the T_g of the rigid phase of this mixture was not clearly identified. As Additive 2 had a lower compatibility with the TPU-rigid segments than Additive 1, a phase separation between the TPU and Additive 2 is expected, as observed in the DSC thermograms of the blend with 10% of Additive 2, which showed a melting peak related to Additive 2 (ca. 117°C).

The increase in the content of Additive 1 caused an increase in the interaction between the phases, leading to an increase in the second transition temperature. In contrast, the increase in the content of Additive 2 led to a greater separation between the rigid and flexible phases because of the formation of rigid areas with less mobility (higher T_g), reducing the temperature observed for the second transition.

The processing of TPU promoted an increase in the melting enthalpy of the material. Seymour and Cooper[6] studied TPUs based on polyester, contain-

ing 38% by weight of MDI, with different average sizes of rigid segments, and noted that an increase in the average size of the rigid segments led to an increase in the melting enthalpy. Thus, the increase in the melting enthalpy of the processed TPU may be associated with an increase in the rigid segment size due to transurethanization reactions. However, Seymour and Cooper[6] observed that a slight increase in the T_g of the rigid phase occurred with an increase in the length of the rigid segments. Processing the neat TPU caused a decrease in the T_g value for the rigid phase, which may be evident that there was a reduction in the average length of the rigid segments. Thus, the increase in the melting enthalpy may be related to a molar mass reduction during the processing, which would increase the chain mobility in the melt and lead to a higher crystallinity degree.

Incorporation of the additive did not lead to the melting enthalpy of mixtures being significantly different to that of the neat processed TPU. A reduction in the melting enthalpy with an increase in the amount of additive is to be expected, since an increase in the quantity of additive reduces the amount of TPU present and, therefore, reduces the amount of TPU crystals. However, an increased mobility of TPU chains with the increase in diurethanes led to almost the same crystallinity degree for blends of TPU/diurethanes, even with the decrease in the TPU content.

Several DSC thermograms showed overlapped melting peaks that may be related with polymorphism. Koberstein and Galambos[7] studied TPU using DSC and X-ray diffraction and found only one type of crystal structure through X-ray diffraction, whereas the DSC thermograms showed two endothermic peaks. Multiple endothermic peaks can be found at high heating rates (20–40°C min^{-1}) for polyurethanes crystallized from the melt, which result from the melting of distinct populations of crystals. During each endothermic process, the crystals do not only melt but also spontaneously mix with the flexible phase. The origin of multiple endothermic peaks is, therefore, dependent on the procedure used in the sample preparation.[7]

Capillary Rheometry

Table III shows the values for the intrinsic viscosity ($[\eta]$), melt flow stability (κ), and correlation coefficient (R) for the samples analyzed. Figures 6 and 7 show the results for intrinsic viscosity ($[\eta]$) versus shear rate and the melt flow stability (κ) versus shear rate, respectively.

Figure 6 shows that the unprocessed TPU had higher intrinsic viscosity values than processed samples under identical conditions. This is due to the higher molar mass of the unprocessed TPU. For the

TABLE III
Intrinsic Viscosity ([η]) and Melt Flow Stability (κ) for Samples Analyzed

| $\dot{\gamma}$ (s⁻¹)	Property	Unprocessed TPU	Processed TPU	TPU + 1% Additive 1	TPU + 2% Additive 1	TPU + 5% Additive 1	TPU + 10% Additive 1	TPU + 1% Additive 2	TPU + 2% Additive 2	TPU + 5% Additive 2	TPU + 10% Additive 2
10	[η] (Log Pa s)	3.601	3.239	3.432	3.321	3.183	3.014	3.357	3.414	3.282	3.068
	κ [(Log Pa s) min⁻¹]	−0.129	−0.072	−0.037	−0.040	−0.045	−0.057	−0.045	−0.056	−0.048	−0.047
	R	−0.962	−0.900	−0.899	−0.913	−0.932	−0.865	−0.867	−0.990	−0.897	−0.882
20	[η] (Log Pa s)	3.449	3.149	3.305	3.226	3.080	2.933	3.245	3.293	3.187	2.943
	κ [(Log Pa s) min⁻¹]	−0.108	−0.068	−0.034	−0.041	−0.044	−0.060	−0.043	−0.053	−0.048	−0.046
	R	−0.944	−0.926	−0.879	−0.937	−0.928	−0.893	−0.858	−0.990	−0.922	−0.883
50	[η] (Log Pa s)	3.283	2.879	3.031	2.946	2.812	2.666	2.960	3.000	2.901	2.668
	κ[(Log Pa s) min⁻¹]	−0.084	−0.058	−0.033	−0.037	−0.042	−0.057	−0.039	−0.047	−0.045	−0.046
	R	−0.951	−0.927	−0.891	−0.963	−0.950	−0.924	−0.893	−0.990	−0.944	−0.937
100	[η] (Log Pa s)	3.135	2.729	2.835	2.744	2.618	2.439	2.793	2.799	2.706	2.459
	κ [(Log Pa s) min⁻¹]	−0.071	−0.055	−0.030	0.034	−0.039	−0.049	−0.040	−0.043	−0.043	−0.044
	R	−0.986	−0.955	−0.926	−0.955	−0.950	−0.930	−0.927	−0.983	−0.964	−0.979
200	[η] (Log Pa s)	2.974	2.550	2.638	2.513	2.398	2.233	2.571	2.558	2.516	2.241
	κ[(Log Pa s) min⁻¹]	−0.060	−0.051	−0.029	−0.029	−0.034	−0.045	−0.035	−0.036	−0.042	−0.040
	R	−0.998	−0.949	−0.932	−0.926	−0.939	−0.952	−0.936	−0.977	−0.969	−0.986
500	[η] (Log Pa s)	2.751	2.330	2.381	2.249	2.171	1.985	2.315	2.316	2.248	2.035
	κ[(Log Pa s) min⁻¹]	−0.047	−0.044	−0.024	−0.022	−0.030	−0.039	−0.030	−0.031	−0.035	−0.042
	R	−0.994	−0.962	−0.848	−0.883	−0.949	−0.955	−0.927	−0.975	−0.933	−0.975
1000	[η] (Log Pa s)	2.536	2.113	2.152	2.007	1.965	1.780	2.132	2.074	2.033	1.830
	κ[(Log Pa s) min⁻¹]	−0.036	−0.034	−0.017	−0.012	−0.024	−0.031	−0.026	−0.022	−0.028	−0.036
	R	−0.984	−0.968	−0.744	−0.616	−0.934	−0.947	−0.915	−0.897	−0.939	−0.977

processed TPU, the intrinsic viscosity values decrease significantly because of the reduction in the molar mass of the polymer following the breaking of chains during the processing. For both additives, samples containing up to 2% of additive, at shear rates up to 200 s^{-1}, showed higher intrinsic viscosity values than processed TPU. This behavior may be related to a reduction in the degradation of TPU during processing due to a lubricant effect of the additives.

Figure 6 also shows that the intrinsic viscosity of blends containing up to 2% of either additives were similar to those found for processed TPU when the shear rate applied was above 200 s^{-1}. On increasing the shear rate, the viscosity of the samples is reduced due to pseudoplasticity. This reduction in viscosity may have masked the effect observed at lower shear rates (up to 200 s^{-1}). Since the intrinsic viscosity is associated with the average molar mass of the polymer,[28] an increase in the amount of low-molar mass molecules, due to incorporation of additives, reduced the average molar mass of the system and reduced the intrinsic viscosity values. Blends with up to 5% of Additive 1 showed higher intrinsic viscosity values than those with up to 5% of Additive 2, under similar test conditions, due to a better lubricant effect between the TPU chains in the case of Additive 1, when compared with Additive 2, as observed in the torque rheometry analysis. The blends with 10% of both additives showed similar intrinsic viscosity values due to the significant reduction in the average molar mass of the blends with these additive levels.

Figure 7 shows that the processing of TPU promoted an increase in melt flow stability. This behavior may be related to the formation of more stable rigid segments formed from transurethanization reactions occurring during processing.[16] Samples with up to 5% of Additive 1 or 2 showed higher
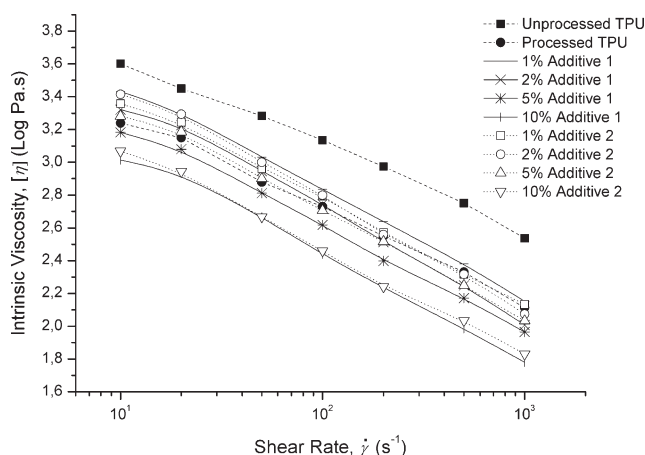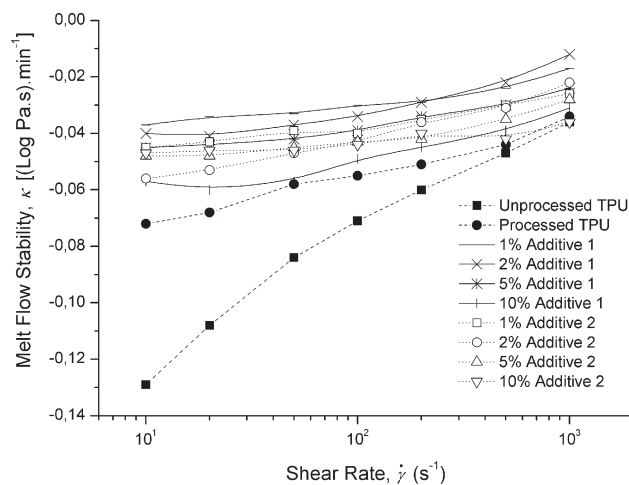
Figure 7 Melt flow stability (κ) versus shear rate ($\dot{\gamma}$) for samples of TPU and TPU + additive.

melt-flow stability values than those found for processed and unprocessed TPU, regardless of the shear rate. The additives have significantly lower molar mass values than that of TPU, and the diurethanes may have decoupled urethane bonds at lower temperatures than those found for TPU, reducing the dissociation rate of the TPU urethane groups because of a trend toward a balance between hydroxyl and isocyanate groups present in the system.

In Figure 7 it can be observed that, when the experiments were carried out using shear rates higher than 500 s^{-1} (inclusive), blends with 10% of Additive 1 or 2 showed melt-flow stability values close to that observed for the processed TPU. This behavior is related to an increase in the mobility of the TPU chains for blends with 10% of additive, which led to an increase in the dissociation rate of the urethane groups of TPU, reducing the melt-flow stability. Increasing the amount of additive reduced the melt-flow stability values because of an increase in the chain mobility and consequent increase in the dissociation rate of the urethane groups. Samples with up to 5% of Additive 1 showed higher melt-flow stability values than samples containing up to 5% of Additive 2, probably due to the lower dissociation rate of TPU urethane groups, because Additive 1 has a lower molar mass and therefore may undergo a higher degree of urethane bond decoupling than Additive 2 under identical conditions.[23] The higher dissociation rate of urethane groups of Additive 1 may have led to a trend toward a balance of isocyanate and hydroxyl groups, reducing the dissociation rate of the urethane groups present in TPU. The samples containing 10% of Additive 1 had lower melt-flow stability than the sample containing 10% of the Additive 2 because of the higher free volume found in the samples with 10% of Additive 1,

Figure 6 Intrinsic viscosity ([η]) versus shear rate ($\dot{\gamma}$) for samples of TPU and TPU + additive.

which may have led to an increase in the dissociation rate of the TPU urethane bonds.

Increasing shear rate resulted in a reduction in the intrinsic viscosity and an increase in the melt-flow stability, which may be related to the pseudoplasticity of the material. Thus, the reduction in viscosity with an increase in the residence time was less significant at higher shear rates.

Finally, the increase in intrinsic viscosity and melt-flow stability with processing may be related to the formation of isocyanurate groups, which have higher thermal stability than urethane groups[27] and can lead to ramifications and even crosslinking. The branching and crosslinking of TPU could reduce the T_m and melting enthalpy; however, this effect was not observed in the DSC analysis.

CONCLUSIONS

In this study, two low-molecular-weight diurethanes were synthesized and blended with TPU, leading to significant changes in the thermal and rheological properties of the material and modifying the TPU processing.

The addition of both diurethanes during mixing with TPU decreased torque values after melting of the samples because of an internal and external lubricant effect of the diurethanes and the reduction of the average molar mass of the samples.

The T_g of soft phase was reduced through processing of the TPU with or without diurethane, while both ΔH_m and T_m increased. The processing promoted a reduction in the average molar mass of TPU and increased molecular mobility, allowing the formation of bigger crystalline structures, and in higher quantity.

When the amount of Additive 1 was increased in the mixture with TPU, there was a reduction of the T_g of rigid phase because of the plasticizer effect of this diurethane in the domains of this phase. So, this additive had better compatibility with the hard segments, as demonstrated by solubility parameter that is closer to the solubility parameter of rigid segment than Additive 2. This fact can justify the physical interactions between rigid segments and Additive 1.

Otherwise, with the increase of the amount of Additive 2 there was an increase in the T_g of rigid phase because of an increase in the separation of soft and rigid phases. As solubility parameter of Additive 2 was lower than Additive 1, it can be stated that Additive 2 interacted mainly with the soft phase, which induced the formation of rigid domains with lower mobility.

The addition of up to 2% of each diurethane increased the melt-flow stability when compared with those observed for processed and unprocessed TPU, which will assist the manufacturing process in

the melt. This phenomenon is related due to a faster balance reached between hydroxyl and isocianate groups with the addition of diurethanes.

Blends containing up to 2% of either diurethane showed higher intrinsic viscosity values than that found for processed unmodified TPU, once the lubricant effect of the diurethanes avoided significant decrease in molar mass of TPU molecules during processing.

Blends containing Additive 1 showed higher melt-flow stability than mixtures containing Additive 2. Additive 1 had lower molar mass and underwent a higher degree of urethane group decoupling than Additive 2, promoting a faster equilibrium between hydroxyl and isocianate groups in the melting.

The processing of unmodified TPU led to a reduction in intrinsic viscosity because of the scission of TPU molecules. However, the processing of TPU led to an increase in the melt-flow stability because of the formation of more stable rigid segments formed from transurethanization reactions.

The melt-flow stability of TPU was higher for shear rates above 500 s^{-1} because of the pseudoplastic behavior of TPU; this masked the influence of residence time on polymer viscosity.

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