

Interfacial rheology of coextruded elastomeric and amorphous glass thermoplastic polyurethanes

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Received: 26 December 2011 / Revised: 28 August 2012 / Accepted: 1 September 2012 / Published online: 29 September 2012
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Abstract In this work, we report on the sensitivity of rheometrical techniques to the nature and size of the interface/interphase in coextruded thermoplastic urethanes (TPUs). In particular, the interphases developed during coextrusion of an amorphous glass (hard) TPU (Isoplast[®] ETPU 301) with one of two elastomeric (soft) TPUs (Estane[®] TPU 58277 and Estane[®] TPU X1175) were studied. Differences in the thickness and nature of the interphase of the two coextruded bilayer films were observed by atomic force microscopy. In one case, the interphase is thicker and rough, and in the other case, it is thinner and flat. Rheology was used in order to probe the type and characteristics of the interphases, with coextruded films having been tested in steady shear, small-amplitude oscillatory shear (SAOS), uniaxial extension, and stress relaxation after a step strain in shear. The results were compared with theoretical predictions assuming zero-thickness interfaces and no interfacial slip. For SAOS and stress relaxation experiments, expressions were deduced in order to enable such a prediction to be made. Of all four rheometrical tests, only stress relaxation after a step shear did not follow the theoretical predictions and, thus, was sensitive enough to detect the presence of the interphase.

Keywords Coextrusion · Multilayer films · Thermoplastic polyurethanes · Interphase · Mutual diffusion

Introduction

When two miscible or partially miscible amorphous polymers are brought into contact at temperatures above the glass, transition temperature mutual diffusion will occur and, given enough time, will lead to an increase in the adhesion between polymers. Furthermore, the interactions between macromolecules at the interface of two polymer melts can be affected by reaction, presence of premade block copolymers, and deformation rates.

The mutual diffusion and chemical reactions occurring in the interfaces between different polymers have been studied by a broad range of different experimental techniques: forward recoil spectrometry (Schulze et al. 2000), dynamic secondary ion mass spectroscopy (Harton et al. 2005), attenuated total reflexion Fourier transform infrared spectrometry (Vaudreuil et al. 2000), scanning electron microscopy (Lamnawar and Maazouz 2008; Lamnawar et al. 2010), transmission electron microscopy (TEM), and atomic force microscopy (AFM) (Jiao et al. 1999; Zhang et al. 2005), and rheology (Carriere and Ramanathan 1995; Qiu and Bousmina 1999; Vaudreuil et al. 2000; Qiu et al. 2002; Macosko and Zhao 2007; Lamnawar and Maazouz 2008; Lamnawar et al. 2010). When the polymers are miscible and/or the chemical reaction occurs across the interface, relatively large interphases, with hundreds of nanometers or even several microns, can be formed. An interesting trait usually noticed in reactive layered

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samples is interfacial roughening. This phenomenon has been observed by several authors (Lyu et al. 1999; Jiao et al. 1999; Zhang et al. 2005) using AFM and TEM, and an important role in its induction has been attributed to the coupling reaction of the reactive polymers, which can be reaction-controlled (Schulze et al. 2000) or diffusion-controlled (Harton et al. 2005). For diffusion–reaction reactive coupling, the progression of the interfacial copolymer formation is controlled by the physics of mass transfer rather than chemical bonding mechanisms as in the reaction-controlled case.

Rheology has been proven to be a valuable tool to study the interphases in polymer melts even if the quantification of the interphase is a challenging task. However, rheology is much easier to use than some of the experimental methods mentioned above. Moreover, some industrial processes involve the flow of multilayer polymer films, a case where it is important to know the kinetic behavior of interphases or interfaces. Thus, it is important to identify which rheometrical techniques are most sensitive to the type of interface and the kinetics of its formation. The present work focuses on the former aspect.

Assuming no slip at the interface and zero interface thickness, the harmonic average viscosity of a stack of parallel multilayers at a fixed stress is given by (Lin 1979)

$$\frac{1}{\eta_{\text{app}}(\tau)} = \phi_A \frac{1}{\eta_A(\tau)} + \phi_B \frac{1}{\eta_B(\tau)} \quad (1)$$

where subscripts *A* and *B* indicate each neat component and ϕ is the volume fraction. If the Cox–Merz law is assumed to be valid, then Eq. 1 can be used to predict dynamic complex shear modulus, G' , and complex viscosity, η^* (Carriere and Ramanathan 1995; Bousmina et al. 1999; Vaudreuil et al. 2000; Levesque et al. 2005; Macosko and Zhao 2007; Lamnawar and Maazouz 2008). However, it is not possible to predict G' and G'' from this equation even assuming that Cox–Merz relation holds.

A negative deviation from Eq. 1 indicates an interfacial slip. An extension to Eq. 1 was first proposed by Lin (1979) and then developed by Bousmina et al. (1999) to explain the interfacial slip. The time evolution of small-amplitude oscillatory shear material functions, especially G^* and η^* , have been extensively used to study the development of the interphases between layers (Qiu and Bousmina 1999; Vaudreuil et al. 2000; Kim et al. 2006; Macosko and Zhao 2007; Lamnawar and Maazouz 2008; Lamnawar et al. 2010). In general, it has been observed that these physical quantities increase when the two polymers diffuse into each other. Different models have been proposed allowing the

mutual diffusion coefficient from the time evolution of G^* and η^* to be determined. Bousmina and Qiu (2000) proposed a model that combines the concepts of the reputation theory and the fast-mode model applied to miscible monodisperse dissimilar polymers brought into close contact in the molten state, allowing the diffusion coefficients to be determined from rheological measurements. Hence, using the dynamic complex shear modulus, G^* , measured in parallel-plate geometry as a function of time and frequency for a sandwich-like assembly with two layers, they found values in good agreement with the literature. The effect of molecular weight distributions was later addressed by the same authors in a different work (Qiu and Bousmina 2002).

Several other authors (Macosko and Zhao 2002; Macosko et al. 2009; Park et al. 2010) have also used steady shear measurements to characterize interfacial slip. The mutual diffusion coefficient of a pair of polyethylenes was measured by Macosko and Zhao (2007) using a coextruded multilayer film with 32 alternating layers. In their analysis, they take into account that the mutual diffusion is a function of concentration. They solve numerically the concentration profile in the multilayers and then, by fitting the experimental data of evolution of complex viscosity over time, the mutual diffusion coefficient as a function of polymer concentration is determined.

The use of shear stress relaxation to investigate planar polymer/polymer interfaces is not common. Qiu et al. (2002) studied the diffusion at symmetric polymer–polymer interfaces. They observed that the shear stress relaxation after a step strain for a polystyrene/polystyrene sandwich is a function of welding time. Specifically, (a) the sandwich samples with longer welding times relaxed more slowly than those with shorter welding times; (b) the magnitude of the shear stress increased with welding time. This was explained in terms of chain diffusion at the interface. As time passes, more and more chains cross the interface and penetrate the other side, creating entanglements and a dense network at the interphase. The initially sharp and weak interface disappears, and it is gradually replaced by a stronger interphase.

It is well known that extensional rheometry is a sensitive tool to probe the interfaces in polymer blends and multilayers. When a molten multilayer film is pulled in uniaxial tension parallel to the layers, the interfacial area per unit of volume increases, amplifying interfacial effects. Levitt et al. (1997) show that at low deformation rates, the extra measured stresses can be related to the interfacial tension, Γ , and the number of interfaces. In fact, they obtained interfacial tension values which are in good agreement with the values measured by

other techniques. The same authors also showed that cross-linking at the interface leads to large strain hardening. Moreover, the cross-linked interface could be modeled with rubber elasticity theory. An intermediate effect was observed for a multilayer system where graft copolymer was formed between the layers.

Silva et al. (2007, 2010a, b) have shown that the modification of the nature of the interfaces in polymer blends through compatibilization can lead to the presence of a very slow relaxation process after a step uniaxial extension. Similar results were obtained by Mechbal and Bousmina (2007) at higher copolymer compatibilizer concentrations, i.e., above a critical concentration of saturation of the interface. This effect was attributed to entanglements in the interfaces and the formation of an elastic interphase.

In this work, we build on the body of work above and study two coextruded bilayer thermoplastic urethane (TPU) films. TPUs are multiblock copolymers usually consisting of hard and soft segments. Hard segments (HS) are composed from diisocyanate and short-chain diols as a chain extender and form a crystalline phase at room temperature, while soft segments (SS) are, in general, polyethers or polyesters and determine low temperature properties. In the present work, the films are composed of a layer of an amorphous glassy TPU, composed almost exclusively by hard segments, while the other layer is an elastomeric one and composed both of hard and soft segments.

In the present work, two different bilayer films, one with a thinner and sharp interphase and the other one with a larger and rough interphase are investigated using a wide range of rheological techniques. The sensibility of these rheological techniques to the nature of the interphase is evaluated. Since no expressions exist in the literature to predict the dynamic moduli and shear relaxation modulus, these are deduced, assuming zero interfacial thickness and no slip between the layers.

Experimental

Materials

One commercial amorphous, glossy aromatic TPU, composed almost exclusively of hard segments, Isoplast[®] ETPU 301, was coextruded at 225 °C alternatively with two different aromatic elastomeric (soft) TPUs: Estane[®] TPU 58277 and Estane[®] TPU X1175. The elastomeric TPUs are composed of hard urethane segments and soft polyester-based segments. They are prepared from a different type of polyester

polyol and have different durometers, 93A on shore scale for Estane[®] TPU 58277 and 85A for Estane[®] TPU X1175. All materials were provided by the Lubrizol Advanced Materials, Inc.

The coextruded films have two layers and were coextruded with a 1:1 (*v/v*) ratio in order to obtain layers with similar thicknesses. Single material films were also extruded (the die temperatures were 230, 210, and 215 °C for Isoplast[®] ETPU 301, Estane[®] TPU 58277, and Estane[®] TPU X1175, respectively). In all cases, the total nominal thickness of the film was 0.75 mm (30 mil).

Rheological measurements

Shear rheometry was performed on a Thermo MARS III rotational rheometer on 20 × 0.75-mm (D × H) disks cut from the extruded film. Prior to the experiments, all disks were vacuum-dried at 70 °C for 8 h. In stress relaxation experiments, a shear step strain of 10 % was applied.

Uniaxial elongational viscosity was measured on a first generation SER fixture (Sentmanat 2004; Sentmanat and Hatzikiriakos 2004) mounted on the same rheometer, under different constant strain rates. Room temperature strip dimensions were approximately 12.7 × 6.0 × 0.75 mm (L × W × H).

Steady shear experiments in the single materials were performed at 225 °C under a nitrogen atmosphere in order to preclude oxidative degradation of the samples, to determine the viscosities of the materials during the coextrusion process, namely, in the feedblock and die. All other rheological experiments were conducted

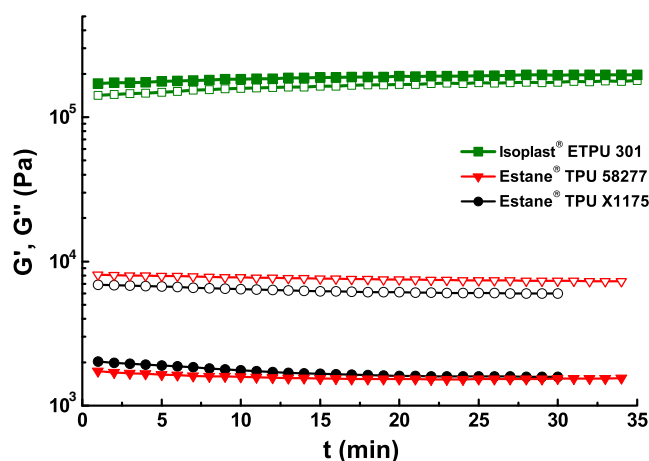


Fig. 1 Dynamic moduli of three TPUs (Isoplast[®] ETPU 301, Estane[®] TPU 58277, and Estane[®] TPU X1175) measured at a constant angular frequency (1 rad s^{-1}) in a nitrogen atmosphere at 175 °C (G' filled symbols, G'' open symbols)

at 175 °C under a nitrogen atmosphere. At this temperature, all the materials show a nearly constant behavior over a long enough time period for the frequency sweeps to be completed (Fig. 1). Moreover, this temperature should be low enough to prevent a significant rate of polymerization/depolymerization reactions but high enough to erase the thermo-mechanical history upon processing. In fact, one of the well-known traits of TPUs is the occurrence at high temperatures of chemical reactions of depolymerization, specially the dissociation of urethane (Yang et al. 1986). Because of the reversibility of most of these reactions, repolymerization takes place when the temperature decreases; this is a further reason for performing the rheological tests at 175 °C. Finally, this temperature allows performing extensional experiments since the sagging is negligible.

Microscopy

The characteristics of the interphases were analyzed by optical microscopy (OM) and atomic force microscopy (AFM). For OM, the films were cut and polished on

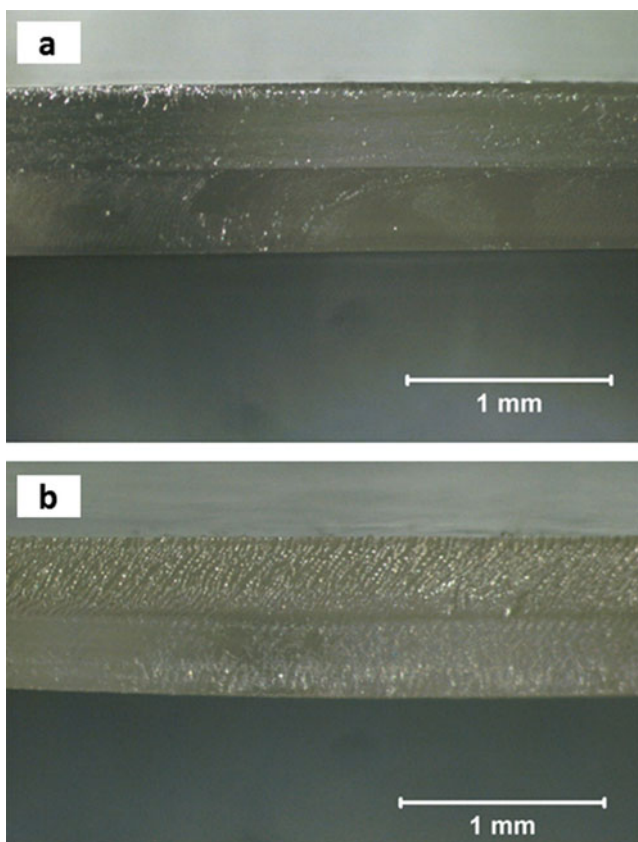


Fig. 2 Optical microscopy images for coextruded bilayer films. **a** Isoplast® ETPU 301/Estane® TPU 58277. **b** Isoplast® ETPU 301/Estane® TPU X1175

a Buehler Metaserv grinder/polisher. A stereo-optical microscope was used to get optical micrographs.

For AFM, a small specimen was cut from the coextruded sheet and microtomed perpendicularly to the cross section of the film with a glass knife at −90 °C. The microtomed surface was examined in a Digital Laboratories Nanoscope IIIa AFM operating in tapping mode. AFM phase images were analyzed using the NanoScope software to obtain a profile showing relative modulus differences across the image.

Results and discussion

Microscopy

The coextruded bilayer films were analyzed by optical microscopy (Fig. 2), and the results show the existence of an interphase with a relatively large thickness in both films. However, the thickness and nature of the

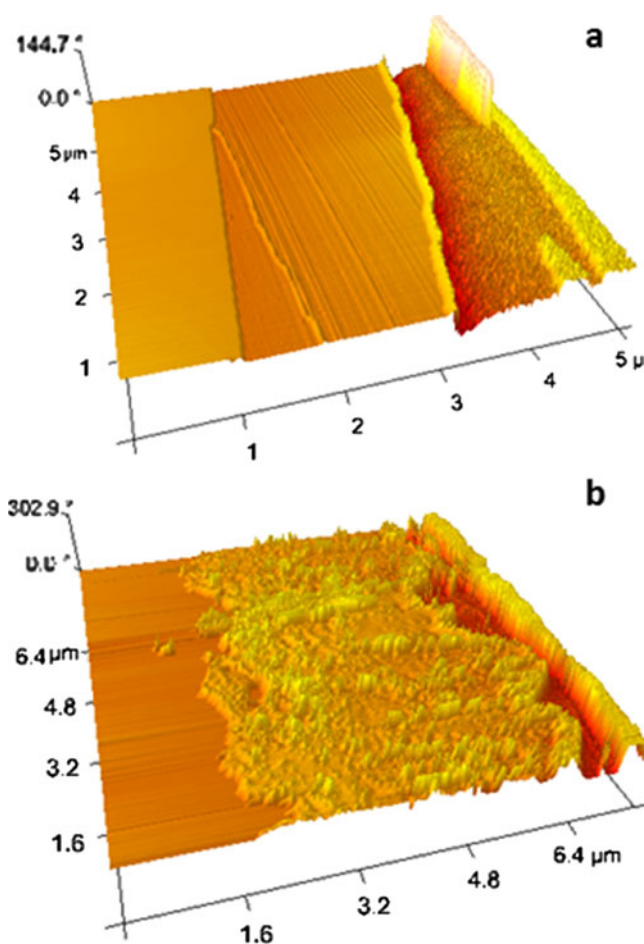


Fig. 3 Three-dimensional AFM phase images. **a** Isoplast® ETPU 301/Estane® TPU 58277. **b** Isoplast® ETPU 301/Estane® TPU X1175

interphase is different in each of the two cases. In the case of Isoplast ETPU 301/Estane TPU 58277 (Fig. 2a), the interphase appears to be sharp, while in the case of the bilayer film with Estane TPU X1175 (Fig. 2b), a rough interphase is observed.

In order to more accurately characterize the interphase and confirm the previous observations with OM, AFM was performed in the cross section of the films.

Figure 3 shows the three-dimensional AFM phase images for both samples. In both cases, three phases are observable. On the left side of the image is the elastomeric layer, on the right is the amorphous glass one, and in between them, a relatively large interphase is observable. The difference between the interphases that were developed in the two samples is clear. In Isoplast ETPU 301/Estane TPU 58277, the edges between the layers and the interphase are very sharp, whereas in Isoplast ETPU 301/Estane TPU X1175, they are

irregular. In addition, the thickness of the interphase is also different in both cases. This can be more clearly observed in Fig. 4. The interphase between Isoplast ETPU 301 and Estane TPU 58277 has 2 μm while the interphase between Isoplast ETPU 301 and Estane TPU X1175 has more than double the thickness, at approximately 5 μm .

It is well known that the hard and soft segments in TPUs are miscible at high temperatures, becoming incompatible at lower temperatures (Velankar and Cooper 2000; Cossar et al. 2004). It thus follows that layer miscibility at coextrusion temperatures during the process is to be expected. This fact explains the large interphase generated during the relatively short contact time between layers (usually between 20 and 40 s, depending on processing conditions) of the coextrusion process. Moreover, the polymerization/depolymerization reactions occurring at high

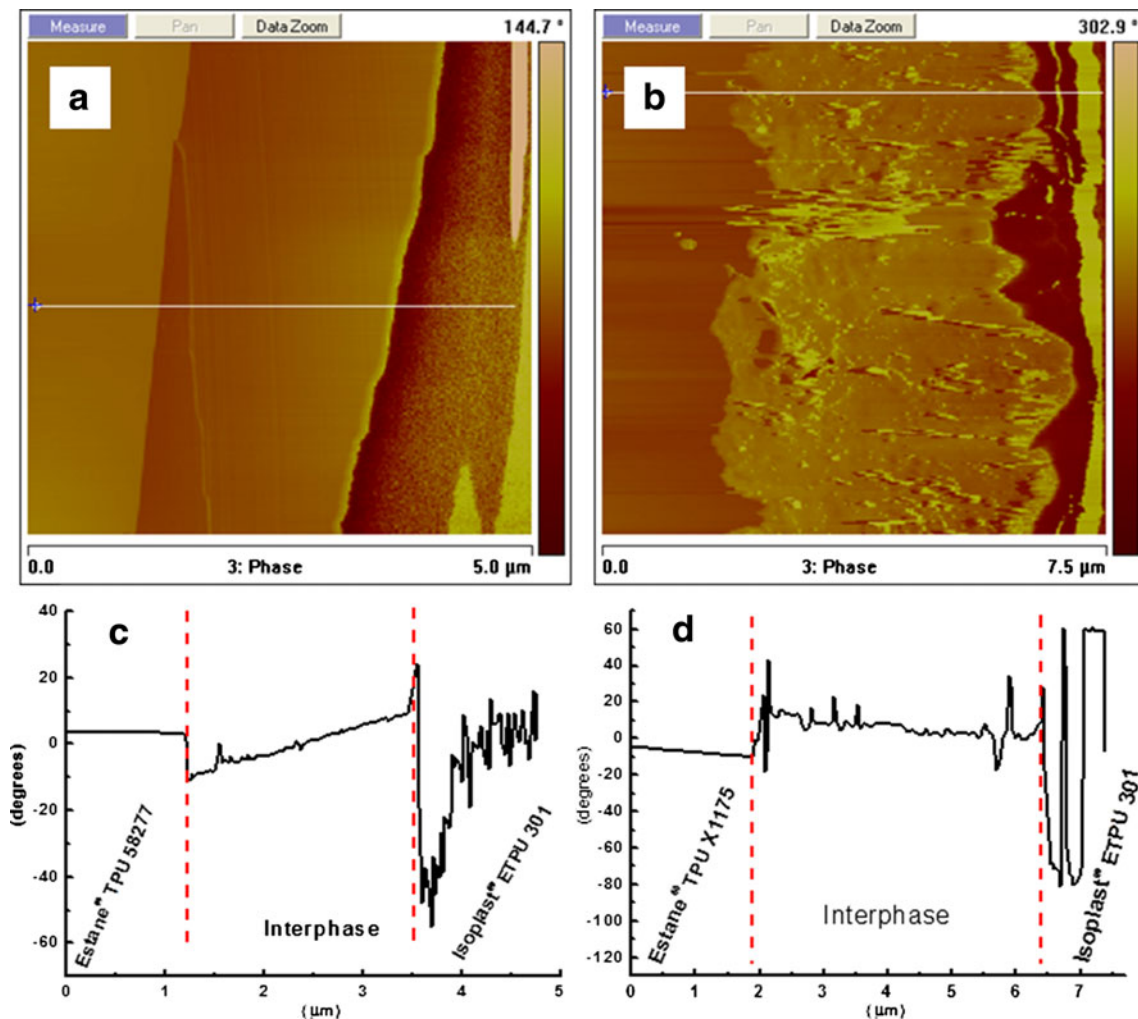


Fig. 4 Two-dimensional AFM phase images of **a** Isoplast[®] ETPU 301/Estane[®] TPU 58277, **b** Isoplast[®] ETPU 301/Estane[®] TPU X1175, and respective section analysis of **c** Isoplast[®] ETPU 301/Estane[®] TPU 58277 and **d** Isoplast[®] ETPU 301/Estane[®] TPU X1175

temperatures may also have an important role on the formation of the interphase.

The results above show that there is a higher degree of diffusion/interpenetration between the layers in Isoplast ETPU 301/Estane TPU X1175 film. The reason for the distinct interphases generated with different elastomeric TPUs is not clear, and a detailed study is beyond the scope of this work. However, two main possibilities should be pointed out. First, the amount of HSs in Estane TPU 58277 is higher than in Estane TPU X1175 which should limit the mobility of Estane TPU 58277 molecular chains. Second, the nature of SSs in Estane TPU 58277 and Estane TPU X1175 is different, and the mobility of SSs itself may be different in each of the two cases. The steady shear viscosities (Fig. 5) can be seen as a first rough indication justifying the higher degree of diffusion/interpenetration in Isoplast ETPU 301/Estane TPU X1175 since Estane TPU 58277 is slightly more viscous than Estane TPU X1175.

The question that remains is then which, if any, rheological technique(s) is/are able to distinguish between these two different interphases: one flat and sharp, Isoplast ETPU 301/Estane TPU 58277, and one diffuse and rough, Isoplast ETPU 301/Estane TPU X1175. This is the main motivation for the present work.

Steady shear

Figure 6 shows a comparison between the steady shear results and the predicted values according to Eq. 1 for both bilayer films. The experimental results follow the predicted viscosity curves and hence show no evidence of interfacial slip or the development of an interphase between the layers. Thus, it can be concluded that for this by-layer systems, the steady shear is not sensitive enough to detect the interphase for low interfacial area/volume ratios.

$$\gamma_0 = \sqrt{(\phi_A \gamma_{0A} \cos \delta_A + \phi_B \gamma_{0B} \cos \delta_B)^2 + (\phi_A \gamma_{0A} \sin \delta_A + \phi_B \gamma_{0B} \sin \delta_B)^2}. \quad (6)$$

Then, if the dynamic moduli of the simple materials are known, the predicted response of multilayer sample can be calculated as follows:

$$G' = \frac{\tau_0}{\gamma_0} \cos \left(\tan^{-1} \left(\frac{\phi_A \gamma_{0A} \sin \delta_A + \phi_B \gamma_{0B} \sin \delta_B}{\phi_A \gamma_{0A} \cos \delta_A + \phi_B \gamma_{0B} \cos \delta_B} \right) \right) \quad (7)$$

$$G'' = \frac{\tau_0}{\gamma_0} \sin \left(\tan^{-1} \left(\frac{\phi_A \gamma_{0A} \sin \delta_A + \phi_B \gamma_{0B} \sin \delta_B}{\phi_A \gamma_{0A} \cos \delta_A + \phi_B \gamma_{0B} \cos \delta_B} \right) \right) \quad (8)$$

Small angle oscillatory shear

Small angle oscillatory shear (SAOS), particularly the storage modulus at low frequencies, can be a very sensitive tool to the relaxation mechanisms occurring at the interfaces (Lamnawar et al. 2010). However, no expression exists to predict the dynamic moduli, G' and G'' , of a multilayer film assuming a zero-thickness interface and no interfacial slip. Such an expression will now be deduced.

Assuming that no slip occurs at the interface and that the thickness of the interphase is zero, the rheological response of a multilayer sample in small oscillatory shear can be predicted. Under these conditions, the stress should be constant throughout the sample, and the total strain, γ_t , would be given by

$$\gamma_t = \phi_A \gamma_A + \phi_B \gamma_B \quad (2)$$

Indexes A and B refer to each phase and ϕ is the volume fraction. Then, if a sinusoidal stress is applied to the material, the response of each phase would be

$$\gamma_A = \gamma_{0A} \sin(\omega t + \delta_A) \quad (3a)$$

$$\gamma_B = \gamma_{0B} \sin(\omega t + \delta_B) \quad (3b)$$

where γ_0 is the maximum strain amplitude, ω is the angular frequency, and δ is the phase angle. Combining Eqs. 2 and 3, and knowing that

$$a \sin x + b \cos x = \sqrt{a^2 + b^2} \sin \left[x + \arctan \left(\frac{b}{a} \right) \right], \quad (4)$$

the strain of the multilayer sample is obtained as function of the viscoelastic material functions of the neat materials:

$$\gamma_t(t) = \gamma_0 \sin(\omega t + \delta_t) \quad (5)$$

with

$$\tan \delta = \frac{\phi_A \gamma_{0A} \sin \delta_A + \phi_B \gamma_{0B} \sin \delta_B}{\phi_A \gamma_{0A} \cos \delta_A + \phi_B \gamma_{0B} \cos \delta_B} \quad (9)$$

where τ_0 is the maximum stress amplitude. If both fluids have the same rheological behavior, the classical expressions of $G' = \frac{\tau_0}{\gamma_0} \cos \delta$ and $G'' = \frac{\tau_0}{\gamma_0} \sin \delta$ are immediately recovered.

Figures 7 and 8 show the viscoelastic material functions for the two bilayer films and their respective predictions. For both Isoplast ETPU 301/Estane TPU 58277 and the Isoplast ETPU 301/Estane TPU X1175

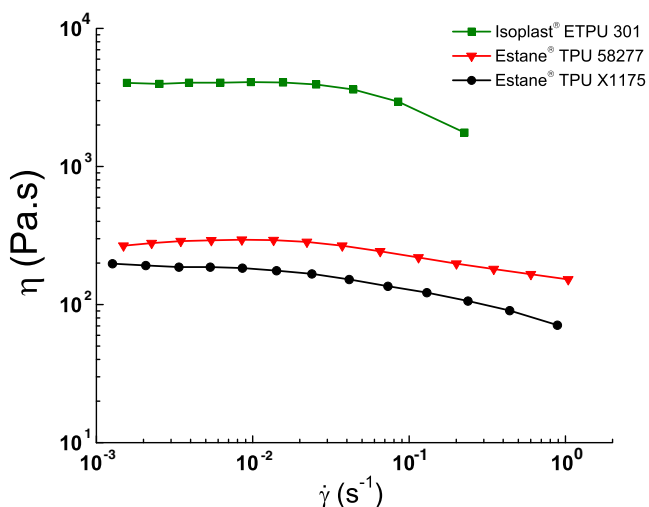


Fig. 5 Flow curves at 225 °C for Isoplast® ETPU 301, Estane® TPU 58277, and Estane® TPU X1175

films, the experimental results agree well with the calculated behavior, indicating that there is no slip between the layers and that the thickness of the interphase is too small to be detected with this technique.

Uniaxial extensional flow

Uniaxial extensional experiments are a fundamentally different way to probe the interfaces in multilayer films. Inversely to what happens in shear, where flow direction is parallel to the interfaces, in extension, the

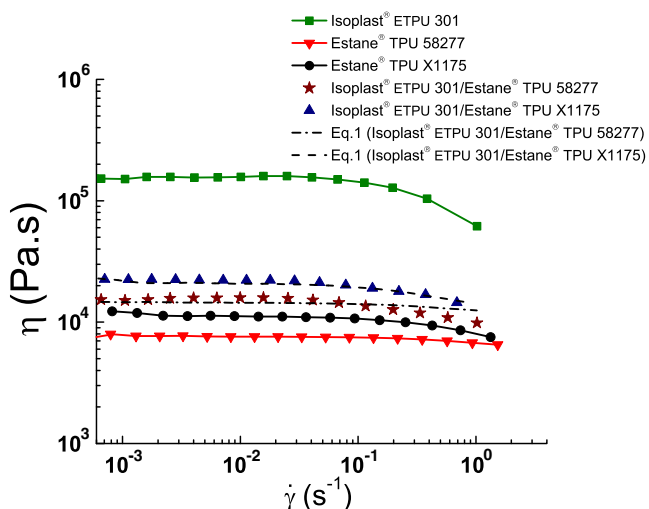


Fig. 6 Flow curves, at 175 °C, for coextruded bilayer films, Isoplast® ETPU 301/Estane® TPU 58277 and Isoplast® ETPU 301/Estane® TPU X1175, and respective predictions according to Eq. 1. In the figure, the results for the correspondent monolayer materials are also represented

interfacial area per volume unit increases over the course of the experiment. This means that any interface/interphase present in the sample will flow, decreasing its thickness as the bulk material of the layers is brought closer to the interface.

Again, the starting point for this study will be the comparison between the experimental results and the predicted ones, assuming no contribution from the interface. In this case, the theoretical prediction is relatively easy to establish. If a multilayer film is subjected to a uniaxial extensional flow and assuming that the layers behave independently of each other, the deformation of both layers will be the same. Then, the total axial force should be the sum of the contributions of each layer. It follows from this that for a multilayer film in which the extensional viscosity will be given by

$$\eta_{E_t}^+ = \phi_A \eta_{E_A}^+ + \phi_B \eta_{E_B}^+ \tag{10}$$

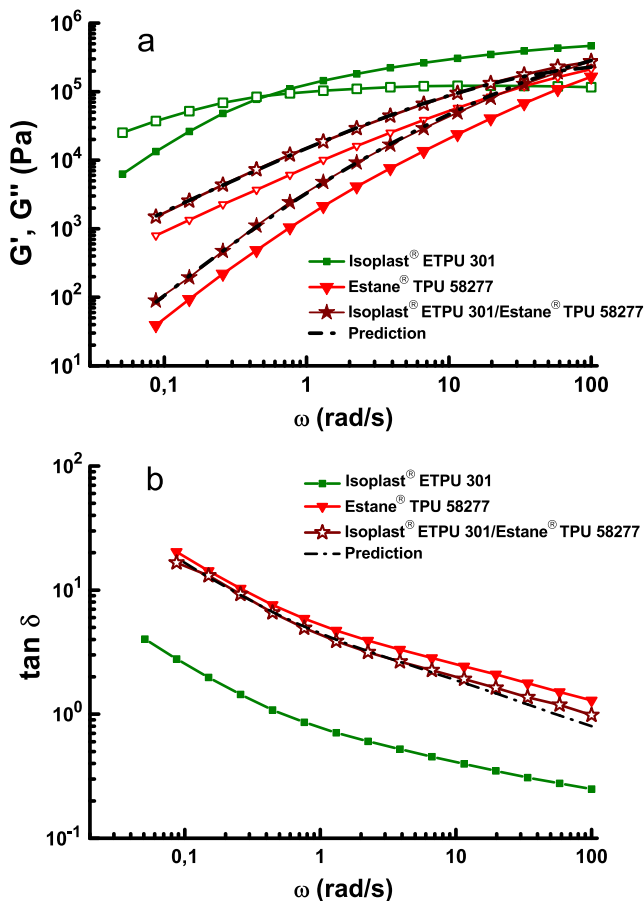


Fig. 7 Small-amplitude oscillatory shear measurements at 175 °C and theoretical predictions for a coextruded bilayer film of Isoplast® ETPU 301/Estane® TPU 58277 at 175 °C. **a** Dynamic moduli (G' filled symbols, G'' open symbols) and **b** loss tangent. In the figure, the results for the correspondent monolayer materials are also represented

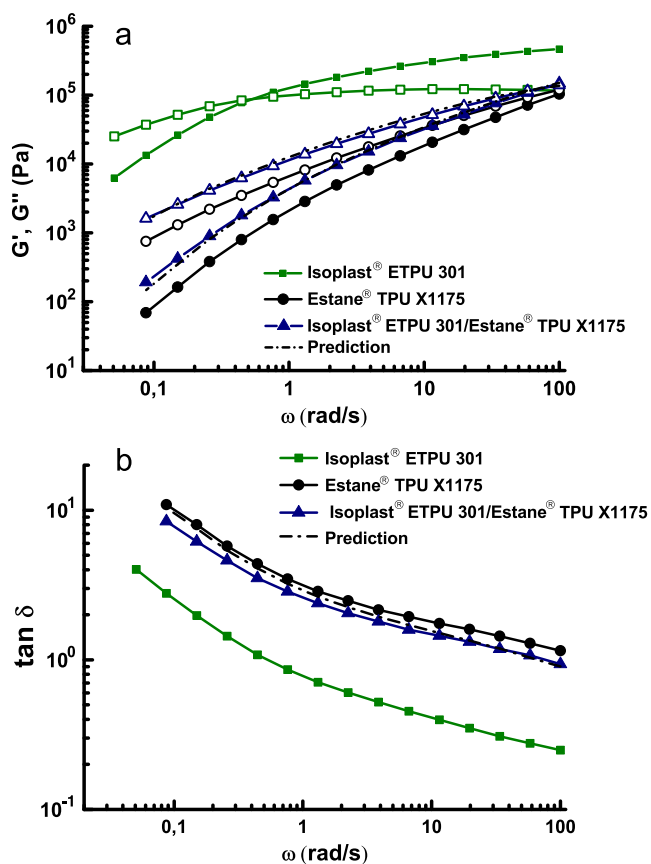


Fig. 8 Small-amplitude oscillatory shear measurements at 175 °C and theoretical predictions for a coextruded bilayer film of Isoplast[®] ETPU 301/Estane[®] TPU X1175 at 175 °C. **a** Dynamic moduli (G' filled symbols, G'' open symbols) and **b** loss tangent. In the figure, the results for the correspondent monolayer materials are also represented

For example, in the limit when the extensional viscosity of one of the components is much higher than the extensional viscosity of the other one, the total viscosity of a film composed by two layers of equal thickness will tend to half of the viscosity of the more viscous one.

The uniaxial extensional viscosities for extruded single materials are shown in Fig. 9. For Isoplast ETPU 301 (Fig. 9a) at low and medium strain rates, the behavior is indicative of strain softening. At high strain rates, the extensional viscosity decreases slightly relatively to the viscoelastic linear regime before assuming a strain-hardening behavior. A similar behavior is observed when strain-induced crystallization occurs (Mchugh et al. 1993). Thus, these results indicate that at high strain rates, the ordered domains grow and become aligned with the direction of flow leading to a large increase of extensional viscosity. In the elastomeric TPUs (Fig. 9b, c) the behavior is again indicative of strain softening at low strain rates. At intermediate rates, the material behaves similarly at first but then the extensional viscosity increases relative to the

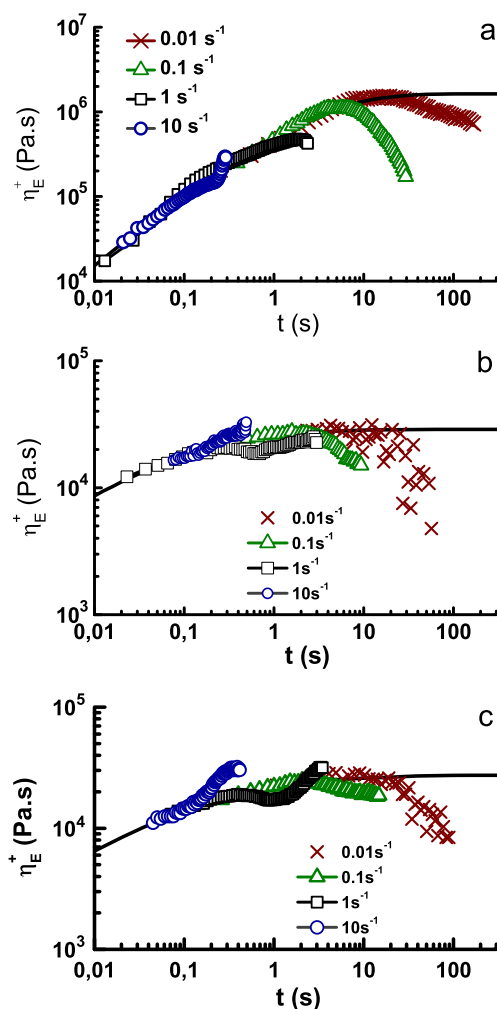


Fig. 9 Extensional results at 175 °C for monolayer extruded films of **a** Isoplast[®] ETPU 301, **b** Estane[®] TPU 58277, and **c** Estane[®] TPU X1175

viscoelastic linear regime. Strain-hardening behavior is observed when high deformation rates are applied.

Figure 10 shows the extensional results for bilayer films and the predictions, assuming no interfacial contribution and/or effects. The shape of theoretical curves and predictions is basically the same, although there are some deviations at 0.1 s⁻¹ that are probably due to experimental errors associated with the high level of difficulty associated with testing these materials. As expected, the results replicate the behavior of more viscous material (Isoplast ETPU 301), so no conclusions can be drawn from these experiments about the existence of a layer interphase between the layers.

Stress relaxation

We have proved in a recent work that stress relaxation experiments are very sensitive to the existence and

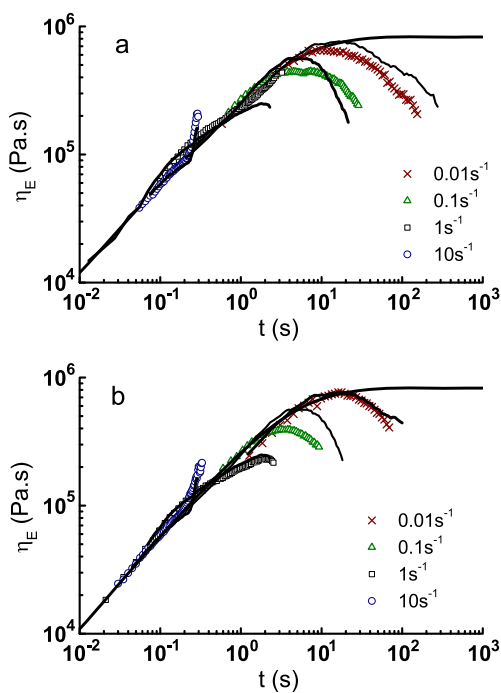


Fig. 10 Extensional results at 175 °C for bilayer films of **a** Isoplast® ETPU 301/Estane® TPU 58277 and **b** Isoplast® ETPU 301/Estane® TPU X1175 and theoretical predictions assuming that layers are deforming independently of each other

nature of interfaces in polymer blends (Silva et al. 2007, 2010a). As in previous cases discussed below, it is also possible to predict the behavior of the bilayer film assuming zero interfacial thickness and no slip between the layers. If the materials are in the viscoelastic linear domain, the relaxation modulus, G , does not depend on the strain and the following relations are valid:

$$G_A(t) = \frac{\sigma(t)}{\gamma_A} \tag{11a}$$

$$G_B(t) = \frac{\sigma(t)}{\gamma_B} \tag{11b}$$

As was explained above, under these conditions, the shear stress is constant throughout the sample. Combining Eqs. 2 and 11 and taking into account that $G_t(t) = \sigma(t)/\gamma_t$, the following expression is obtained:

$$\frac{1}{G_t(t)} = \frac{\phi_A}{G_A(t)} + \frac{\phi_B}{G_B(t)} \tag{12}$$

A deformation of 10 % was applied for approximately 0.01 s to both the single and the bilayer materials, and the relaxation modulus was measured. The results and their respective predictions for the relaxation modulus normalized to its initial value are shown in Fig. 11. First, it can be observed that Isoplast ETPU 301 and the different grades of Estane have very different re-

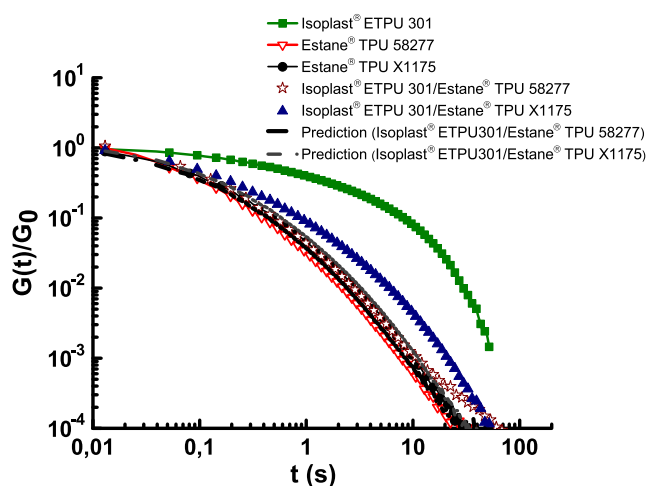


Fig. 11 Normalized relaxation modulus at 175 °C for coextruded bilayer Isoplast® ETPU 301/Estane® TPU 5827, Isoplast® ETPU 301/Estane® TPU X1175, and for the monolayer films. A step strain of 10 % was applied in all cases

laxation kinetics, with the two grades of Estane relaxing much faster and very similarly to each other. Equation 12 predicts that in both films, the kinetics of relaxation should resemble the relaxation kinetics of the material that relaxes faster. However, the coextruded materials do not have the same behavior. Isoplast ETPU 301/Estane TPU 58277 follows the behavior of the soft layer until $t = 10$ s, as predicted theoretically, and then exhibits an extra shoulder. From these results, it is clear that, as expected, in the case of Isoplast ETPU 301/Estane TPU 58277, the short term relaxation dynamics is dominated by the soft layer, with the influence of the hard layer only being felt at very long times, when the soft phase has already relaxed. In the case of Isoplast ETPU 301/Estane TPU X1175, the film exhibits a longer relaxation time compared to the theoretical predictions throughout the entire relaxation process. These results are indicative of the presence of a large and rough interphase which contributes positively to the relaxation modulus and are in good agreement with the previous optical microscopy observations.

Conclusions

This paper aimed at establishing which, if any, rheometrical techniques were sensitive to the nature of the interphase in coextruded sheets of amorphous glass and elastomeric TPUs. Two TPU bilayer films were used: Isoplast ETPU 301/Estane TPU 58277 and Isoplast ETPU 301/Estane TPU X1175. As observed by AFM, the films have interphases with different natures and

thicknesses: the former has a sharp and thinner one and the latter, a rough and larger one. Since no predictive expressions existed in the literature to predict the respective material functions assuming zero interfacial thickness and no interfacial slip, for both SAOS and stress relaxation experiments, these were deduced and validated against the experimental data.

The results for steady shear, SAOS and uniaxial extensional experiments all follow essentially the theoretical predictions assuming zero interfacial thickness and no interfacial slip, which means that for these hard TPU/soft TPU bilayer systems, these rheological techniques are not sensitive to the nature of the interphase. This may partially be due to the fact that these films only had one interface/interphase and thus have a relatively low interfacial area per volume unit of the samples. This shortcoming could presumably be overcome by increasing the number of layers in the film, possibly using layer-multiplying die technology such as that of Baer and coworkers (see for example, Baer et al. (2000)). However, the very different viscosity levels of the amorphous glass and elastomeric TPUs would probably lead to interfacial instabilities in multilayer coextrusion, which would make the exercise very difficult, if not impossible. Only shear stress relaxation experiments were able to detect rheologically the presence of an interphase in Isoplast ETPU 301/Estane TPU X1175, as observed by AFM, via slower relaxation kinetics relative to the theoretical prediction.

Acknowledgements The authors would like to acknowledge Lubrizol Advanced Materials, Inc. and NSF STC Center CLiPS–Center for Layered Polymer Systems for financial support. Ricardo Andrade would also like to acknowledge the financial support of FCT-Foundation for Science and Technology, Portugal, through grant no. SFRH/BD/62152/2009. The authors would like to express their sincere gratitude to Prof. Savvas G. Hatzikiriakos for providing his lab in performing the extensional studies of the materials. They would also like to thank Tom Braden for extruding the bilayer films. Estane[®] TPU and Isoplast[®] ETPU are trademarks of The Lubrizol Corporation.

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