INFLUENCE OF INTERFACIAL TENSION ON THE MORPHOLOGY OF POLYMER BLENDS

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Abstract

The transient interfacial tension σ has been measured by means of a temperature controlled pendent/sessile drop apparatus and the influence of molecular weight, polydispersity and temperature on σ have been analyzed. The results show that the polymer pairs PB/PBD/PDMS used in this work cannot be considered fully immiscible and, to a certain extent, diffusion is always present. The interfacial tension changes significantly in time and decreases while increasing the polydispersity when the dispersed phase molecular weight is lower than the one of the continuous phase. This is attributed to the migration of short molecules from the drop into the matrix. Minor changes are reported for the reversed systems. The larger the molecular weight asymmetry across the interface, the more the interfacial tension is eligible to changes. A kinetic model is applied for σ(t) which enables a qualitative and quantitative investigation of the rates of transport of the migrating species.

The impact of the interfacial tension on the flow-induced morphology is examined by means of in-situ techniques for 1% concentrated blends at the temperature of 23°C and at viscosity ratio λ of 1. Depending on the type of interfacial response, the morphology development in the early stages is dominated by either diffusion or coalescence. The results are compared with the drop size evolution calculated from a drainage model for sharp interfaces, using either an immobile or partially mobile interface formulation.

Introduction

The mixing of two or more polymers is a common industrial route to produce materials with tailor-made properties. Among the many morphological phenomena that occur during preparation and processing of polymer blends, the interfacial tension is a crucial one. In many cases in literature, mutual solubility is assumed negligible [1 - 4] because the mixing of different polymers is thermodynamically unfavorable [5]. Moreover, polymers consist of long molecules and possess high viscosities; consequently the kinetics of polymer-polymer diffusion is expected to be slow compared to the experimental time-scale [6]. However, if a large asymmetry in molecular weight across the interface is considered, the smaller (i.e. faster) molecules, can diffuse from one phase into the other giving rise to mass transport in the same time-scale as the experiments. These transport phenomena drive changes in the interfacial thickness as function of time and, therefore, in the time evolution of the interfacial tension [7]. Although many studies have been performed on break up for the single drop and coalescence for two or more droplets, only a limited literature is available on mutual diffusion combined with coalescence and break-up phenomena [8 - 13].

The goal of this work is to study the evolution of interfacial tension in time and temperature as function of molecular weight and molecular weight asymmetry across the interface. Measurements of the volume changes of a single drop in the matrix are performed

to estimate the relevance of diffusion in the experimental time-scale and characteristic times for diffusion are calculated using a double exponential model [13]. The influence of interfacial tension on the drop size evolution in time is investigated by Small-Angle Light Scattering (SALS) and optical microscopy and compared with prediction of a drainage model.

Materials and methods

The materials selected in this study, molecular weights, polydispersities, viscosities and densities at 23^oC are reported in Table 1.

Table 1. Material properties.

Sample	M_n	M_w/M_n	Viscosity Pa·s	Density g/cm^3
PB (H25)	635	2.1	3.7	0.8742
PB (H300)	1300	1.65	44.5	0.8980
PB (H1200)	2100	1.8	307.6	0.9031
PBD	8000	1.1	13.6	0.8911
PDMS	62700	1.8	10.9	0.9726

Measurements of interfacial tension as function of time and with temperature have been carried out by means of a sessile/pendant drop apparatus [14, 15, 16]. PBD/PDMS and PB635/PDMS blend morphologies are investigated with in-situ techniques. The SALS patterns have been analyzed applying the theory of Debye-Bouche for randomly arranged systems with a two-phase structure [17] while the optical images were analyzed manually.

Interfacial tension

One of the first mathematical models proposed to predict the time dependence of interfacial tension for a polymer blend [18], consists of a single exponential equation. Later, a double exponential model was reported [19] and the time dependence of interfacial tension was attributed mainly to the diffusion of the components in the vicinity of the phase boundary and to the hydrodynamic relaxation of the droplet. The case in which diffusion is due to polydispersity of the materials has been published recently [13] showing that the double exponential model still holds. The basis of this model is the dependence of the interfacial tension on the molecular weight of the polymers. For a binary system it can be shown that interfacial tension decreases while decreasing the molecular weight of one phase and keeping constant the molecular weight of the second phase. Due to this difference, the lower molecular weight chains migrate to the interface to lower the interfacial tension (i.e. the Gibbs

energy of the system). For a generic A/B binary system, it can be demonstrated that the interfacial tension varies in time according to Eq.1.

$$\sigma = \sigma_s + \Delta\sigma_{s,A} e^{-1/\tau_A} + \Delta\sigma_{s,B} e^{-1/\tau_B} \tag{1}$$

whith σ is the interfacial tension, σ_s the steady-state value, τ_A and τ_B characteristic times, $\Delta\sigma_{s,A}$ and $\Delta\sigma_{s,B}$ contribution of the different migrating components to the interfacial tension behavior of the whole system.

Sharp interface drainage model

Coalescence can be seen as a four stages process: (1) the collision between two droplets; (2) the Stokes drag force is the driving force to drain the matrix film trapped between the two coalescing droplets; (3) the rupture of the aforementioned film; (4) the drop coalescence. According to this four step model, there exists a minimum distance between the droplets, h_0, at which hydrodynamic interactions become significant and collision starts. The next stage is the drainage of this film which occurs with a rate of dh/dt. While the thickness of the films reduces, also the drainage rate is reducing in time. A critical value of the film thickness, h_{cr}, which is governed by van der Waals forces, can be defined. When this critical value is reached, due to the rising instabilities at the interface, rupture of the film occurs and drops coalesce. The minimum contact time required to obtain coalescence is the time to achieve film rupture. Assuming that the contact time is equal to the drainage time, it is possible to estimate a maximum radius, R, below which coalescence occurs. Two different cases are presented in relation to the mobility of the interfaces:

Immobile interfaces: $R = \left(\dfrac{32}{9}\right)^{1/4} \left(\dfrac{h_{cr}\sigma}{\eta_m\dot{\gamma}}\right)^{1/2}$ (2)

Partially mobile interfaces: $R = \left(\dfrac{4}{\sqrt{3}}\dfrac{h_{cr}}{p}\right)^{2/5} \left(\dfrac{\sigma}{\eta_m\dot{\gamma}}\right)^{3/5}$ (3)

where η_m is the viscosity of the continuous phase, λ is the viscosity ratio ($\lambda = \eta_d/\eta_m$, with η_d the dispersed phase viscosity) and $\dot{\gamma}$ is the shear rate. The main problem is to get the right value for h_{cr}. Two different models have been proposed [20] which allow the prediction of h_{cr} values in a partially mobile regime. Model I is based on the approximation of constant pressure and interfacial tension in the region outside the film. However, the region in which σ changes from the "equilibrium" value to an approximate constant external value will be the region in which the two continuous phase-concentration boundary layers meet. The thickness of these layers grows with time and this region tends to move outside the film. This phenomenon is taken into account in model II, in which the Marangoni term becomes weaker as time progress and the drainage tends asymptotically to the rate in absence of mass transfer. It is reported that Model I suffices for practical purposes whenever the transfer is from drop into the matrix, while Model II applies when mass transport is from the matrix into the drop. However, the molecular diffusivity of the pairs is input parameters to the model II

and its value is not known. Although the model I does not apply, Eq.4, proposed for the model I, will be used also when diffusion is from the matrix into the drop.

$$h_{cr} \approx \left(\frac{AR}{8\pi\sigma} \right)^{1/3}$$

(4)

where A is the Hamaker constant (O(10^{-21} J)). This expression shows proportionality to the parameters, therefore a qualitative, more than a quantitative, discussion will be presented. The values calculated for immobile and partially mobile interfaces are meant as limits for the evolution of the morphology.

Interfacial tension results

M_n dispersed phase < M_n continuous phase

In Table 2 the initial radius of the drop phases and the variations in the radius after 4 hours, ΔR_{4h}, are reported at room temperature. As no external factors influenced the drop volume during the measurements, any variation is attributed to mutual diffusion [12]. The mutual solubility between PB635 and PDMS is higher than the mutual solubility for the PBD8000/PDMS system. Since the diffusion layer around a drop was estimated to be at least of the order of magnitude of ΔR, the system PB635/PDMS has a thicker interface compared with the system PBD/PDMS. Comparing the three grades of PB, the rate of change of the radius increases with the molecular weight.

Table 2. Drop radius reduction over a period of 4 hours.

Drop phase	R_0 [mm]	ΔR_{4h} [μm]
PB 635	1.13	209
PB 1300	1.25	13
PB 2100	1.44	0
PBD 8000	1.22	6

At T=23°C, a reduction in interfacial tension, which corresponds to the thickening of the interface, is observed, see Figure 1, left. This reduction was attributed to some solubility of the lower molecular weight in the corresponding receiving matrix phase [13]. Proceeding in time, a minimum value of the interfacial tension is reached. This is the time at which depletion of the interphase occurs due to the limited material contained in the source phase and the continuous transport from the interface to the receiving phase. As a result of the interphase depletion, the interfacial tension increases again. In the final stage, a plateau value for the interfacial tension, corresponding to the equilibrium conditions, is reached. As the temperature is increased, the minimum reached goes down and shifts to the right. The higher the temperature, the lower the viscosity of the materials and, therefore, the chains will have higher mobility (more chains to the interface, lower interfacial tension). Increasing the

amount of low molecular weight material at the interface, longer time is needed to complete the diffusion process (i.e. the minimum shifts to the right). The same conclusion can be drawn for the other two grades of PB reported in Figure 2. For the PBD/PDMS blend (Figure 1 right), a fast reduction for the two higher temperatures and a fast increase for the two lower one are followed by the plateau. Diffusion in this case is only a minor phenomenon.

M_n dispersed phase > M_n continuous phase

The diffusion is from the matrix into the drop. A fast reduction in interfacial tension is observed in time for both cases and at all temperatures investigated. Considering that the drop is much smaller than the matrix, the limiting phenomenon for diffusion is the fast saturation of the drop phase (see Figure 3).
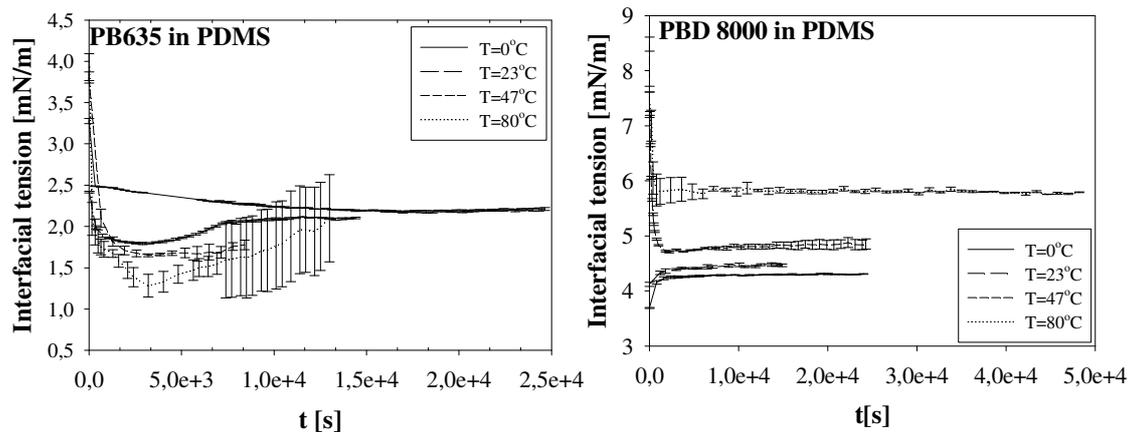

Figure 1. Interfacial tension as function of time and temperature for the lowest (left) and the highest (right) molecular weight dispersed phase in PDMS.
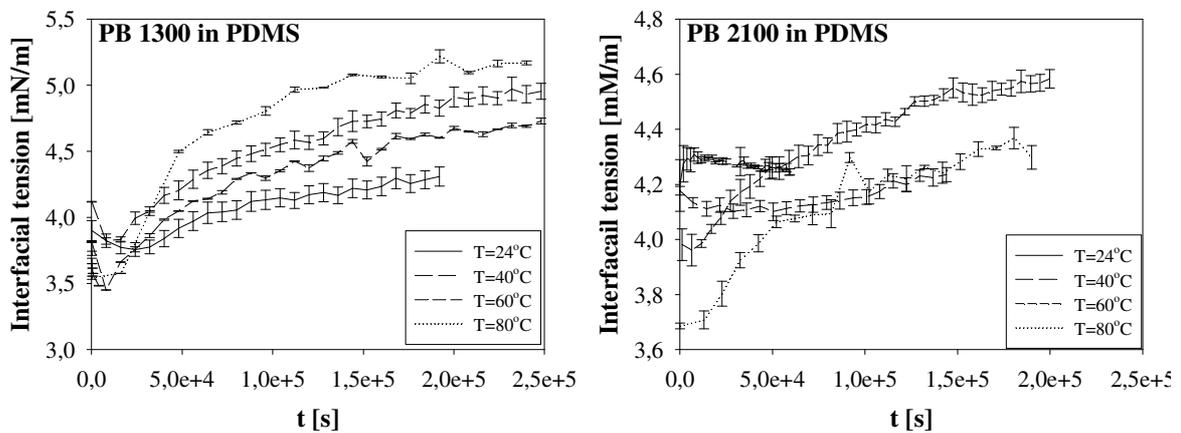

Figure 2. Interfacial tension as function of time and temperature for PB 1300 and PB 2100.
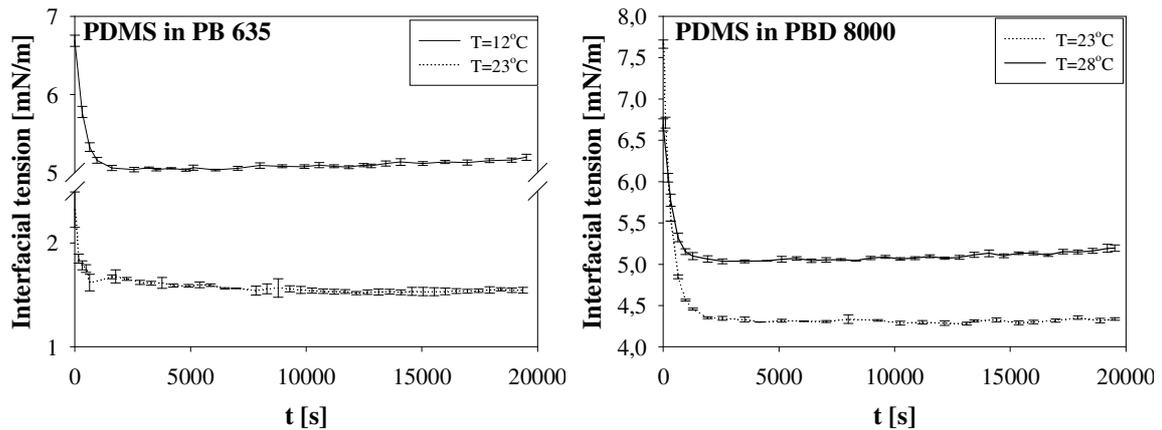
Figure 3. Interfacial tension as function of time and temperature for the reversed systems.

Influence of temperature on steady state interfacial tension

Figure 4 left shows steady values of the interfacial tension (the last value was taken if no plateau was reached yet) as a function of temperature. It is observed that the steady interfacial tension decreases while increasing the polydispersity. For the broader molecular weight distribution systems, the lower molecular weight part will preferentially sit at the interface, effectively lowering the interfacial tension [13, 21, 22].
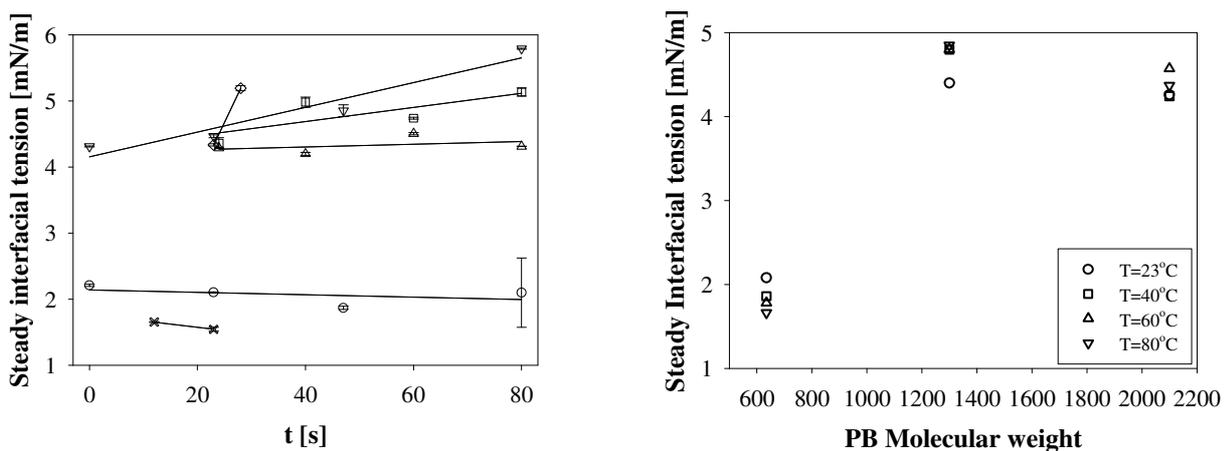

Figure 4. Left: Interfacial tension as function of temperature for PB 635 (○), PB 1300 (□), PB 2100 (△), PBD 8000 (▽) in PDMS, PDMS in PB 635 (x), PDMS in PBD 8000 (◇). Right: Influence of the drop molecular weight on the steady interfacial tension value.

Influence of molecular weight on steady state interfacial tension

Figure 4 (right) shows the steady interfacial tension as function of the molecular weight for the different temperatures. The blends having as drop phase PB635, PB2100 and PB1300 and as matrix PDMS62700 are taken into account. Increasing the molecular weight of the dispersed phase, the interfacial tension increases and eventually reaches a plateau [23, 24].
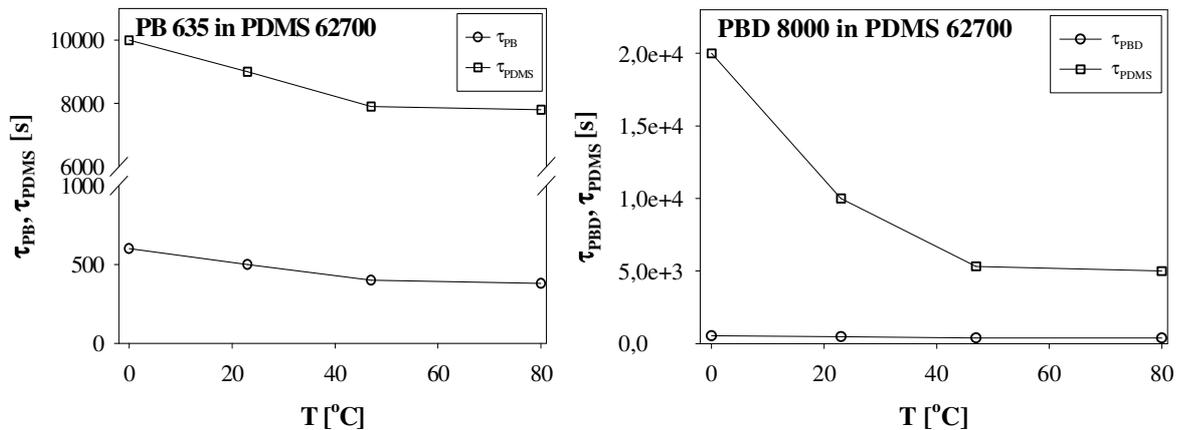
Fitting of the diffusion times

Figure 5. Prediction of diffusion times $\tau_{PB,PBD}$ and τ_{PDMS} at four different temperatures for the most diffusive (PB 635 drop phase) and the less diffusive (PBD 8000 drop phase) polymer pairs.

Eq.2 was fitted on the data shown in Figure 1-3 in order to get the characteristic times of transport, τ_{drop} and τ_{matrix}. The results for two different blends are reported in Figure 5.

The data demonstrates that the short chains component of PB diffuse more rapidly than the short chains component of PBD supporting the interpretation given above of the interfacial tension behavior in time. The same trend for τ_{drop} and τ_{matrix} has been found for all the blends under investigation.

Morphology prediction for low concentrated blends

Figure 6 (left) reports the time evolution of the average drop radii obtained with in-situ techniques and of the interfacial tension at 23oC for the 1% in weight concentrated PB 635 blend. Clearly the morphology follows the trend of the interfacial tension. Two parallel phenomena are going on: the diffusion, which reduces the drop radii due to mass transport, and the coalescence, which leads to increasing radii. In the first 3000s of the experiment, diffusion is very strong and therefore, despite coalescence, a reduction in the drop size occurs. Proceeding in time, diffusion slows down and coalescence takes over resulting in increasing radii till a plateau value is reached. In order to prove that the reduction in drop size is due to diffusion, the same experiment has been repeated with a 48 hours old blend. The reduction in drop size is not present anymore and the average radius of the droplets increases due to coalescence (Figure 6 right).
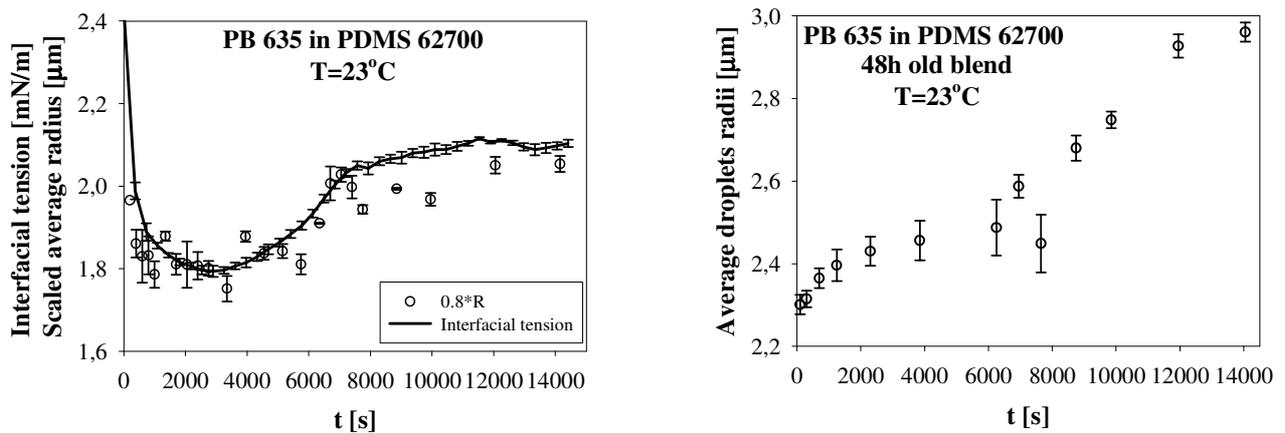
Figure 6. Interfacial tension and average drop radii obtained for the fresh 1% concentrated PB 635/PDMS blend (left) and drop radius evolution in time for the same blend after 48h (right).

A comparison of the experimental average radii with the radii calculated with the drainage model is reported in Figure 7 for the same blend. For all the other blends investigated, experiments are carried out at room temperature and at $\lambda=1$. The average radii follow the typical coalescence behavior whenever the interfacial tension does not change much in time.
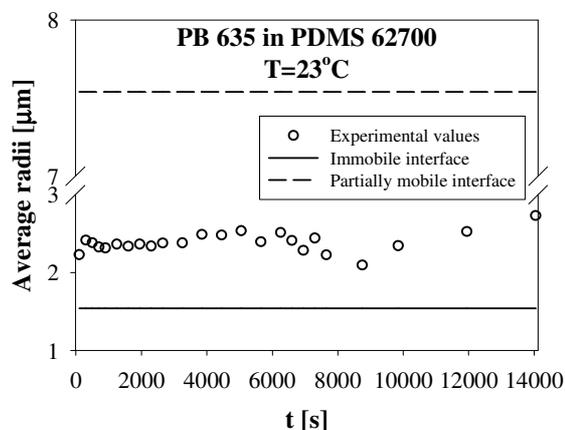

Figure 7. Experimental radii limited by the radii predicted using the immobile and partially mobile formulations for the 1% in PB concentrated blend.

Conclusions

Interfacial tension measurements show that interfacial tension changes in time for all the polymer pairs under investigation and a time scale for diffusion can be derived. Characteristic times for the mass transport have been calculated, supporting the diffusion

process hypothesis. It has been shown that changes in interfacial tension are more pronounced when the asymmetry in molecular weight across the interface is higher. From the experiments discussed it can be concluded that increasing the polydispersity the interfacial tension decreases, increasing the molecular weight of the drop phase the interfacial tension increases and eventually reaches a plateau. Increasing the temperature, according to the polymer pairs characteristics, different trends in the steady interfacial tension values are reported. It has been shown that the morphology of 1% in weight concentrated blend is affected by the diffusion process and a relation between the morphology and the interfacial tension has been highlighted.

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