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Influence of composition on the linear viscoelastic behavior and morphology of PP/HDPE blends

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Abstract

In this paper the influence of temperature and composition on the dynamic behavior and morphology of polypropylene (PP)/high-density polyethylene (HDPE) blends were studied. The blend composition ranged from 5 to 30 wt% of dispersed phase (HDPE) and the temperatures ranged from 180 to 220 °C. The interfacial tension between PP and HDPE at temperatures of 180, 200 and 220 °C was obtained from fitting Palierne's emulsion model [1] to the experimental data of PP/HDPE blends with different compositions and from the weighted relaxation spectra of PP/HDPE blends with different compositions, following Gramespacher and Meissner [2] analysis. The interfacial tension between PP and HDPE as inferred from the rheological measurements was shown to depend on PP/HDPE blend composition. However, the results indicated that there is a range of PP/HDPE blend composition for which interfacial tension between PP and HDPE is constant. Considering these values, it was shown that interfacial tension between PP and HDPE decreases linearly with increasing temperature. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Interfacial tension; Linear viscoelasticity

1. Introduction

Most polymers are immiscible thermodynamically, forming when blended multiphase materials. The properties of immiscible polymer blends can be optimized by controlling the blend morphology, which in turn is strongly dependent on the rheological behavior of the blend. In the case of immiscible blends, the rheological properties depend on the blend composition, properties of the components as well as the morphology and interactions between phases, characterized by the interfacial tension between the polymers forming the blend [3].

Among various methods to measure interfacial tension between two liquids only a few are suitable for molten polymers because of their high viscosity. In general, the equilibrium methods are most commonly used. These methods involve the evaluation of a profile of either sessile, spinning or pendant drop [4]. Dynamic methods based on the breaking thread and imbedded fiber retraction [5–8] can be also used. However, both equilibrium and dynamic methods cannot be used to evaluate the interfacial tension between PP and HDPE due to experimental difficulties encountered. The equilibrium and dynamic methods rely on the visualization of a drop (in the case of sessile, spinning or pendant drop) or fiber (in the case of breaking thread or imbedded fiber retraction) in a matrix. The refraction indexes of molten PP and HDPE are the same order of magnitude [9], making the distinction between phases impossible unless artifacts such as addition of carbon black to one of the phases [10] are used. Consequently, reported values of interfacial tension for polypropylene (PP)/polyethylene (PE) polymer pair are very scarce.

Recently, a large effort has been conducted to increase the understanding of the relationship between viscoelastic properties and the morphology of blends. Many theoretical models have been developed to predict the linear viscoelastic behavior of polymer blends [1,2,11–16]. These models relate the dynamic response of polymer blends to their morphology, composition and interfacial tension between the components. Therefore, using these models, it is possible to infer interfacial tension from the dynamic behavior of the blend once the blend morphology has been characterized. Two of these models are briefly discussed below.

Making the assumption that small strains do not alter the polymer blends morphology and that interfacial tension is independent of local area variation, Graebling et al. [12–15], using Palierne's Emulsion Model [1], developed a constitutive equation that predicts the complex shear modulus ($G^*(\omega)$) of a blend, as a function of its morphology, the

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interfacial tension between its components and the complex shear modulus of the pure phases, given by:

$$G^* = G^*_{\rm m}\frac{40\left(\frac{\gamma}{R_{\rm v}}\right)[G^*_{\rm m} + G^*_{\rm d}] + [2G^*_{\rm d} + 3G^*_{\rm m}][16G^*_{\rm m} + 19G^*_{\rm d}] + 3\phi\left[4\left(\frac{\gamma}{R_{\rm v}}\right)[2G^*_{\rm m} + 5G^*_{\rm d}] + [G^*_{\rm d} - G^*_{\rm m}][16G^*_{\rm m} + 19G^*_{\rm d}]\right]}{40\left(\frac{\gamma}{R_{\rm v}}\right)[G^*_{\rm m} + G^*_{\rm d}] + [2G^*_{\rm d} + 3G^*_{\rm m}][16G^*_{\rm m} + 19G^*_{\rm d}] - 2\phi\left[4\left(\frac{\gamma}{R_{\rm v}}\right)[2G^*_{\rm m} + 5G^*_{\rm d}] + [G^*_{\rm d} - G^*_{\rm m}][16G^*_{\rm m} + 19G^*_{\rm d}]\right]} \tag{1}$$

where G^*, $G^*_{\rm m}$, $G^*_{\rm d}$ are the complex shear moduli of the blend, matrix and dispersed phase, respectively; γ is the interfacial tension between the components of the blend; ϕ is the volume fraction of dispersed phase and $R_{\rm v}$ is the volume average radius of dispersed phase defined by:

$$R_{\rm v} = \frac{\sum_i R_i\phi_i}{\sum_i \phi_i} \tag{2}$$

where R_i is the radius of each droplet and ϕ_i the volume fraction of each droplet.

In order for the constitutive equation to be valid the ratio $R_{\rm v}/R_n$ should be smaller than 2, with R_n defined as:

$$R_n = \frac{\sum_i n_iR_i}{\sum_i n_i} \tag{3}$$

where R_i is the radius of each droplet and n_i the number of droplets with a radius R_i.

In the case when the ratio $R_{\rm v}/R_n$ is higher than 2, each radius and volume fraction must be taken into account individually, resulting in a much more complex expression for $G^*(\omega)$.

The model described above can be used to infer interfacial tension if a secondary plateau is observed in the storage modulus curve [15]. This secondary plateau occurs because of the form relaxation of the dispersed phase droplets. Using the model described above, Graebling et al. [15] determined the interfacial tension between polystyrene (PS) and polyethylmethacrylate (PEMA) at 180 °C using a PS/PEMA blend. The authors also showed that there was a good agreement between the dynamic behavior of polydimethylsiloxane/polyethylene-diol (PDMS/POE-DO) and polystyrene/polymethylmethacrylate (PS/PMMA) blends and the theoretical prediction of their model. However, they could not infer interfacial tension for PDMS/POE-DO and PS/PMMA blends because no secondary plateau was observed in the storage modulus ($G'(\omega)$) of the blend as function of frequency.

In order to evaluate the interfacial tension between two polymers using the linear viscoelastic behavior of blends, Gramespacher and Meissner [2] developed a constitutive equation for an emulsion based on the work of Choi and Schowalter [11] and on a linear mixing rule. This constitutive equation considers the complex modulus of a blend as a combination of the contribution of the shear moduli of the viscoelastic phases plus the contribution of the interface. These researchers obtained the following equations for the complex storage and loss moduli of the blend when submitted to a small amplitude oscillatory shear:

$$G^*(\omega) = \phi G^*_{\rm d}(\omega) + (1-\phi)G^*_{\rm m}(\omega) + G^*_{\rm interface}(\omega) \tag{4}$$

$$G'(\omega) = \phi G'_{\rm d}(\omega) + (1-\phi)G'_{\rm m}(\omega) + \frac{\eta}{\tau_1}\left(1 - \frac{\tau_2}{\tau_1}\right)\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2} \tag{5}$$

$$G''(\omega) = \phi G''_{\rm d}(\omega) + (1-\phi)G''_{\rm m}(\omega) + \frac{\eta}{\tau_1}\left(1 - \frac{\tau_2}{\tau_1}\right)\frac{\omega\tau_1}{1+\omega^2\tau_1^2} \tag{6}$$

with

$$\eta = \eta_{\rm m}\left[1 + \left(\frac{5K+2}{2K+2}\right)\phi + \left(\frac{5(5K+2)^2}{8(K+1)^2}\right)\phi^2\right] \tag{7}$$

$$\tau_1 = \left(\frac{\eta_{\rm m}R}{\gamma}\right)\frac{(19\,K+16)(2\,K+3)}{40(K+1)} \times\left(1 + \phi\frac{5(19\,K+16)}{4(K+1)(2\,K+3)}\right) \tag{8}$$

$$\tau_2 = \left(\frac{\eta_{\rm m}R}{\gamma}\right)\frac{(19\,K+16)(2\,K+3)}{40(K+1)} \times\left(1 + \phi\frac{3(19\,K+16)}{4(K+1)(2\,K+3)}\right) \tag{9}$$

where G^*, $G^*_{\rm m}$, $G^*_{\rm d}$ are the complex shear moduli of the blend, matrix and dispersed phase, respectively; G'', $G''_{\rm m}$, $G''_{\rm d}$ are the loss moduli of the blend, matrix and dispersed phase, respectively; G', $G'_{\rm m}$, $G'_{\rm d}$ are the storage moduli of the blend, matrix and dispersed phase, respectively; ω is the frequency of oscillation; η, $\eta_{\rm m}$, $\eta_{\rm d}$ are the Newtonian viscosities of the blend, matrix and dispersed phase, respectively; $K = \eta_{\rm d}/\eta_{\rm m}$ the viscosity ratio; γ the interfacial tension between the components of the blend; ϕ the volume

Table 1
Materials used in this work

Polymers	$\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$	Melt index (g/10 min)	Zero shear stress viscosity (η_o) at 180 °C (Pa s)	Zero shear stress viscosity (η_o) at 200 °C (Pa s)	Zero shear stress viscosity (η_o) at 220 °C (Pa s)
PP	340,000	4.5	8	27,000	17,200	10,700
HDPE	140,000	3.2	8	10,900	9,040	8,050

fraction of dispersed phase and R is the radius of the monodispersed droplets.

The term τ_1 is the form relaxation time of the dispersed phase droplets and corresponds to an extra relaxation time in the discrete relaxation spectrum of the blend [2,17]. The blend relaxation spectrum is thus a combination of the relaxation spectra of the different phases of the blend (bulk) and an additional peak τ_1, from which the interfacial tension between the components of the blend can be inferred. Gramespacher and Meissner [2] used the relaxation spectrum of polystyrene/polymethylmethacrylate (PS/PMMA) blend to measure the interfacial tension between PS and PMMA, at 170 °C. Their result was in good agreement with the interfacial tension determined from recovery after melt elongation for the same blend. Macaúbas and Demarquette [18] also used this method to evaluate the interfacial tension between polypropylene (PP) and polystyrene (PS), at 200 °C. Their results were in good agreement with the interfacial tension between PP and PS obtained by the pendant drop method.

Some studies have shown that may be there is an influence of blend composition on the determination of interfacial tension between the components of the blend using dynamic data [3,19,20]. However, no systematic study of the effect of the blend composition on the dynamic data of the blends has been carried out.

In this work, PP/HDPE blends with different compositions were investigated. The effects of blend composition and temperature on the morphology and on the linear viscoelastic behavior of the blends were studied. The possibility of inferring interfacial tension between PP and HDPE using small amplitude oscillatory shear measurements of blends with different compositions was addressed. Finally the effect of temperature on the interfacial tension between PP and HDPE was studied.

2. Experimental

2.1. Materials

Commercial polypropylene (PP) from Polibrasil SA, and high-density polyethylene (HDPE) from Ipiranga Petroquímica SA were used in this work. The characteristics of the polymers are listed in Table 1.

2.2. Blending

Blends of PP/HDPE were prepared in different weight concentrations (PP/HDPE: 95/5, 90/10, 85/15, 80/20, 75/25 and 70/30). The blends were prepared in a Werner & Pfeiderer twin-screw extruder, model ZSK-30 with six zones of temperatures, ranging from 170 to 210 °C along the barrel of the extruder.

2.3. Rheological measurements

Samples for rheological tests were obtained by compression molding. Discs of 25 mm diameter and 1 mm in thickness were molded at a temperature of 200 °C, under an isostatic pressure of 18 MPa, during 30 min.

Rheological tests of the samples were carried out using a controlled shear rheometer (model SR-5000 from Rheometric Scientific) under dry nitrogen atmosphere. A parallel-plate configuration was used with a gap size of 0.6 mm and a plate diameter of 25 mm. Strain and stress sweeps tests were performed for all blends and pure polymers to define the linear viscoelasticity region. Dynamic frequency sweeps were performed for all blends and pure polymers at temperatures of 180, 200 and 220 °C. The stress varied from 10 to 500 Pa and the strain from 0.8 to 4%. The zero-shear viscosity of the individual phases necessary to calculate the interfacial tension was determined by Carreau model [21] using the curve Eta*(Pa s) × frequency (rad/s) obtained from dynamic frequency sweeps tests.

2.4. Morphological characterization

The morphology of the blends was characterized by Scanning Electron Microscopy (SEM) using a Cambridge microscope, model Stereoscan 240. The samples were fractured in liquid nitrogen and then covered with gold using a Balzers sputter coater, model SCD-050.

The average diameter and volume fraction of the dispersed phase were calculated using the SEM photomicrographs. About 300 particles were used to calculate these parameters. For the calculation of average size of the dispersed phase, the Saltikov's correction [22] was used. This correction takes into account the polydispersity of the dispersed phase droplets and the fact that the fracture in the sample does not always occur at the maximum diameter of the droplets.

3. Results and discussion

3.1. Morphology

Fig. 1 shows the morphology of PP/HDPE (80/20) blend

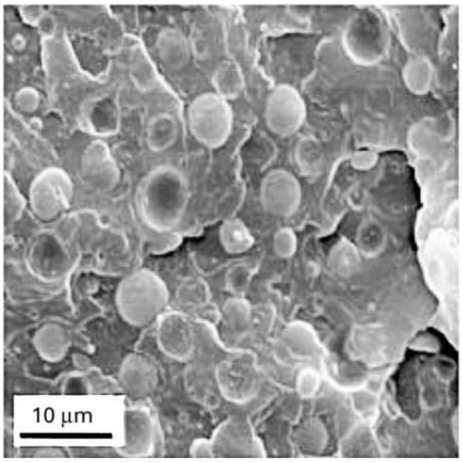

Fig. 1. Morphology of PP/HDPE (80/20) blend after compression molding.

after compression molding. A droplet dispersion morphology type can be observed. This type of morphology was observed for all blends after compressing molding. Fig. 2 shows the number average radius (R_n) and volume average radius (R_v) of the dispersed phase as a function of HDPE concentration in PP/HDPE blends. The volume and average radii are defined by Eqs. (2) and (3), respectively. They are represented by different symbols and the continuous lines are just guides for the eyes.

It can be seen from Fig. 2 that the number average radius and volume average radius of the dispersed phase increases as a function of increasing concentration of HDPE in PP/HDPE blends. This fact can be due to an increase of coalescence of dispersed phase with the increase of dispersed phase concentration. This phenomenon has been already observed by other researchers [23,24]. It can also be seen from Fig. 2 that a marked increase of the droplet diameter sets in at dispersed phase contents of about 10%. Wallheinke et al. [24] observed in their studies with thermoplastic polyurethane/polypropylene (TPU/PP) and thermoplastic polyurethane/polyethylene (TPU/PE) blends (for compositions ranging from 0.1 to 20 wt% of dispersed phase) that a marked increase of the droplet diameter sets in at a much lower dispersed phase concentration of about 1%. The coalescence process could explain the difference between the results of Wallheinke et al. [24] and the results obtained here. Coalescence depends on two principal parameters: the number of droplets collisions and the ability of the blend to drain the film of matrix phase entrapped between two droplets of the dispersed phase until the critical thickness for coalescence to occur is reached [25]: when the number of droplets collisions and the ability of film drainage are high, the coalescence can occur at low dispersed phase concentration. The number of droplets collisions is proportional to the square of the dispersed phase concentration and is inversely proportional to the droplet size [25]. Film drainage is a complex phenomenon that depends on the interfacial tension between both polymers and is inversely proportional to the viscosity of the matrix [24]. The lower the interfacial tension and the lower the viscosity ratio dispersed phase/matrix, the slowest is the film drainage. In the case of PP/HDPE blends, the interfacial tension between PP and HDPE is much smaller than the interfacial tension between TPU and Polyolefins (around 1 mN/m vs 8.2 and 9.4 mN/m for TPU/PP and TPU/PE polymer pair [24], respectively). Also, the viscosity ratio of HDPE/PP studied here is smaller than the one for TPU/PE studied by Wallheinke et al. [24] (less than 1 compared to 3.54). These differences of rheological behavior and interfacial tension could explain the differences of magnitude of coalescence observed in the case studied here and the case of Wallheinke et al. [24].

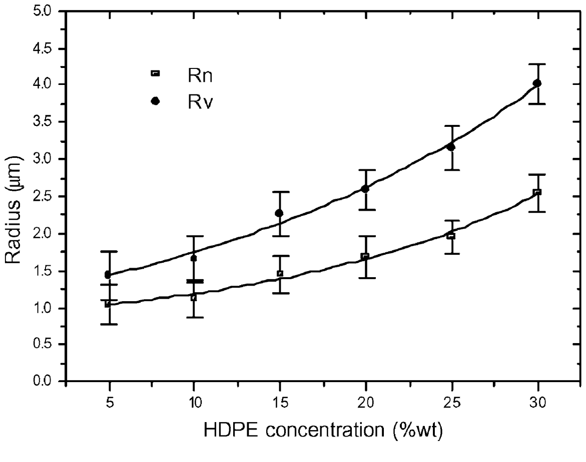

Fig. 2. Number average radius (R_n) and volume average radius (R_v) of the dispersed phase as a function of HDPE concentration in PP/HDPE blend.

The polydispersities (R_v/R_n) of the dispersed phase for PP/HDPE blends with different compositions are shown in Table 2. It can be seen that the polydispersity tends to increase when HDPE concentration in PP/HDPE blends increases. This is due to a greater coalescence for more concentrated blends, which could lead to an increase of heterogeneity of size distribution of dispersed phase [26]. However, for each blend studied here the polydispersity of the inclusions does not exceed 2. This condition is necessary if one wants to use the viscoelastic data of the blend to determine the interfacial tension between its components [15].

Table 2
Polydispersities (R_v/R_n) of the dispersed phase for PP/HDPE blends with different compositions

PP/HDPE blend composition	R_n (μm)	R_v (μm)	R_v/R_n
95/5	1.05 ± 0.27	1.43 ± 0.33	1.36
90/10	1.12 ± 0.24	1.66 ± 0.31	1.48
85/15	1.45 ± 0.26	2.27 ± 0.29	1.56
80/20	1.68 ± 0.29	2.59 ± 0.28	1.54
75/25	1.95 ± 0.23	3.15 ± 0.30	1.61
70/30	2.54 ± 0.25	4.01 ± 0.27	1.59

3.2. Rheological measurements

Figs. 3 and 4 show the storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli of the PP/HDPE blends with different compositions and of the pure phases when submitted to oscillatory shear at a temperature of 220 °C. It can be seen that for low frequencies the storage moduli ($G'(\omega)$) of the PP/HDPE blends for every composition are greater than those of the pure phases and are increasing when the dispersed phase (HDPE) concentration is increasing. These observations were made for all temperatures studied in this work (180, 200 and 220 °C). The enhancement of elasticity of the blends when compared to the pure phases, at low frequencies, has already been reported by many researchers for different polymer blends [2,3,12–16,18,27–29]. This behavior can be attributed to a form relaxation process of the dispersed phase droplets when slightly sheared. When the dispersed phase (HDPE) concentration increases, it is observed that the diameter of dispersed phase increases and the relaxation process of the dispersed phase becomes longer, leading to an increase of the storage modulus.

It can be seen from Fig. 3, that no well defined secondary plateau can be distinguished in the storage modulus curve ($G'(\omega)$), for PP/HDPE blends with low dispersed phase concentration (5 and 10% of HDPE). A small shoulder can be observed for PP/HDPE blends with higher dispersed phase concentration. This behavior corroborates the predictions of Graebling et al. [14] who studied the influence of dispersed phase concentration on the secondary plateau. The authors observed that increasing the dispersed phase concentration increases both G_p and the width of the secondary plateau.

In order to infer the interfacial tension between PP and HDPE from the rheological data, Palierne's emulsion model was fit to the experimental data for the different blend compositions studied. It was observed that for PP/HDPE blends with low dispersed phase concentration (5 and 10% of HDPE) it was not possible to obtain a good agreement between experimental data and Palierne's emulsion model most likely because no well defined secondary plateau could be observed in the storage modulus curve ($G'(\omega)$) for these blends. For blends with higher dispersed phase concentration, it was observed that fitting the experimental data of storage modulus ($G'(\omega)$) over the complete experimental frequency range yielded to results that differed from a fitting over a limited frequency range located around the position of small shoulder of storage modulus ($G'(\omega)$). This behavior has been observed by other researchers [30]. Table 3 shows the values of interfacial tension between PP and HDPE at temperatures of 180, 200 and 220 °C obtained fitting Palierne's emulsion model to the experimental data for the different PP/HDPE blend compositions over a limited frequency range located around the position of small shoulder of storage modulus ($G'(\omega)$) (range of frequencies that corresponds to the form relaxation of the dispersed phase droplets). It can be seen that the values of interfacial tension between PP and HDPE obtained from PP/HDPE blend compositions ranging from 85/15 to 75/25 seem to be constant. It can also be seen that the value of interfacial tension between PP and HDPE obtained from PP/HDPE 70/30 blend is higher than the one obtained from PP/HDPE blend compositions ranging from 85/15 to 75/25.

Table 3
Interfacial tension between PP and HDPE obtained from fitting Palierne's emulsion model to the experimental data of PP/HDPE blends with different compositions at temperatures of 180, 200 and 220 °C

PP/HDPE blend composition	Interfacial tension (mN/m)		
	180 °C	200 °C	220 °C
95/5	–	–	–
90/10	–	–	–
85/15	2.44 ± 0.35	1.99 ± 0.44	1.75 ± 0.50
80/20	2.64 ± 0.54	2.37 ± 0.50	1.72 ± 0.11
75/25	2.52 ± 0.27	2.07 ± 0.15	1.61 ± 0.18
70/30	3.75 ± 0.19	3.17 ± 0.27	2.27 ± 0.37

Fig. 5 shows the weighted relaxation spectra of PP/HDPE (80/20) blend and of PP and HDPE pure phases at 220 °C.

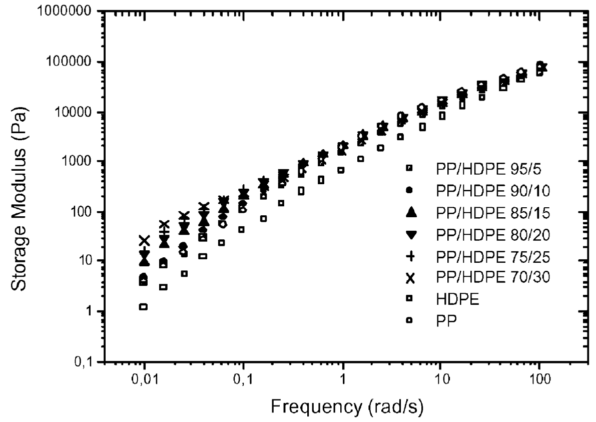

Fig. 3. Storage ($G'(\omega)$) moduli of the PP/HDPE blends with different compositions and of the pure phases at 220 °C.

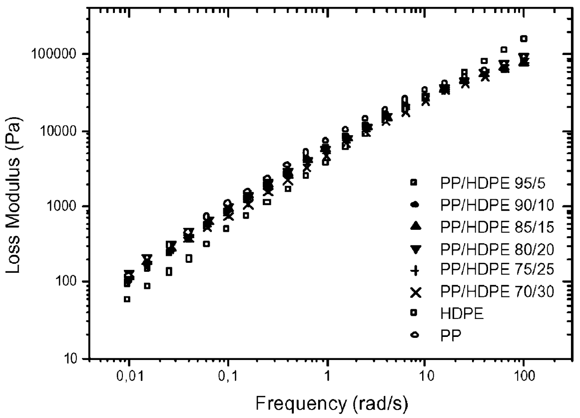

Fig. 4. Loss ($G''(\omega)$) moduli of the PP/HDPE blends with different compositions and of the pure phases at 220 °C.

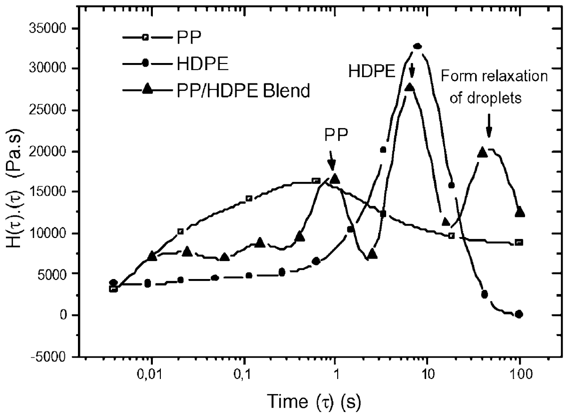

Fig. 5. Weighted relaxation spectra of PP/HDPE (80/20) blend and of PP and HDPE pure phases at 220 °C.

The relaxation spectra can be calculated by several methods [31–34]. In this work the relaxation spectra were calculated using a nonlinear regression method from the storage modulus raw data. The mathematical method is available in the stress rheometer SR-5000 software package from Rheometrics [34,35]. In the relaxation spectrum of PP/HDPE (80/20) blend (Fig. 5) it is possible to identify three peaks, which are related to these relaxation times. Two peaks are related to the relaxation times of the blend phases—PP and HDPE—(bulk), since they have the same order of magnitude as the ones of the pure phases. The remaining peak can be associated to the form relaxation time of the dispersed droplets. This type of relaxation spectrum was observed for all blends studied here.

Tables 4–6 show the form relaxation times of the dispersed phase droplets obtained from the relaxation spectra of the PP/HDPE blends with different compositions at temperatures of 180, 200 and 220 °C, respectively. From Tables 4 to 6, it can be seen that for each temperature the form relaxation times of the dispersed droplets increase when the HDPE concentration increases. This can be explained if we recall that the form relaxation of the dispersed droplets results from a balance between two forces [36]: a shearing force, proportional to $\eta\dot{\gamma}$ (where η is the viscosity and the $\dot{\gamma}$ is the shear rate) that tends to deform the droplets of the dispersed phase and a cohesive force, proportional to the ratio γ/d (where γ is the interfacial tension between two polymers and d is the diameter of the droplet) that contributes to the retraction of the dispersed phase into a spherical shape. When the HDPE concentration increases, the diameter of the dispersed phase increases. The force proportional to interfacial tension decreases and the form relaxation time of the dispersed droplets becomes longer.

The value of the form relaxation time of the dispersed droplets for each blend at each temperature was used to evaluate the interfacial tension as a function of temperature using Gramespacher and Meissner analysis [2]. The calculated values of interfacial tension between PP and HDPE are also reported in Tables 4–6. It can be seen that the values of interfacial tension between PP and HDPE vary from 1.53 to 3.68 mN/m (180 °C), 1.10 to 2.81 mN/m (200 °C) and 1.01 to 2.32 mN/m (220 °C). It can also be seen that for PP/HDPE blend composition ranging from 85/15 to 75/25, the interfacial tension seems to be constant. Such behavior corroborates the results obtained from fitting Palierne's emulsion model to the experimental data (see Table 3).

In order to verify if the relaxation times obtained experimentally from the relaxation spectrum analysis could really be associated with the form relaxation time of the dispersed phase droplets, we compared their values to the ones predicted by Palierne's emulsion model. In his work, Palierne [1] derived an equation to predict the longest form relaxation time of the dispersed phase droplets (τ_P), for an emulsion of Newtonian uniform size droplets immersed in a Newtonian matrix. An estimation of the longest form relaxation time of the dispersed phase droplets (τ_P) due to interfacial tension is given by:

$$\tau_P = \frac{R_v \eta_m}{4\gamma} \frac{(19K + 16)(2K + 3 - 2\phi(K - 1))}{10(K + 1) - 2\phi(5K + 2)} \tag{10}$$

where $K = \eta_d/\eta_m$ where η_d, η_m are the Newtonian viscosities of the dispersed phase and matrix, respectively; γ is the interfacial tension between the components of the blend; ϕ is the volume fraction of dispersed phase, and R_v is the volume average radius of droplets given by Eq. (2).

The zero shear stress viscosity of the matrix (PP), η_m, and of the dispersed phase (HDPE), η_d, used in the calculation are reported in Table 1 and the values of R_v are reported in Table 2. The value of interfacial tension used was obtained from the data of Rao et al. [10] who measured the interfacial

Table 4
Form relaxation time of the dispersed droplets and interfacial tension between PP and HDPE obtained from the relaxation spectra of PP/HDPE blends with different compositions at 180 °C

PP/HDPE blend composition	Form relaxation time of the dispersed droplets τ_1 (s)	Interfacial tension (mN/m)
95/5	37.83	1.53 ± 0.40
90/10	39.81	1.89 ± 0.41
85/15	39.81	2.69 ± 0.52
80/20	59.67	2.57 ± 0.44
75/25	76.32	2.64 ± 0.32
70/30	79.59	3.68 ± 0.37

Table 5
Form relaxation time of the dispersed droplets and interfacial tension between PP and HDPE obtained from the relaxation spectra of PP/HDPE blends with different compositions at 200 °C

PP/HDPE blend composition	Form relaxation time of the dispersed droplets τ_1 (s)	Interfacial tension (mN/m)
95/5	35.94	1.10 ± 0.28
90/10	35.94	1.41 ± 0.31
85/15	36.31	1.98 ± 0.38
80/20	43.29	2.36 ± 0.41
75/25	61.62	2.18 ± 0.27
70/30	69.31	2.81 ± 0.29

Table 6
Form relaxation time of the dispersed droplets and interfacial tension between PP and HDPE obtained from the relaxation spectra of PP/HDPE blends with different compositions at 220 °C

PP/HDPE blend composition	Form relaxation time of the dispersed droplets τ_1 (s)	Interfacial tension (mN/m)
95/5	26.83	1.01 ± 0.26
90/10	31.62	1.09 ± 0.24
85/15	35.94	1.44 ± 0.27
80/20	39.81	1.72 ± 0.31
75/25	51.80	1.72 ± 0.22
70/30	55.62	2.32 ± 0.26

tension between polypropylene (PP) and linear low density polyethylene (LLDPE) using the breaking thread method. The values of interfacial tension they obtained ranged from 0.2 to 2.6 mN/m at 220 °C. So, in order to obtain one value of interfacial tension between PP and PE at 220 °C to evaluate the longest form relaxation time of the dispersed phase droplets (τ_P) predicted by Palierne's emulsion model, an average of the values measured by Rao et al. [10] was used. The value obtained was $\gamma = 1.58$ mN/m. The values of the longest form relaxation time of the dispersed phase droplets (τ_P) predicted by Palierne's emulsion model [1] are shown in Table 7. It can be seen from Table 7 that the values of the longest form relaxation time of the dispersed phase droplets (τ_P) predicted by Palierne's emulsion model [1] corroborate the experimental values for PP/HDPE blend composition ranging from 85/15 to 75/25. It can also be seen that the values of the form relaxation time of the dispersed droplets for PP/HDPE blends 95/5, 90/10 and 70/30 obtained experimentally from the relaxation spectra analysis are different from values obtained by Palierne's emulsion model [1]. These results corroborate the observation made for values of interfacial tension obtained from fitting Palierne's emulsion model to the experimental data (see Table 3) and from the relaxation spectra of the blends (see Tables 4–6). These results confirm the possibility of the existence of a range of compositions for which it is possible to infer the interfacial tension between PP and HDPE from rheological data. If the dispersed phase concentration is small (in this case ≤10%) no well defined secondary plateau can be observed in the storage modulus curve ($G'(\omega)$) for these blends and it was not possible to obtain a good agreement between experimental data and Palierne's emulsion model. The form relaxation time of the dispersed phase droplets is lower and the distinction of the peaks associated with the relaxation of the bulk and the form relaxation of the dispersed phase droplets is difficult. Coupling effects between the peaks could then make the determination of the form relaxation time of the dispersed phase droplets less reliable [27]. On the other hand, if the dispersed phase concentration is large (in this case ≥30%) the distance between the particles becomes small and steric interaction cannot be excluded. So, these cooperative phenomena could take effect on the rheological behavior of the blend [3,27].

The values of interfacial tension obtained using the rheological data of PP/HDPE blends with compositions ranging from 85/15 to 75/25 were used to evaluate the influence of temperature on the interfacial tension between PP and HDPE. Fig. 6 shows the interfacial tension between PP and HDPE as a function of temperature. The values of interfacial tension were obtained by averaging the values of interfacial tension obtained from fitting Palierne's emulsion model to the experimental data and from the weighted

Table 7
Values of form relaxation time of the dispersed droplets obtained experimentally (τ_1) and predicted by Palierne's emulsion model (τ_P)

PP/HDPE blend composition	τ_1 (s)	τ_P (s)
95/5	26.83	19.60
90/10	31.62	23.69
85/15	35.94	33.75
80/20	39.81	40.18
75/25	51.80	51.07
70/30	55.62	68.04

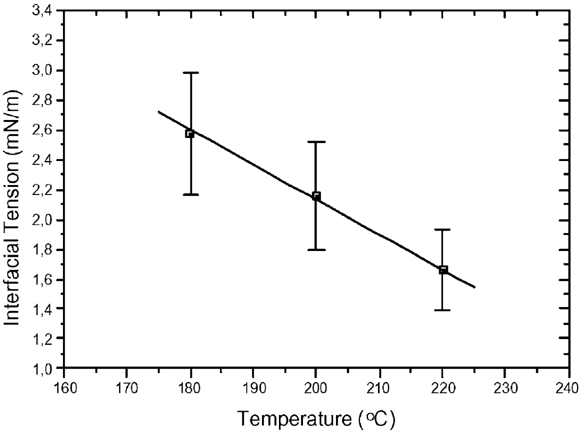

Fig. 6. Interfacial tension between PP and HDPE as a function of temperature.

relaxation spectra of PP/HDPE blends with compositions ranging from 85/15 to 75/25. The symbols represent the experimental data and the straight line represents the best fit obtained by linear regression. It can be seen that the interfacial tension decreases linearly with increasing temperature following the equation below:

$$\gamma = 6.73 - 0.023\,T \tag{11}$$

where γ is the interfacial tension and T is the temperature

The linear decrease of interfacial tension with temperature is expected thermodynamically and has already been reported by many researchers for different polymer pairs [37–40]. The temperature coefficient ($\partial\gamma/\partial T$) was found to be equal to (-0.023×10^{-3} N/mK) and corroborated the values obtained for other polymer pairs [9].

4. Conclusions

In this work, blends of PP/HDPE with different compositions were investigated. The effects of dispersed phase concentration (ranging from 5 to 30 wt%) and temperature (ranging from 180 to 220 °C) on the morphology and linear viscoelastic behavior of the blends were studied. The linear viscoelastic behavior of the blends was used to evaluate the interfacial tension between the components of the blends.

All blends studied showed a droplet dispersion morphology type. The number average radius and volume average radius of the dispersed phase increased as a function of increasing HDPE concentration in PP/HDPE blend due to increase of coalescence.

The interfacial tension between PP and HDPE at temperatures of 180, 200 and 220 °C was obtained fitting Palierne's emulsion model to the experimental data of PP/HDPE blends with different compositions and from the weighted relaxation spectra of PP/HDPE blends with different compositions, following Gramespacher and Meissner [2] analysis. The results seemed to indicate that there is a range of PP/HDPE blend compositions for which it is possible to use rheological data in order to calculate interfacial tension between PP and HDPE. This range of PP/HDPE blend compositions was used to evaluate the influence of temperature on the interfacial tension between PP and HDPE. It was shown that the interfacial tension between PP and HDPE decreases linearly with the increase of temperature.

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