

Influence of coalescence and interfacial tension on the morphology of PP/HDPE compatibilized blends

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Abstract

In this paper, the compatibilization of polypropylene (PP)/high-density polyethylene (HDPE) blend was studied through morphological and interfacial tension analysis. Three types of compatibilizers were tested: ethylene–propylene–diene copolymer (EPDM), ethylene–vinylacetate copolymer (EVA) and styrene–ethylene/butylene–styrene triblock copolymer (SEBS). The morphology of the blends was studied by scanning electron microscopy. The interfacial tension between the components of the blends was evaluated using small amplitude oscillatory shear analysis. Emulsion curves relating the average radius of the dispersed phase and the interfacial tension to the compatibilizer concentration added to the blend were obtained. It was shown that EPDM was more efficient as an emulsifier for PP/HDPE blend than EVA or SEBS. The relative role of interfacial tension reduction and coalescence reduction to particle size reduction was also addressed. It was observed that the role of coalescence reduction is small, mainly for PP/HDPE (90/10) blends compatibilized by EPDM, EVA or SEBS. The results indicated that the role of coalescence reduction to particle size reduction is lower for blends for which interfacial tension between its components is low at compatibilizer saturation. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Blends; Interfacial tension; Rheology

1. Introduction

Due to their relatively low cost and versatile properties, polyolefins represent one of the principal commodity thermoplastics [1]. As a consequence, their blends have attracted much interest [1–8]. It is well known that the impact strength of polypropylene (PP) increases at low temperatures through the addition of polyethylene (PE) [1–5]. Unfortunately, PP and PE are highly immiscible resulting in a blend with poor adhesion among its phases, coarse morphology and consequently poor mechanical properties. The compatibility between the phases of a blend can be improved by the addition of compatibilizers, which results in a finer and more stable morphology, better adhesion between the phases of the blends and consequently better properties of the final product. Blom et al. [6] showed that the addition of ethylene–vinylacetate copolymer (EVA) or ethylene–propylene–diene copolymer (EPDM) in PP/PE blends resulted in an increase of impact strength of the blend. Flaris and co-workers [2,3] showed that the addition of styrene–ethylene/butylene–styrene triblock

copolymer (SEBS) in PP/PE blends reduced the size of the dispersed phase.

The efficiency of the compatibilization can be evaluated using the emulsion curve introduced by Favis [9]. This curve correlates the size of the dispersed phase (in the case of a droplet dispersion morphology type) to the concentration of compatibilizer added to the blend. It has been shown that this change of the morphological characteristics, from coarse to fine particles, is related to a reduction of interfacial tension between the phases forming the blend and to a reduction of the dispersed phase particles coalescence [10,11]. However, studies correlating emulsion curves to interfacial tension reduction and coalescence suppression are still scarce due to the experimental difficulties encountered in the determination of interfacial tension between two molten polymers.

Among the various methods that exist 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 [12]. Dynamic methods based on the breaking thread and imbedded fiber [13–16] can also be used. However, both equilibrium and dynamic methods cannot be used to evaluate the interfacial

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tension between PP and high-density polyethylene (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) in a matrix. The refraction index of molten PP and HDPE is the same order of magnitude [17], making the distinction between phases impossible unless artifacts, such as addition of carbon black to one of the phases [18], which could alter the interfacial tension value, are used. Consequently, reported values of interfacial tension for PP/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 [19–24]. 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.

In this work, blends of PP/HDPE compatibilized with EPDM, EVA, SEBS were investigated. The effects of addition of the three compatibilizers on the morphology of PP/HDPE blends and on the interfacial tension between PP and HDPE were studied. The rheological behavior of the blends was used to evaluate the interfacial tension between the blend components. The relative role of interfacial tension reduction and coalescence reduction to particle size reduction was also addressed.

2. Experimental

2.1. Materials

Commercial PP from Polibrasil S.A., and HDPE from Ipiranga Petroquímica S.A. were used in this work. EPDM from Du Pont, EVA from Scientific Polymer, and SEBS from Shell Chemical were used as compatibilizers. The properties of the polymers and compatibilizers are listed in Tables 1 and 2, respectively.

2.2. Blending

Blends of PP/HDPE were prepared in an 80/20, 90/10,

Table 1
Properties of the polymers

Polymers	\bar{M}_w (g/mol)	\bar{M}_w/\bar{M}_n	Melt index (g/10 min)	Zero-shear stress viscosity (η_0) at 220 °C (Pa s)
PP	340,000	4.5	8	10,700
HDPE	140,000	3.2	8	8,050

Table 2
Properties of the compatibilizers

Compatibilizers	\bar{M}_w (g/mol)	\bar{M}_w/\bar{M}_n
EPDM	320,000	1.88
EVA	46,000	1.92
SEBS	74,000	1.03

and 99/1 weight concentrations. Concentrations of compatibilizers (EPDM, EVA or SEBS) ranging from 0 to 20 wt% with respect to the dispersed phase HDPE were used for all PP/HDPE blend compositions. The blends were prepared in a Werner and Pfeiderer twin-screw extruder, model ZSK-30 with six zones of temperatures, ranging from 170 to 210 °C along the barrel of the extruder. Both the non-modified and compatibilized blends were prepared in two steps. The compatibilizers (EPDM, EVA or SEBS) were first mixed with the minor phase (HDPE) and then blended with the matrix (PP). In the case of the non-modified blends, the minor phase was processed twice in order to have undergone the same thermomechanical history.

2.3. Rheological measurements

Samples for rheological tests were obtained by compression molding. Discs of 25 mm diameter and 1 mm 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 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 a temperature of 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 using Carreau's model [25], which was fitted to the curve Eta^* (Pa. s) versus 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 minor phase were determined using the SEM photomicrographs. About 300 particles were used to evaluate these parameters. For the determination of average size of the minor phase, the Saltikov's correction [26] was used. This correction takes into account the polydispersity of the samples and the fact

that the fracture in the sample does not always occur at the maximum diameter of the dispersed phase droplets.

3. Results and discussion

3.1. Effect of compatibilizer addition on the morphology of PP/HDPE blends

Fig. 1 shows a typical PP/HDPE blend morphology. In this case, it is shown a PP/HDPE (80/20) blend morphology. A droplet dispersion morphology type can be observed. This morphology type was observed for all PP/HDPE blend compositions studied here. Fig. 2 shows a typical compatibilized PP/HDPE blend morphology. In this case, it was added 10 wt% of EPDM with respect to the minor phase HDPE of the PP/HDPE (80/20) blend. It can be seen that the compatibilizer addition results in a decrease of the dispersed phase diameter. Figs. 3–5 show the volume average radius (R_v) of the dispersed phase as a function of EPDM, EVA and SEBS concentration added to the PP/HDPE (80/20), (90/10), and (99/1) blends, respectively. The volume average radius (R_v) is defined as:

$$R_v = \frac{\sum_i (R_i \phi_i)}{\sum_i \phi_i} \quad (1)$$

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

It can be seen that the volume average radius of the dispersed phase decreases exponentially with increasing concentration of EPDM, EVA or SEBS added to the PP/HDPE blends, following an emulsion curve.

The following exponential equation provides a good estimate of the average radius dependency on the copolymer

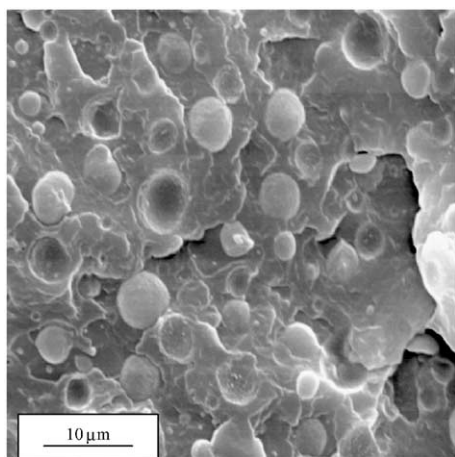


Fig. 1. Morphology of PP/HDPE (80/20) blend without compatibilizer addition.

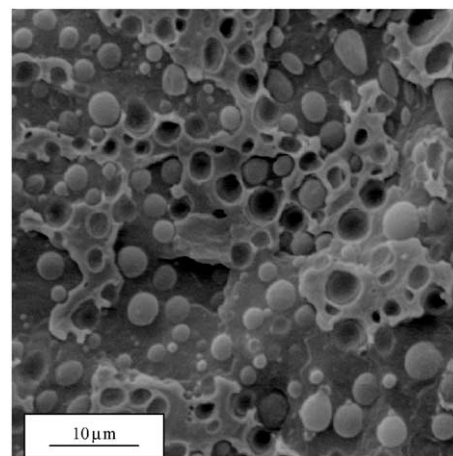


Fig. 2. Morphology of PP/HDPE (80/20) blend compatibilized with 10 wt% of EPDM with respect to the dispersed phase HDPE.

concentration [27]:

$$\frac{R_{vc} - R_\infty}{R_0 - R_\infty} = \exp(-n_1 c) \quad (2)$$

where R_{vc} is the volume average radius for a concentration c of compatibilizer, R_0 is the average radius for a blend without compatibilizer, R_∞ is a constant that corresponds to the radius at infinite concentration of compatibilizer, and n_1 is a constant that determines the efficiency of the compatibilizer as an emulsifier.

In order to compare the three compatibilizers efficiencies, we picked up a compatibilizer concentration $c_{R0.05}$ at which $(R_{vc} - R_\infty)/(R_0 - R_\infty) = 0.05$. For concentrations higher than $c_{R0.05}$, the decrease of R_{vc} value can be considered negligible. Table 3 presents the constants R_∞ and n_1 for Eq. (2), as well as the concentration $c_{R0.05}$ obtained for PP/HDPE (80/20), (90/10), and (99/1) blends. It can be seen that n_1 values are larger for EPDM than for SEBS or EVA for all PP/HDPE blends studied. Also, R_∞ and $c_{R0.05}$

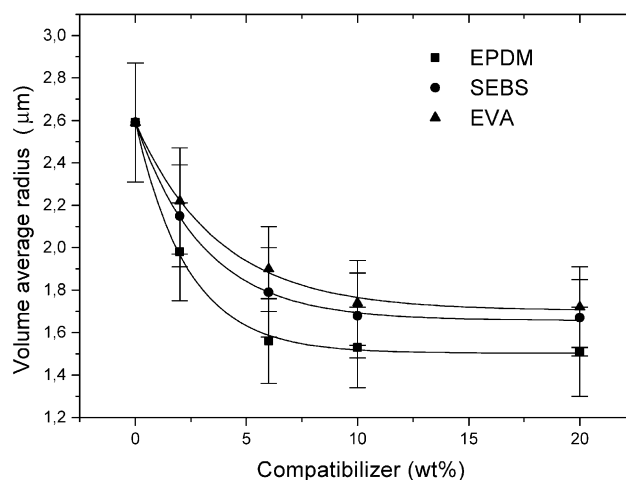


Fig. 3. Volume average radius (R_v) of the dispersed phase as a function of EPDM, EVA or SEBS concentration added to the PP/HDPE (80/20) blend.

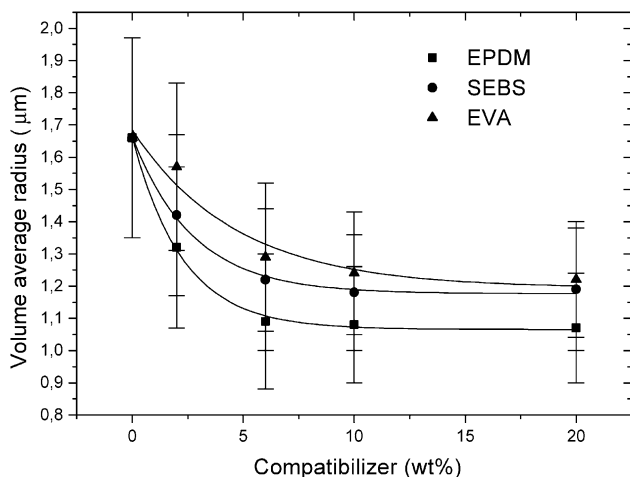


Fig. 4. Volume average radius (R_v) of the dispersed phase as a function of EPDM, EVA or SEBS concentration added to the PP/HDPE (90/10) blend.

values are smaller for EPDM than for SEBS or EVA. These results indicate a higher efficiency of EPDM than SEBS or EVA as an emulsifier for PP/HDPE blend. In other words, a smallest concentration of EPDM than of EVA or SEBS is necessary for the dispersed phase size to reach a minimum value.

The better efficiency of EPDM as an emulsifier for PP/HDPE blends can be the result of a better interaction between the PE and PP regions present in its backbone, with HDPE and PP homopolymers of the blend. EVA and SEBS have PE regions in their backbones that are very compatible with PE homopolymer, but VA and styrene segments are not compatible with PP [28]. Another possibility for the better efficiency of EPDM as an emulsifier is its greater molecular weight, although other researchers [29] have reported that the molecular weight of the copolymer did not affect the compatibilizer critical concentration or the equilibrium particle size of the dispersed phase.

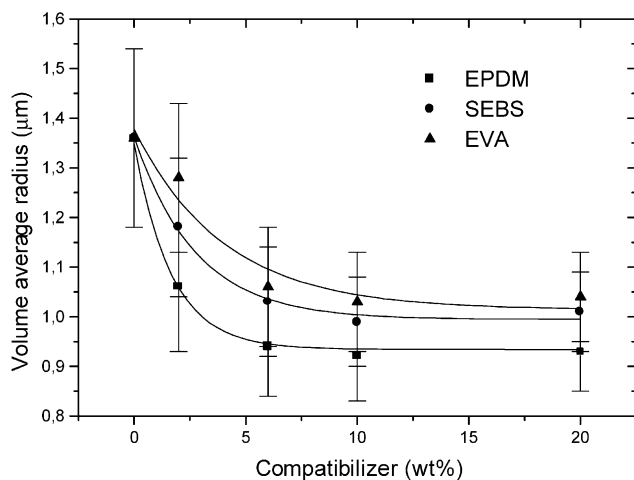


Fig. 5. Volume average radius (R_v) of the dispersed phase as a function of EPDM, EVA or SEBS concentration added to the PP/HDPE (99/1) blend.

The dispersed phase polydispersities (R_v/R_n) for PP/HDPE blends were also obtained. The number average radius (R_n) is defined as:

$$R_n = \frac{\sum_i n_i R_i}{\sum_i n_i} \quad (3)$$

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

The dispersed phase polydispersities (R_v/R_n) for PP/HDPE (80/20), (90/10), and (99/1) blends compatibilized with EPDM, EVA or SEBS, are given in Table 4. It can be seen that the polydispersity decreases with the increase of EPDM, EVA or SEBS concentration added to the PP/HDPE blend. This fact can be due to the decrease of dispersed phase coalescence with the increase of compatibilizer concentration, which leads to an increase of homogeneity of the dispersed phase size distribution. It can also be seen that EPDM is more efficient to decrease the polydispersity of PP/HDPE blends. In addition, for each blend studied here the polydispersity of the inclusions does not exceed 2. This condition is necessary if one wants to use the blend viscoelastic data to determine the interfacial tension between its components.

3.2. Effect of compatibilizer addition on the interfacial tension between PP and HDPE

The effect of compatibilizer addition on the interfacial tension between PP and HDPE was evaluated using the weighted relaxation spectra of PP/HDPE blends compatibilized by EPDM, EVA or SEBS, following Gramespacher and Meissner analysis. In their work, Gramespacher and Meissner [23] observed that the relaxation spectrum of a blend is a combination of three peaks. Two of them are related to the relaxation times of the different phases of the blend (bulk). The remaining peak can be associated to the form relaxation time (τ_1) of the dispersed phase particles. From this additional peak, the interfacial tension between the components of the blend can be inferred using the following equation:

$$\tau_1 = \left(\frac{\eta_m R}{\gamma} \right) \frac{(19K + 16)(2K + 3)}{40(K + 1)} \times \left(1 + \phi \frac{5(19K + 16)}{4(K + 1)(2K + 3)} \right) \quad (4)$$

where $K = \eta_d/\eta_m$ is the viscosity ratio; η_m , η_d are the matrix and dispersed phase Newtonian viscosities, respectively; γ is the interfacial tension between the components of the blend; ϕ is the volume fraction of dispersed phase and R is the radius of the monodispersed droplets.

In a previous work [30], it was shown that the interfacial tension between PP and HDPE inferred from the rheological measurements may depend on blend concentration. However, the results indicated that there is a range of

Table 3
Fitting parameters of Eq. (2)

PP/HDPE blend composition	Compatibilizer	R_{∞} (μm)	n_1	$c_{R0.05}$ (%)
99/1	EPDM	0.68	0.57	5.3
	EVA	0.76	0.31	9.6
	SEBS	0.73	0.35	8.5
90/10	EPDM	0.77	0.55	5.4
	EVA	0.86	0.32	9.3
	SEBS	0.83	0.35	8.5
80/20	EPDM	1.11	0.51	5.9
	EVA	1.18	0.30	9.9
	SEBS	1.16	0.34	8.7

blend composition for which interfacial tension is constant. The range observed varied from 15 to 25 wt% of dispersed phase concentration. Considering these results, the effect of compatibilizer addition on the interfacial tension between PP and HDPE was evaluated using PP/HDPE (80/20) blends.

The emulsion model of Gramespacher and Meissner [23] was not originally derived for being used for compatibilized blends and should not be used to evaluate the interfacial tension between polymers forming a compatibilized blend. Recently, Jacobs et al. [31] studied the influence of block copolymers addition, P(S-*b*-MMA), to polystyrene (PS)/poly(methyl methacrylate) (PMMA) blends on the relaxation behavior of the blends. The relaxation spectrum of the compatibilized blends obtained presented four peaks. Three of them corresponded to the ones described by Gramespacher and Meissner [23], i.e. two peaks related to the relaxation times of the different phases of the blend (bulk) and one third peak (τ_1) related to the form relaxation time of the dispersed phase particles. The fourth peak was an additional characteristic relaxation time, called τ_{β} . τ_{β} was shown to be longer than the form relaxation time and to depend on the amount and the nature of the block copolymer used. The authors derived formulas for the form relaxation time and for the additional relaxation time (τ_{β}) rewriting Palierne's model [19] for the case of compatibilized blends. Both relaxation times (τ_1 and τ_{β}) were shown to depend on the interfacial tension between the components forming the blend and the interfacial modulus of the blend.

Fig. 6 shows the weighted relaxation spectrum of PP/

Table 4
The dispersed phase polydispersities (R_w/R_n) for PP/HDPE (80/20), (90/10), and (99/1) blends

(%)	EPDM			EVA			SEBS		
	99/1	90/10	80/20	99/1	90/10	80/20	99/1	90/10	80/20
0	1.36	1.48	1.54	1.36	1.48	1.54	1.36	1.48	1.54
2	1.36	1.48	1.52	1.36	1.48	1.54	1.35	1.46	1.53
6	1.34	1.43	1.39	1.34	1.45	1.45	1.32	1.42	1.42
10	1.35	1.44	1.42	1.36	1.47	1.51	1.36	1.46	1.49
20	1.35	1.46	1.41	1.35	1.47	1.52	1.36	1.45	1.50

HDPE (80/20) blend compatibilized with 10 wt% of EPDM and PP and HDPE pure phases at 220 °C. The relaxation spectrum can be calculated by several methods. In this work, the relaxation spectrum was calculated using a non-linear regression method from the storage modulus raw data, following the work of Baumgartel and Winter [32]. The mathematical method is available in the stress rheometer SR-5000 software package from Rheometrics. It can be seen from Fig. 6 that it was possible to identify only three peaks from the relaxation spectrum of PP/HDPE (80/20) blend compatibilized with 10 wt% of EPDM differently from Jacobs et al. who observed four relaxation times. This behavior was observed for all compatibilized blends studied here. Two peaks corresponded to the relaxation times of the blend phases—PP and HDPE—(bulk). The value of the relaxation time corresponding to the remaining peak was of the same order of magnitude of the form relaxation time obtained for non-modified PP/HDPE blend in a previous work [30]. The remaining peak was therefore associated to the form relaxation time of the dispersed droplets.

The differences between the relaxation spectra obtained by Jacobs et al. [31] and the relaxation spectra obtained in this work can be explained by the differences of magnitude of the values of the form relaxation times. The form

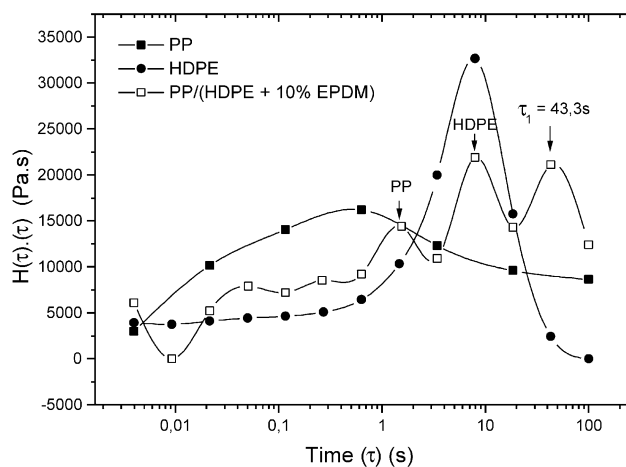


Fig. 6. Weighted relaxation spectra of PP/HDPE (80/20) blend compatibilized with 10 wt% of EPDM and PP and HDPE pure phases at 220 °C.

relaxation time (τ_1) and the additional characteristic relaxation time (τ_β) values for PS/PMMA compatibilized blends studied by Jacobs et al. [31] ranged from 5 to 8 s and 50 to 100 s, respectively. The form relaxation time (τ_1) values obtained in this work are of the same order of magnitude of the additional characteristic relaxation time (τ_β) values for PS/PMMA compatibilized blends obtained by Jacobs et al. [31]. It can be concluded that the additional characteristic relaxation times (τ_β) for PP/HDPE compatibilized blends are situated in a range of frequencies, that is not possible to obtain experimentally.

In this work, due to the low compatibilizer concentrations (maximum of 4 wt% with respect to the whole blend weight) used to modify the PP/HDPE (80/20) blend and due to the fact that only three peaks were observed on the relaxation spectra of all blends studied here, it was assumed that the emulsion model developed by Gramespacher and Meissner [23] could be used to evaluate interfacial tension between PP and HDPE to which compatibilizer had been added. The contribution of the dispersed phase was then considered as a sum of the contribution of the dispersed phase of HDPE and the contribution of the compatibilizer (EPDM, EVA or SEBS). Such an assumption has already been used by other researchers [27,33].

Table 5 shows the form relaxation time of the dispersed droplets obtained from the relaxation spectrum of the compatibilized blends with EPDM, EVA and SEBS. From Table 5, it can be seen that the form relaxation time of the dispersed droplets is shifted to higher values, when a compatibilizer is added to the blend. This can be explained if we recall that the relaxation of the dispersed droplets is due to a balance between two forces [34]: 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 dispersed phase droplets 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 EPDM, EVA or SEBS is added to the blend, it would be expected that the interfacial tension between PP and HDPE and also the dispersed phase size decrease. It will be shown later in the paper that the dispersed phase size reduction is greater than the interfacial tension reduction, when EPDM, EVA or SEBS is added to the blend, resulting in an increase of the cohesive force value. Nevertheless, it can also be seen in Table 5 that the viscosity of the dispersed phase increased with the increase of the EPDM, EVA or SEBS concentration added, resulting in an increase of the shearing force. The increase of the relaxation time values with the increase of the compatibilizer concentration observed for PP/HDPE blends compatibilized with EPDM, EVA or SEBS can indicate that in the case of PP/HDPE blends compatibilized with EPDM, EVA or SEBS, the value of the shearing force was greater than the cohesive force.

Fig. 7 shows the interfacial tension between PP and HDPE obtained from Gramespacher and Meissner analysis [23] as a function of amount of EPDM, EVA or SEBS added to PP/HDPE (80/20) blend at 220 °C. It can be seen that for the three types of compatibilizers, the interfacial tension decreases as a function of increasing compatibilizer concentration, following a typical behavior of an emulsion curve.

A similar expression as the one used for the radius of the dispersed phase can be used to estimate the dependency of the interfacial tension on the copolymer concentration [27]:

$$\frac{\gamma_c - \gamma_\infty}{\gamma_0 - \gamma_\infty} = \exp(-n_2c) \quad (5)$$

where γ_c is the interfacial tension between PP and HDPE to which a concentration c of compatibilizer has been added, γ_0 is the interfacial tension between PP and HDPE without compatibilizer, γ_∞ is a constant that corresponds to interfacial tension at infinite concentration of compatibilizer, and

Table 5

Form relaxation times of the dispersed phase for PP/HDPE (80/20) blends compatibilized with EPDM, EVA, and SEBS

Compatibilizer	(%)	η_0 (HDPE/compatibilizer) (10^4 Pa. s)	τ_1 (s)	γ (mN/m)
EPDM	0	0.81 ± 0.113	39.81	1.72 ± 0.31
	2	0.93 ± 0.068	39.81	1.38 ± 0.23
	6	0.98 ± 0.076	39.81	1.21 ± 0.20
	10	1.36 ± 0.064	43.29	1.18 ± 0.20
	20	1.58 ± 0.069	45.87	1.16 ± 0.22
EVA	0	0.81 ± 0.113	39.81	1.72 ± 0.31
	2	0.86 ± 0.078	39.81	1.50 ± 0.24
	6	0.91 ± 0.096	39.81	1.38 ± 0.21
	10	1.55 ± 0.046	43.29	1.31 ± 0.20
	20	1.67 ± 0.096	43.29	1.32 ± 0.21
SEBS	0	0.81 ± 0.113	39.81	1.72 ± 0.31
	2	0.88 ± 0.094	39.81	1.47 ± 0.22
	6	0.97 ± 0.077	39.81	1.35 ± 0.21
	10	1.42 ± 0.070	43.29	1.25 ± 0.20
	20	1.59 ± 0.079	43.29	1.26 ± 0.20

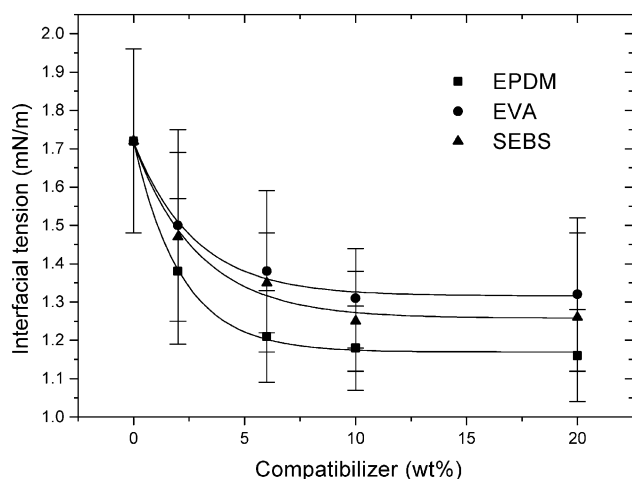


Fig. 7. The interfacial tension between PP and HDPE as a function of amount of EPDM, EVA or SEBS added to PP/HDPE (80/20) blend at 220 °C.

n_2 is a constant that determines the compatibilizer efficiency to decrease the interfacial tension.

In order to compare the three compatibilizers efficiency, we picked up a compatibilizer concentration $c_{\gamma 0.05}$ at which $(\gamma_c - \gamma_\infty)/(\gamma_0 - \gamma_\infty) = 0.05$. For concentrations higher than $c_{\gamma 0.05}$, the decrease of γ_c value can be considered negligible. Table 6 presents the constants γ_∞ and n_2 for Eq. (5), as well as the concentration $c_{\gamma 0.05}$. It can be seen that n_2 value is larger for EPDM than for SEBS or EVA. Also, γ_∞ and $c_{\gamma 0.05}$ values are smaller for EPDM than for SEBS or EVA. These results indicate that EPDM is more efficient in decreasing the interfacial tension between PP and HDPE than SEBS or EVA is.

3.3. Relative role of interfacial tension reduction and coalescence reduction to particle size reduction

As mentioned in Section 1, the dispersed phase size reduction, when a compatibilizer is added to a blend can be attributed to two different phenomena: an interfacial tension reduction and also a coalescence reduction of the dispersed phase particles [10,11]. In order to quantify the effect of the compatibilizer addition on each of these phenomena individually, an analysis similar to the one developed by Lepers et al. [11] was used in this work.

The total particle size reduction (TR_vR) was calculated for PP/HDPE (99/1), (90/10), and (80/20) blends compatibilized with EPDM, SEBS or EVA using the

following equation:

$$TR_vR = \frac{R_{v0} - R_{v\infty}}{R_{v0}} \times 100\% \quad (6)$$

where R_{v0} is the volume average radius of the dispersed phase of the blend without compatibilizer and $R_{v\infty}$ is the volume average radius of the blend at infinite concentration of compatibilizer.

The interfacial tension reduction (γR) was calculated using:

$$\gamma R = \frac{\gamma_0 - \gamma_\infty}{\gamma_0} \times 100\% \quad (7)$$

where γ_0 is the interfacial tension between PP and HDPE without compatibilizer addition and γ_∞ is the interfacial tension between PP and HDPE at infinite concentration of compatibilizer.

The particle size reduction can be attributed to the sum of an interfacial tension reduction and a coalescence reduction. Therefore, the coalescence reduction can be calculated as follows:

$$CR = TR_vR - \gamma R \quad (8)$$

Table 7 shows the total particle size reduction (TR_vR), the interfacial tension reduction (γR) and the coalescence reduction for PP/HDPE (99/1), (90/10), and (80/20) blends compatibilized with EPDM, SEBS or EVA. It can be seen that the total particle size reduction values are equal to the interfacial tension reduction values for PP/HDPE blends compatibilized with EPDM, SEBS or EVA, when the dispersed phase concentration is 1%. In this case, the particle size reduction results solely from the interfacial tension reduction. Therefore, for PP/HDPE blends with a composition (99/1), the coalescence can be considered negligible, due to high dilution. It can also be seen that the particle size reduction due to coalescence reduction is small. For example, PP/HDPE (90/10) blends compatibilized with EPDM, EVA or SEBS (CR amounts to 4, 2, and 2%, respectively). The values obtained in this work corroborate the ones obtained by Macaúbas and Demarquette [27], who observed a reduction of particle size due coalescence reduction of 6% for PP/PS (90/10) blends compatibilized with SEBS. However, the values are much smaller than the ones obtained by Lepers et al. [11], who observed a particle size reduction due coalescence reduction of 31% for

Table 7

Total particle size reduction (TR_vR), interfacial tension reduction (γR) and coalescence reduction of the PP/HDPE (80/20), (90/10), and (99/1) blends at interface saturation

Compatibilizer	TR_vR (%)			γR (%)	CR (%)		
	99/1	90/10	80/20		99/1	90/10	80/20
EPDM	31	35	41	31	–	4	10
EVA	24	26	33	24	–	2	9
SEBS	27	29	35	27	–	2	8

Table 6

Fitting parameters of Eq. (5)

Compatibilizer	γ_∞ (μm)	n_2	$c_{\gamma 0.05}$ (%)
EPDM	1.21	0.53	5.6
EVA	1.33	0.33	9.2
SEBS	1.28	0.34	8.8

Table 8
Residual coalescence of PP/HDPE (80/20) and (90/10) blends at interface saturation

Compatibilizer	ResC (%)	
	80/20	90/10
EPDM	63	15
EVA	85	32
SEBS	79	25

PP/PET (90/10) blends compatibilized with SEBS-*g*-MA. This discrepancy may be explained by differences of the values of interfacial tension between the polymers forming the blend at compatibilizer saturation. The value of interfacial tension between PP and HDPE obtained in this work at interface saturation was 1.18 mN/m and the value of interfacial tension between PP and PS obtained by Macaúbas and Demarquette [27] was 2.23 mN/m. In the case of the work of Lepers et al. [11], the value of interfacial tension between PP and PET at interface saturation was 7.1 mN/m. The results indicate therefore that the role of coalescence reduction on emulsion curve is lower for blends for which interfacial tension between its components at interface saturation is low.

The residual coalescence (ResC) for PP/HDPE (90/10) and (80/20) blends compatibilized with EPDM, EVA or SEBS was calculated considering the plateau of the dispersed phase size value for the PP/HDPE (99/1) blend compatibilized by EPDM as a baseline diameter representing the case of full coalescence suppression. The Residual coalescence was calculated using the following equation:

$$\text{ResC} = \frac{R_{v\infty} - R_{v99/1EPDM}}{R_{v99/1EPDM}} \times 100\% \quad (9)$$

where $R_{v\infty}$ is the volume average radius of the blend at infinite concentration of compatibilizer and $R_{v99/1EPDM}$ is the volume average radius of the PP/HDPE (99/1) blend at EPDM saturation.

Table 8 shows the residual coalescence for PP/HDPE (90/10) and (80/20) blends compatibilized with EPDM, SEBS, and EVA. It can be seen that the PP/HDPE (80/20) blends show a higher residual coalescence than that the PP/HDPE (90/10) blends, which is expected that the dispersed phase coalescence increases, when the dispersed phase concentration increases [35]. It can also be seen from Table 8 that the residual coalescence for PP/HDPE (90/10) and (80/20) blends compatibilized with EPDM show a lower value than that the PP/HDPE (90/10) and (80/20) blends compatibilized with EVA and SEBS. These results indicate a higher efficiency of EPDM than SEBS and EVA as an emulsifier for PP/HDPE blends. The residual coalescence phenomenon was also observed by Lepers et al., who obtained a residual coalescence of 30% for PP/PET (90/10) blends compatibilized with SEBS-*g*-MA. It can be observed that the residual coalescence factor obtained in

this work for PP/HDPE (90/10) blends compatibilized with EPDM is lower than the residual coalescence factor obtained by Lepers et al. [11]. Once again these different results can be explained by different values of interfacial tension between the polymers forming the blends.

4. Conclusions

In this work, blends of PP/HDPE compatibilized with EPDM, EVA, SEBS were investigated. The effects of addition of three compatibilizers on the morphology of PP/HDPE blends and on the interfacial tension between PP and HDPE were studied.

All blends studied showed a droplet dispersion morphology type. The volume average radius of the disperse phase decreased exponentially as a function of increasing concentration of compatibilizers added to the blend, following an emulsion curve. It was shown that EPDM is more efficient as an emulsifier than the others.

The effect of compatibilizer addition on the interfacial tension between PP and HDPE at a temperature of 220 °C was evaluated using the weighted relaxation spectra of the blends, following Gramespacher and Meissner [23] analysis. It was shown that the interfacial tension decreases exponentially as a function of increasing concentration of compatibilizers. It was also shown that EPDM is more efficient to decrease the interfacial tension than the others, corroborating with morphology results.

The relative role of interfacial tension reduction and coalescence suppression to particle size reduction was estimated quantitatively by a comparison of the interfacial tension reduction at the plateau value with the emulsion curve. It was observed that the role of reduction of particle size due to coalescence reduction is small, for PP/HDPE (90/10) blends, when compared with other blends. These results could indicate that the role of coalescence reduction to particle size reduction is lower for blends for which interfacial tension between its components is low at compatibilizer saturation.

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