Influence of Temperature, Molecular Weight, and Polydispersity of Polystyrene on Interfacial Tension Between Low-Density Polyethylene and Polystyrene

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ABSTRACT: In this work, the influence of temperature, molecular weight, and polydispersity of polystyrene on interfacial tension between low-density polyethylene (LDPE) and polystyrene (PS) was evaluated using the pendant drop method. It was shown that interfacial tension between LDPE and PS decreases with increasing temperature for all LDPE–PS pairs studied. The temperature coefficient $(\partial\gamma/\partial T)$ (where λ is interfacial tension and T is temperature) was higher for lower molecular weight and larger polydispersity of PS. The interfacial tension between LDPE and PS at a temperature of 202°C increased when the molecular weight of polystyrene was varied from 13,000 to 30,000. When the molecular weight of PS was further increased, the interfacial tension was shown to level off. The effect of polydispersity on interfacial tension between PS and LDPE, at a temperature of 202°C, was studied using PS with a constant-number average molecular weight and varying polydispersity. The interfacial tension was shown to decrease with increasing polydispersity. However, the influence of polydispersity was lower for PS of higher molecular weight. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2423–2431, 1999

Key words: polymer blends; interfacial tension; molecular weight; polydispersity; pendant drop method

INTRODUCTION

For the past 30 years, polymer blends have gained an increasing popularity in the field of polymer science and industry.[1] The growth in the use of polymer blends is mainly due to the possibility of those materials to combine the properties of their components, to a lower cost of development (when compared to the development of new molecules), and to easier processing (when compared to multilayer products). The properties of polymer blends depend strongly on the quality of their morphology, which is controlled by the thermodynamic properties of the blend, the rheological properties of their components, and the processing conditions and the composition of the blend.[2]

Interfacial tension between the components of the blend is one of the most accessible parameters that describes the thermodynamics of the blends. Unfortunately, research in the field of interfacial tension between molten polymers has been limited because of experimental difficulties encountered in its determination. Wu[3,4] summarized all the data published up to the beginning of the 1980s. Most previous experimental studies reported the effect of temperature on interfacial tension between polymers. Within the last 10 years some effort has been made to evaluate the effect of molecular weight and polydispersity on

interfacial tension between molten polymers but the results are still scarce. In particular, Anastasiadis et al.[5–7] and Nam and Jo[8] studied the effect of molecular weight on interfacial tension between poly (dimethylsiloxane) (PDMS) and polystyrene (PS), between poly(methyl methacrylate) (PMMA) and PS, between hydrogenated polybutadiene (HPBD) and PS, and between polybutadiene (PBD) and PS respectively, but the ranges of molecular weight studied were very small. Only two studies have been reported in the literature regarding the effect of molecular weight on interfacial tension between polymers for a larger range of molecular weight[9–10]: Ellingson et al.[9] reported the influence of molecular weight of PS on the interfacial tension between PS and PMMA for molecular weight ranging from 2,000 to 200,000, and Kamal et al.[10] reported the influence of molecular weight of PS on the interfacial tension between PS and polypropylene (PP) for molecular weights ranging from 1,600 to 380,000. All those authors showed that interfacial tension between two polymers increases when the molecular weight of one of the polymer increases; they also suggested that interfacial tension values appears to follow a $\overline{M_n}^{-z}$ type of dependence ($\overline{M_n}$ is the average molecular weight number of one of the polymers) with $0.5 < z < 1$. The experimental data of Ellingson et al.[9] and of Kamal et al.[10] suggested that the interfacial tension as a function of the average molecular weight number could level off when the average molecular weight number is above the molecular weight of entanglements. As far as the influence of polydispersity is concerned, only two studies have been reported up to date. Nam and Jo[8] studied the effect of polydispersity of PS on interfacial tension between trimodal blends of PS and PBD for polydispersities of PS ranging from 1.10 to 1.45 for polymers with low molecular weight. Kamal et al.[11] worked on the determination of interfacial tension between bimodal blends of PS and PP. In both studies the results seemed to indicate that interfacial tension decreases with increasing polydispersity. However, in spite of all the effort spent to study the influence of molecular weight and polydispersity on interfacial tension between polymers, the data are still scarce in the literature.

In this work the influence of temperature, molecular weight, and polydispersity of PS on the interfacial tension between low-density polyethylene (LDPE), using two different molecular weights, and polystyrene was studied. The results

Table I   Polymer Used in this Work

Polymer	$\overline{M_n}$	$I = \overline{M_w}/\overline{M_n}$
PE$_1$	3,500	2.00
PE$_2$	82,300	4.00
PS$_{mono}^{2,360}$	2,360	1.05
PS$_{mono}^{3,700}$	3,700	1.03
PS$_{mono}^{12,400}$	12,400	1.06
PS$_{mono}^{18,100}$	18,100	1.07
PS$_{mono}^{29,100}$	29,100	1.08
PS$_{mono}^{41,200}$	41,200	1.07
PS$_{mono}^{107,200}$	107,200	1.07
PS$_{mono}^{200,600}$	200,600	1.11
PS$_{mono}^{339,500}$	339,500	1.16
PS$_{mono}^{679,000}$	679,000	1.12

have been obtained using a pendant drop apparatus described elsewhere.[12]

MATERIALS

Pure PS and LDPE were used in this work to study the influence of temperature, molecular weight, and polydispersity on interfacial tension. The characteristics of the resins are reported in Table I. Pure resins were chosen because the presence of additives could influence the interfacial tension results.[13] The polymers used to evaluate the influence of temperature and molecular weight on interfacial tension had the following characteristics:

1. LDPE: two types of polyethylene were used in this study:

- PE$_1$: a low molecular weight polyethylene with $\overline{M_n} = 3,500$ and $I = 2.0$.

- PE$_2$: a high molecular weight polyethylene with $\overline{M_n} = 82,000$ and $I = 4.0$

2. PS: Monodisperse samples with molecular weight ranging from 12,000 to 400,000 were used in this study.

The molecular weight of the PS and LDPE used in this study were provided by the supplier (Aldrich Chemical Co.) and were verified using gel permeation chromatography (GPC). The following procedures were used in the determination of the molecular weight by GPC: The PS samples were dissolved in tetrahydrofuran (THF) at 30°C,

Table II Composition of Polydisperse Polystyrene for $\overline{M_n}$ = 18,100

Abbreviation	$I = \overline{M_w}/\overline{M_n}$	Weight Ratio of the Different PS Used in the Blend						
		$PS_{mono}^{2,360}$	$PS_{mono}^{3,700}$	$PS_{mono}^{12,400}$	$PS_{mono}^{18,100}$	$PS_{mono}^{29,100}$	$PS_{mono}^{41,200}$	$PS_{mono}^{107,200}$
$PS_{poli3}^{18,100}$	1.14			33.8	25	41.2		
$PS_{poli5}^{18,100}$	1.55		5.2	18.6	13.8	22.6	39.8	
$PS_{poli7}^{18,100}$	2.68	3.1	3.6	13.1	9.6	15.8	27.9	26.9

and the PE samples were dissolved in trichlorobenzene (TCB) at 140°C. The equipment used was a GPC 150 C from Waters Inc. In both cases, the GPC columns were calibrated with standard polymers.

In order to study the effect of polydispersity of polystyrene on interfacial tension between polyethylene and polystyrene, monodisperse polystyrene samples were mixed in different weight proportions to obtain polystyrene samples with varying polydispersity and constant-number average molecular weight ($\approx$18,100) and ($\approx$107,100). The polydisperse polystyrene samples were prepared by solution blending in order to ensure proper mixing. The weighted proportions of the polystyrene were mixed and dissolved in tetrahydrofuran (THF). After dissolution, the samples were allowed to dry in a vacuum oven at a temperature of 110°C for 72 h. It was checked by Fourier transform infrared (FTIR) spectroscopy to ensure that such a procedure was adequate for complete removal of the solvent and lack of thermal degradation. The two molecular weights of PS used ($\approx$18,100 and $\approx$107,100) were chosen to study the effect of the polydispersity of polystyrene on interfacial tension below and above the molecular weight of entanglement. The polydispersities of the PS mixtures were calculated from the mixing ratios. Table II and Table III show the composition, polydispersities, and abbreviations used for the polydisperse samples of PS with an average molecular weight number of 18,100 and 107,100, respectively.

EXPERIMENTAL

The interfacial tension was measured with an apparatus based on the pendant drop method. This method to measure interfacial tension between polymers has been reviewed extensively by several authors.[3,5,12,14–16] Basically the pendant drop method involves the determination of the profile of a pendant drop of one denser liquid into another. The shape of the pendant drop is related to the difference of density and interfacial tension between the two liquids. The interfacial tension between the two liquids can be inferred from the following equation:

$$\gamma = \frac{\Delta \rho g a^2}{B} \tag{1}$$

where λ is the interfacial tension between the two liquids, $\Delta\rho$ is the difference of density between the two liquids, a is the radius of curvature of the pendant drop at the apex, and B is a shape factor that depends on the geometrical shape of the drop.

The apparatus used in this work is similar to the one used by Demarquette and Kamal.[16] It basically consists of three parts: an experimental cell where the pendant drop of the polymer is formed, an optical system to monitor the evolution of the pendant drop, and a data acquisition system to infer the interfacial tension from the geometrical profile of the drop. The apparatus

Table III Composition of Polydisperse Polystyrene for $\overline{M_n}$ = 107,200

Abbreviation	$I = \overline{M_w}/\overline{M_n}$	Weight Ratio of the Different PS Used in the Blend						
		$PS_{mono}^{18,100}$	$PS_{mono}^{29,100}$	$PS_{mono}^{41,200}$	$PS_{mono}^{107,200}$	$PS_{mono}^{200,600}$	$PS_{mono}^{339,500}$	$PS_{mono}^{679,000}$
$PS_{poli3}^{107,200}$	1.40			16.9	25	58.1		
$PS_{poli5}^{107,200}$	1.93		9.1	9.3	13.7	32	35.9	
$PS_{poli7}^{107,200}$	2.98	4.4	6.4	6.4	9.6	22.4	25.1	25.6

used in this work was totally automatic—it acquired the image of the drop and inferred the interfacial tension on-line automatically without the input of the user during the whole duration of the experiment.

EXPERIMENTAL RESULTS

Material Characterization

It can be seen from eq. (1) that in order to evaluate interfacial tension between two liquids using the pendant method, it is necessary to know the difference of density between those two liquids under the same experimental conditions. The densities of the polymers used in this work were determined theoretically, using results from equations of state or experimentally using a mercury dilatometer. The different methods used are presented below:

(1) PE₁

The density of PE_1 at a temperature of 202°C was inferred from the data of Demarquette,[17] who worked with a PE of similar molecular weight. It was also measured with a mercury dilatometer, and both results were corroborated. The value of 0.753 g/cm³ was taken in the calculation of interfacial tension.

(2) PE₂

According to Tait's equation,[18] the specific volume of a polymer as a function of temperature and pressure can be written as

$$V(T, P) = V(0, T)\{1 - 0{,}0894 \ln[1 + P/B(T)]\}$$
(2a)

where $V(0,T)$ and $B(T)$ are the Tait's equation parameters (respectively, the specific volume at zero pressure and a function of temperature) and P is the pressure. Using pressure–volume–temperature (PVT) data, it is possible to infer the Tait's equation parameters $B(T)$ and $V(0,T)$. In this work, the Tait's equation parameters used for PE_2 were

$$B = 1929 \exp(-4{,}70 \times 10^{-3}T)$$
(2b)

$$V(0, T) = 1{,}14 \exp(6{,}95 \times 10^{-4}T)$$
(2c)

where T is the temperature in °C.

These parameters were chosen because they were inferred from PVT data of polymers with similar molecular weight to the one used in this work.[19]

The density of PE_2 as a function of temperature for temperatures ranging from 200°C to 240°C was also determined experimentally using a mercury dilatometer, and it was verified that the theoretical results from the equation of state corroborated the experimental results within the experimental errors. Therefore, the values of density considered in this work to evaluate interfacial tension were the ones obtained using the equations of state.

(3) PS

The density values of PS were taken from an empirical equation of state proposed by Fox and Flory[20]; the equation was obtained for molecular weights between 3,000 and 85,000. The equations of state taken for the density of polystyrene as a function of temperature used in this work were

$$\text{If } \overline{M_n} < 50{,}000 \quad d = 1{,}09\text{-}0{,}00068T \quad \text{(3a)}$$

$$\text{If } \overline{M_n} > 50{,}000 \quad d = 1{,}10\text{-}0{,}00068T \quad \text{(3b)}$$

The density values generated from these equations corroborated the ones inferred from PVT measurements of PS samples with different molecular weights reported in the literature.[21]

Interfacial Tension Results

Interfacial tension for the polymer pairs PE–PS was determined using drop profiles obtained experimentally using a pendant drop apparatus. The experimental results are presented in Figures 1–3.

DISCUSSION

Effect of Temperature

The effect of temperature on interfacial tension was studied for the PE_2–PS polymer pair for three types of PS: two monodisperse samples with two different molecular weights and a polydisperse sample with the same molecular weight as one of the monodisperse samples. Figure 1 shows the interfacial tension for the polymer pairs mentioned above as a function of temperature. The
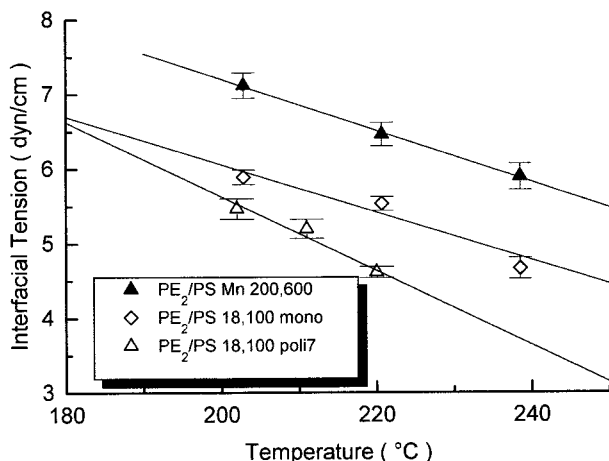
Figure 1 Interfacial tension between PE_2 and PS as a function of temperature for three different samples of PS.

Figure 3 Interfacial tension between PE_2 and PS as a function of polystyrene polydispersity at a temperature of 202°C for two molecular weights of polystyrene: $\overline{M}_n = 18,100$ and $\overline{M}_n = 107,200$.

different symbols represent the experimental data for the different PS samples, and the straight lines represent the best fit obtained by linear regression. For all the polymer pairs studied here, it can be seen that interfacial tension decreases linearly as a function of temperature. This is expected thermodynamically, as an increase of temperature decreases the free energy of mixing at the interface, resulting in a decrease of interfacial tension.

Table IV shows the coefficients of the lines obtained by fitting the interfacial tension as a function of temperature; a represents an extrapolation of the interfacial tension at 0°C, and b represents the temperature coefficient. The temper-
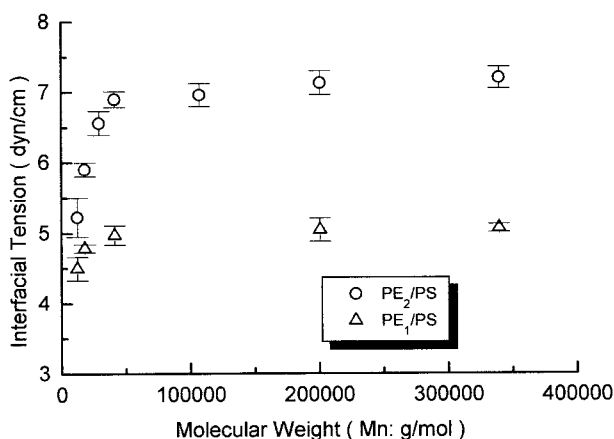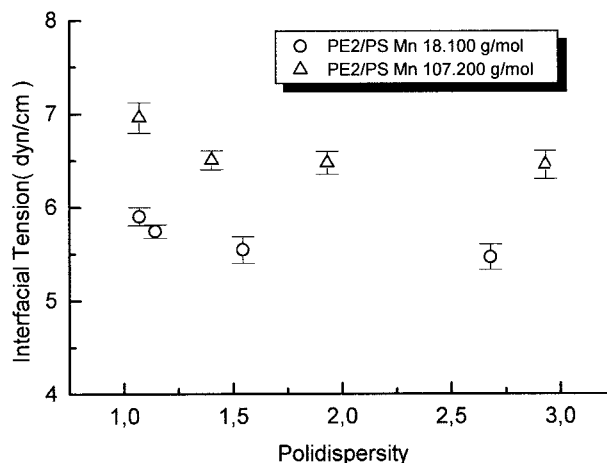
ature coefficients are of the same order of magnitude as the ones reported in the literature.[3,5–8,10,17] It can be seen that the temperature coefficient for the polydisperse system is higher than the one for the monodisperse system. Also, the temperature coefficients seem to decrease with increasing molecular weight. This phenomenon can be explained thermodynamically as follows: The temperature coefficient corresponds to the entropy change of interface formation per unit area at constant volume; when the molecular weight decreases or the polydispersity increases, the conformational restrictions of the polymer decrease, therefore increasing the entropy change of interface formation. These results corroborate the theoretical predictions of Broseta et al.[22] Such a trend has already been shown by other researchers. Kamal et al.[10] showed that for PS–PP systems, the temperature coefficients were of the order of 0.04 dyne.cm^{-1}.°C^{-1} for monodisperse systems, whereas for polydisperse systems they

Figure 2 Interfacial tension between PE_1 and PS and between PE_2 and PS as a function of molecular weight of PS at a temperature of 202°C.

Table IV Linear Regression Coefficients of the Dependence of Interfacial Tension on Temperature $\gamma = a - bt$

Polymer Pair	a (dyne/cm)	b (dyne/cm/°C)	r^2
PE/PS$_{\text{mono}}^{200,600}$	13.23	0.030	0.998
PE/PS$_{\text{mono}}^{18,100}$	13,27	0,036	0.976
PE/PS$_{\text{poli7}}^{18,100}$	14,44	0,044	0,961

were of the order of 0.07 dyne.cm^{-1}.°C^{-1}. Nam and Jo[9] showed that for polystyrene–polybutadiene systems of low molecular weight, the temperature coefficients increased linearly as a function of polydispersity of PS for polydispersities ranging from 1.1 to 1.5.

Effect of Molecular Weight

The effect of molecular weight on interfacial tension was studied for PE$_1$–PS and PE$_2$–PS polymer pairs at a temperature of 202°C. The molecular weight of PS varied from 13,000 to 400,000. Figure 2 shows the interfacial tension data as a function of the average molecular weight number of PS for both polymer pairs, PE$_1$–PS and PE$_2$–PS.

It can be seen that for both types of PE, the interfacial tension between PE and PS increases as a function of molecular weight of polystyrene. Figure 2 suggests that the influence of molecular weight of PS on interfacial tension between PS and PE decreases significantly when the molecular weight of PS exceeds 45,000 (the value at which entanglements occur for polystyrene[23]). Similar behavior has been observed by Kamal et al.[10] and Ellingson et al.,[9] who studied the effect of molecular weight of PS on the interfacial between PS and PP and PS and PMMA, respectively.

All the reported studies on the effect of molecular weight on interfacial tension between polymers showed a dependence of interfacial tension on molecular weight as given by the following equation:

$$\gamma = \gamma_\infty - C_1(\overline{M_n})_1^{-z} - C_2(\overline{M_n})_2^{-z} \qquad (4)$$

where γ is the interfacial tension, γ_∞, C_1, C_2, and z are constants and $(\overline{M_n})_1$ and $(\overline{M_n})_2$ are the average molecular weight number s of polymers 1 and 2, respectively. γ_∞ refers to the limiting value of interfacial tension for infinite molecular weight of both polymers, and C_1 and C_2 reflect the dependence of the interfacial tension on molecular weight.

If the molecular weight of one of the polymer is constant, eq. (4) reduces to

$$\gamma = \gamma_{\infty 1} - C_1(\overline{M_n})_1^{-z} \qquad (5)$$

where $\gamma_{\infty 1}$ refers to the limiting value of interfacial tension for infinite molecular weight of poly-
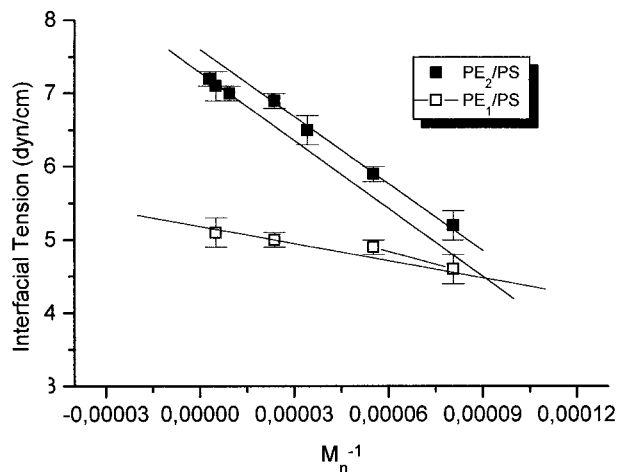

Figure 4 Interfacial tension between PE$_1$ and PS and between PE$_2$ and PS as a function of $\overline{M_n}^{-1}$ ($\overline{M_n}$ is for polystyrene) at a temperature of 202°C.

mer 1 (this value incorporates $C_2(\overline{M_n})_2$ as $(\overline{M_n})_2$ is kept constant).

Gaines et al.[24–25] studied the effect of molecular weight on interfacial tension for a limited range of molecular weights and found that the interfacial tension between n-alkanes and perfluoroalkane ($C_{12,5}F_{27}$) was proportional to $\overline{Mn}^{-2/3}$. Anastasiadis et al.[5–7] concluded that for systems including PDMS–PS, PMMA–PS, and HPB–PS, the exponent z in eq.(5) could depend on polydispersity; however the range of molecular weight studied by these authors was small. Kamal et al.[10] and Ellingson et al.[9] studied the effect of molecular weight of PS on the interfacial tension between PS and PP and between PS and PMMA, respectively, for larger ranges of molecular weight than the ones studied by Gaines et al. or Anastasiadis et al. Kamal et al.[10] and Ellingson et al.[9] fitted their experimental data using eq. (4); they concluded that the quality of the fit was the same for $z = \frac{1}{2}$, $\frac{2}{3}$, or 1 and observed deviations from the power law relationship at high molecular weights.

Figures 4–6 show the interfacial tension between PE and PS at a temperature of 203°C for both types of PE as a function of $\overline{M_n}^{-1/2}$, $\overline{M_n}^{-2/3}$, and $\overline{M_n}^{-1}$, respectively. The symbols represent the experimental data and the best-fitting lines (obtained by linear regression). It can be seen that for all the different values of z, the power law fits the experimental data only if it is considered two separate ranges of molecular weights. For the interfacial tension between PE$_1$ and PS, the two ranges of molecular weight correspond to below
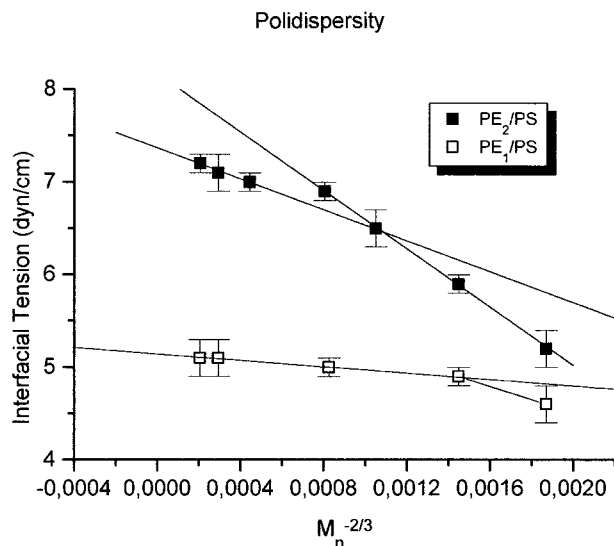
Polidispersity

Figure 5 Interfacial tension between PE$_1$ and PS and between PE$_2$ and PS as a function of $\overline{M_n}^{-2/3}$ (M_n is for polystyrene) at a temperature of 202°C.

and above 30,000, and for PE$_2$ and PS to below and above 45,000. Those critical molecular weights are referred as $\overline{M_c}$ in the rest of the text.

Table V shows the parameters γ_∞ and C_1 for both polymers pairs PE$_1$–PS and PE$_2$–PS for z = ½, z = ⅔, and z = 1, respectively. It can be seen that the quality of the fit is the same for the three values of z. The values of γ_∞ for both ranges of molecular weight for both polymer pairs increase when z decreases. This is expected mathematically. It can be seen that (γ_∞ and C_1 are larger
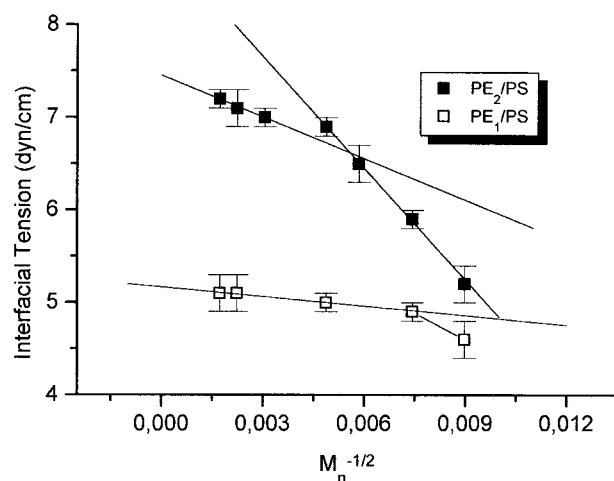

Figure 6 Interfacial tension between PE$_1$ and PS and between PE$_2$ and PS as a function of $\overline{M_n}^{-1/2}$ (M_n is for polystyrene) at a temperature of 202°C.

Table V   The Effect of Molecular Weight on Interfacial Tension: Parameters for Eq. (5)

	Interfacial Tension Between PE$_1$ and PS (dyn/cm)			
	Range of Molecular Weight $\overline{M_n}$	$\gamma_{\infty 1}$	C_1	r^2
$Z = 1$	12,400–30,000	5.55	15748	1.000
	30,000–339,000	5.11	5028	0.990
$Z = \frac{2}{3}$	12,400–30,000	5.93	952	1.000
	30,000–339,000	5.14	170	0.992
$Z = \frac{1}{2}$	12,400–30,000	6.33	258	1.000
	30,000–339,000	5.16	33	0.988

	Interfacial Tension Between PE$_2$ and PS (dyn/cm)			
	Range of Molecular Weight $\overline{M_n}$	$\gamma_{\infty 1}$	C_1	r^2
$Z = 1$	12,400–45,000	7.54	29415	0.998
	45,000–339,000	7.27	30046	0.989
$Z = \frac{2}{3}$	12,400–45,000	8.22	1009	0.999
	45,000–339,000	7.35	820	0.988
$Z = \frac{1}{2}$	12,400–45,000	8.93	409	0.998
	45,000–339,000	7.45	140	0.991

when $\overline{M_n} < \overline{M_c}$ for both polymer pairs and each value of z. This could be due to the weaker influence of molecular weight for higher molecular weights of PS, as shown in Figure 2.

Comparing the values of C_1 for both polymer pairs, it can be seen that the dependence of molecular weight on interfacial tension is lower for PE$_1$–PS polymer pairs than for the PE$_2$–PS polymer pair. This behavior is probably due to the interfacial tension between the two polymers being proportional to the sum of the inverse of the molecular weight of the two polymers. This has been shown theoretically by Broseta,[22] who suggested that the interfacial tension between two polymers could be expressed as

$$\gamma = \gamma_\infty \left[1 - \frac{\pi^2}{12\chi} \left(\frac{1}{N_A} + \frac{1}{N_B} \right) + \cdots \right] \quad (6a)$$

with

$$\gamma = \left(\frac{\chi}{6} \right)^{1/2} b\rho_0 kT \quad (6b)$$

where γ is the interfacial tension, χ is the Flory–Huggins interaction parameter between the cor-

responding monomers, T is the temperature, k is the Boltzman constant, b is the effective length of the monomer units, ρ_o is the monomer density at the interface, and N_A and N_B represent the degree of polymerization of each polymers.

The degree of polymerization of PE_1 is about 25 times smaller than that of PE_2. Therefore, the correcting factor for the molecular weight in eq. (6a) corresponding to the molecular weight of PE is much higher for PE_1 than for PE_2, decreasing the influence of the molecular weight of PS on the interfacial tension between PE_1 and PS.

Effect of Polydispersity

The effect of polydispersity on interfacial tension between PE and PS was studied for PE_2 and PS with values of polydispersity ranging from 1 to 3 at a temperature of 202°C. The polydispersity of PS was varied, keeping constant the average molecular weight number. Two molecular weights of polystyrene were studied ($\overline{M_n}$ = 18,000 and $\overline{M_n}$ = 114,000).

Figure 3 shows the interfacial tension between PE_2 and PS for both molecular weights of PS as a function of the polydispersity of PS. It can be seen that the interfacial tension decreases with increasing polydispersity. This could be due to the migration of the short chains of the polydisperse systems to the interface, which results in a broadening of the thickness of the interface and therefore lowering the interfacial tension. Similar results have been shown by Nam and Jo[8] and Kamal et al.[9] It seems, from Figure 3, that the influence of polydispersity is higher for lower molecular weights of polystyrene. The value 18,000 corresponds to a molecular weight below the molecular weight of entanglement of polystyrene. Therefore, it is expected that the mobility of the short chains of the 18,000 molecular-weight systems will be higher than when the 114,000 molecular-weight system is used, which explains the results observed here.

CONCLUSIONS

In this work the effect of temperature, molecular weight, and polydispersity of polystyrene on the interfacial tension between low-density polyethylene and polystyrene was studied. It was shown that interfacial tension decreases linearly with temperature. The temperature coefficient was shown to be larger for lower molecular weight and higher polydispersity. The interfacial tension between low-density polyethylene and polystyrene increased with increasing molecular weight of the polystyrene, but the influence of molecular weight was smaller when using polymers with a molecular weight above the molecular weight of entanglement. The experimental data of interfacial tension as a function of molecular weight could be fitted to a type of power law if two molecular-weight ranges were considered: one below and the other above the molecular weight of entanglement. The influence of the molecular weight of polystyrene on interfacial tension between polystyrene and polyethylene was shown to be smaller for lower molecular weights than for higher molecular weights of polyethylene. The interfacial tension decreased as a function of polydispersity of polystyrene when the average molecular weight number was kept constant. The decrease of interfacial tension with polydispersity was more intense for polystyrenes with molecular weights below the molecular weight of entanglement.

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