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Danilo J. Carastan^a; Elaine Palmezan^a; Renato N. Shimizu^a; Nicole R. Demarquette^a

^a Materials Engineering Department, Polytechnic School of the University of São Paulo, 05508-900 São Paulo/SP, Brazil

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Interfacial tension between polystyrene and a liquid crystal polymer

DANILO J. CARASTAN, ELAINE PALMEZAN, RENATO N. SHIMIZU and NICOLE R. DEMARQUETTE*
Materials Engineering Department, Polytechnic School of the University of São Paulo, Av. Prof. Mello Moraes 2463,
05508-900 São Paulo/SP, Brazil

In this work contact angles formed by drops of polystyrene (PS) on a surface of liquid crystalline polymer (LCP) Vectra A910 were measured as a function of temperature for temperatures ranging from 180 to 230°C. The values were used together with the surface tensions of both polymers to evaluate the interfacial tension between PS and the LCP. In order to validate the method used to evaluate this interfacial tension, the interfacial tension between polypropylene (PP) and PS was evaluated using values of contact angles formed by a drop of PP on PS and the values of surface tension of both polymers in the molten state. The values of interfacial tension between PP and PS corroborated well the values obtained using the pendant drop method. The values of interfacial tension between PS and the LCP were shown to decrease linearly with temperature.

1. Introduction

Blends of thermotropic liquid crystalline polymers (LCPs) and isotropic thermoplastics form a special group of materials called self-reinforcing blends or *in situ* composites [1]. The LCPs usually form fibrous phases that give rise to enhanced mechanical properties, with the advantage of being easier to process in comparison with solid fibre-reinforced composites. Most of the studies on these blends deal with the mechanical properties, morphology stability and rheological properties of these materials. There are some review papers available on these subjects [2–4]. One very important parameter in the study of a multicomponent polymeric system is the interfacial tension between its components. It is the most accessible parameter that describes the thermodynamic and structural conditions of the interfaces in blends and composites, influencing their morphology and indicating if there is good or bad adhesion between two phases [5]. Unfortunately, there are very few interfacial tension data between liquid crystal polymers and thermoplastics because of the difficulties encountered when working with LCPs [5].

Several experimental methods, such as the contact angle method [6], embedded fibre retraction method [7], breaking thread method [8, 9] and rheological method [10] have been used to evaluate the interfacial tension between a LCP and a thermoplastic. However, a large variation of interfacial tension values for the same polymer pair (thermoplastic/LCP) can be found in the literature. When the thermoplastic has a much lower

melting temperature than the LCP, most methods to evaluate interfacial tension cannot be used because of the probable thermal degradation of the lower melting point polymer. Even though both polymers can be heated for short times for melt blending, degradation is likely to occur in methods that require a longer time of analysis, such as the pendant drop method. In this case the polymers must be kept at high temperatures during all the experimental time, and the drop may take several hours to reach equilibrium. Thus, the only technique that can be used is the contact angle method; unlike all the other methods, it does not require that both polymers be in the molten state, so that lower temperatures can be used for the experiments. The contact angle method is a relatively simple way to determine the interfacial tension between a pair of polymers. A sessile drop of one of them is deposited on the surface of the other and the contact angles formed by this drop are measured.

If the polymer forming the drop rests on the surface of a solid polymer, as in figure 1 (a), the interfacial tension between both polymers can be inferred using Young's equation, given by [11]:

$$\gamma_1 = \gamma_{12} + \gamma_2 \cos \theta \quad (1)$$

where γ_1 is the surface tension of polymer 1 in the solid state, γ_{12} is the interfacial tension between the solid and the molten polymer, γ_2 is the surface tension of polymer 2 in the molten state and θ is the contact angle between the polymers.

If both polymers are in the molten state two contact angles, θ_1 and θ_2 , can be measured, see figure 1 (b), and

*Corresponding author. Email: nick@usp.br

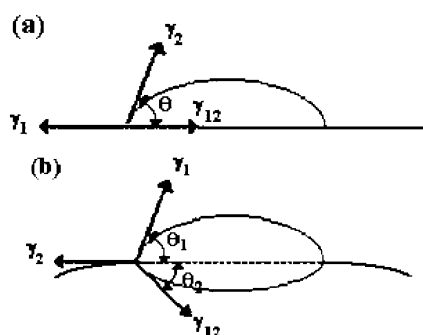


Figure 1. Evaluation of contact angles in: (a) a drop of molten polymer on a solid polymer surface; (b) a drop of molten polymer on a molten polymer surface.

the interfacial tension can be inferred from equation (2) [12]:

$$\gamma_2 = \gamma_1 \cos \theta_1 + \gamma_{12} \cos \theta_2 \quad (2)$$

where γ_1 and γ_2 are the surface tensions of polymer 1 and 2 in the molten state, respectively, γ_{12} is the interfacial tension between both polymers and θ_1 and θ_2 are defined in figure 1 (b). For both cases, in equations (1) and (2) γ_1 and γ_2 have to be determined using other techniques.

In this work the interfacial tension between polystyrene (PS) and a commercial LCP was measured as a function of temperature for temperatures ranging from 180 to 230°C using the method discussed above. In order to see if the method leads to reliable values of interfacial tension, it was first tested to evaluate interfacial tension between polypropylene (PP) and PS as a function of temperature. The values of interfacial tension between PP and PS obtained were compared with values obtained using the pendant drop method.

2. Experimental

2.1. Materials

Commercially available polypropylene (HY6100 from Polibrasil) and polystyrene (Lustrex HH-101 from Estireno do Brasil) were used in this work; their characteristics are summarized in table 1. PP was an isotactic polypropylene. The liquid crystal polymer studied in this work was a random copolymer of

4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid (HBA/HNA), namely Vectra A-910 from Ticona Polymers.

2.2. Contact angle measurements

Two systems were studied in this work: (i) drops of molten PP over a molten surface of PS, and (ii) drops of molten PS over a solid surface of Vectra. The drops of PP and PS were obtained by cutting polymer filaments in very small pieces. The PS surfaces used in this work were thin discs (25 mm diameter and 1 mm thick) obtained by moulding in a hydraulic press at 200°C. The Vectra surfaces were small discs (10 mm diameter and 0.5 mm thick) obtained by compressing single pellets between two silicon wafers using a hot stage (Mettler Toledo FP-82 HT) at 270°C. The silicon wafers were used in order to obtain a very smooth surface, since it is well known that surface roughness affects the contact angle values [21].

For each experiment, a disc of PS or Vectra was placed over the flat surface of a cylindrical steel support inside an experimental chamber. A polymer solid drop was then placed on the disc (PP on PS and PS on Vectra) and the polymer pairs were heated in the chamber at the temperature desired for the evaluation of interfacial tension. The system was kept in an argon atmosphere to avoid polymer degradation. After the time necessary for the systems to reach mechanical equilibrium (about 6 h), each sample was removed from the chamber together with the steel support and quenched in water inside a beaker; the samples could thus maintain their shapes at room temperature as close as possible to the equilibrium shapes at the experiment temperature. The thermal expansion coefficients of the polymers used in his work are quite similar, in the range of $3\text{--}6 \times 10^{-4} \text{C}^{-1}$, so deformation in cooling caused by a difference of thermal expansion coefficients is unlikely to happen. The time spent in the transportation of a sample from the chamber to the beaker was around 2–3 s. Effects of non-uniform cooling, such as warpage, were discounted, once the samples were small and thin, resulting in rapid and uniform cooling.

The PS/LCP contact angles were directly measured using a goniometer. The PP/PS systems were first embedded in polyester-based resin Serifix® (Struers) and carefully cut with a diamond disc rotary cutter (ISOMET 11-1180 Low Speed Saw) in the middle of each drop along the vertical plane, so that the angles of figure 1 (b) could become visible. Experimental errors arising from cutting the samples away from the middle of the drop and in a plane making an angle, δ , with the vertical plane will be addressed later in the paper. Problems in distinguishing each phase of the system

Table 1. Materials used in this work.

Material (trade name)	Supplier	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$
PP (HY6100)	Polibrasil	–5	165
PS (Lustrex HH-101)	Estireno do Brasil	95	–
Vectra A-910	Ticona Polymers	–	260

prevented the angles from being measured using a reflected light microscope. However, it was possible to measure these angles using a goniometer because of the contrast obtained by the illumination of the apparatus.

2.3. Surface tension measurements

As shown above, in order to determine the interfacial tension between two polymers using the contact angle method, one has to determine the surface tension of both polymers using other methods. The surface tensions of molten PP and PS were measured directly using an apparatus based on the pendant drop method, in which the geometrical profile of a pendant drop of a liquid is determined. The interfacial tension between PP and PS was also evaluated by this method, to be compared with the results obtained by the contact angle method. The apparatus used in this work is similar to that used by Demarquette and Kamal [13], consisting basically of an experimental cell where the pendant drop is formed, an optical system to monitor the evolution of the drop and a data acquisition system to infer the surface tension from the geometrical profile of the drop. More details on the pendant drop apparatus used in this work can be found in Arashiro and Demarquette [14] and in Morita *et al.* [15]. The densities of the polymers necessary for the determination of surface or interfacial tensions by the pendant drop method were obtained from PVT data [16].

The surface tension of Vectra, necessary for the determination of interfacial tension between Vectra and PS, was evaluated by extrapolating values obtained previously with the contact angle method with low molecular mass liquids at room temperature [17, 18]. This extrapolation was made using a value of $\partial\gamma/\partial T = -0.06 \text{ mN mK}^{-1}$ for Vectra [6]. It was possible to assume that the surface tension of Vectra decreases linearly with temperature as this polymer undergoes no thermal transition in the range of temperature considered [19].

3. Results and discussion

Figure 2 presents the surface tension of polystyrene and polypropylene as a function of temperature. It can be seen that for both polymers the surface tension decreases linearly with increasing temperature. This is expected thermodynamically, as an increase of temperature decreases the free energy at the surface resulting in a decrease of surface tension. The linear decrease of surface tension with increasing temperature has been reported previously by many researchers for different polymers [16, 20]. The data were fitted to a straight line by linear regression. The coefficients of the

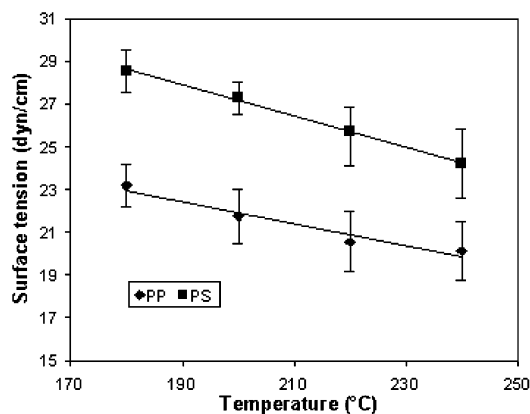


Figure 2. Surface tension of polypropylene and polystyrene as a function of temperature.

linear regression are reported in table 2, together with the coefficients for the surface tension of Vectra. The temperature coefficients ($\partial\gamma/\partial T$) found in this study corroborate the values obtained for other polymers [20].

Figure 3 shows typical drops of molten PS on a surface of solid Vectra (a), and of molten PP on a surface of molten PS (b). Tables 3 and 4 present all the values of contact angle measured for the systems PS/Vectra and PP/PS, respectively. The values of contact angle for the system PS/Vectra represent the average of around 12 angles measured along the whole circumference of each drop. A similar procedure could not be performed for the PP/PS system as the angle was measured only at the cutting plane. Table 5 presents the average contact angles formed by the drops of the two polymeric systems for different temperatures. It can be seen that the contact angle decreases with increasing temperature. This is expected as the surface tension of the polymers decreases with increasing temperature. It can also be seen that there is a large scatter of the values for θ_2 -PP/PS and θ -PS/Vectra.

The scatter obtained for θ_2 -PP/PS can be explained by the lack of precision of the measuring technique, although much care was taken during the process of cutting the samples. In order to identify the reason for this scatter, and see if it could be attributed to deviations from optimal cutting conditions, the error analysis developed by Kim and Jeong [21] was applied in this work to one of the experimental drops of the

Table 2. Linear regression coefficients of $\gamma = a - bT$ for PS, PP and Vectra.

Material	$a/\text{mN m}^{-1}$	$b/\text{mN mK}^{-1}$	R^2
PS	41.73	0.0728	0.9981
PP	32.38	0.0523	0.9504
Vectra	36 [16, 17]	0.06 [6]	1

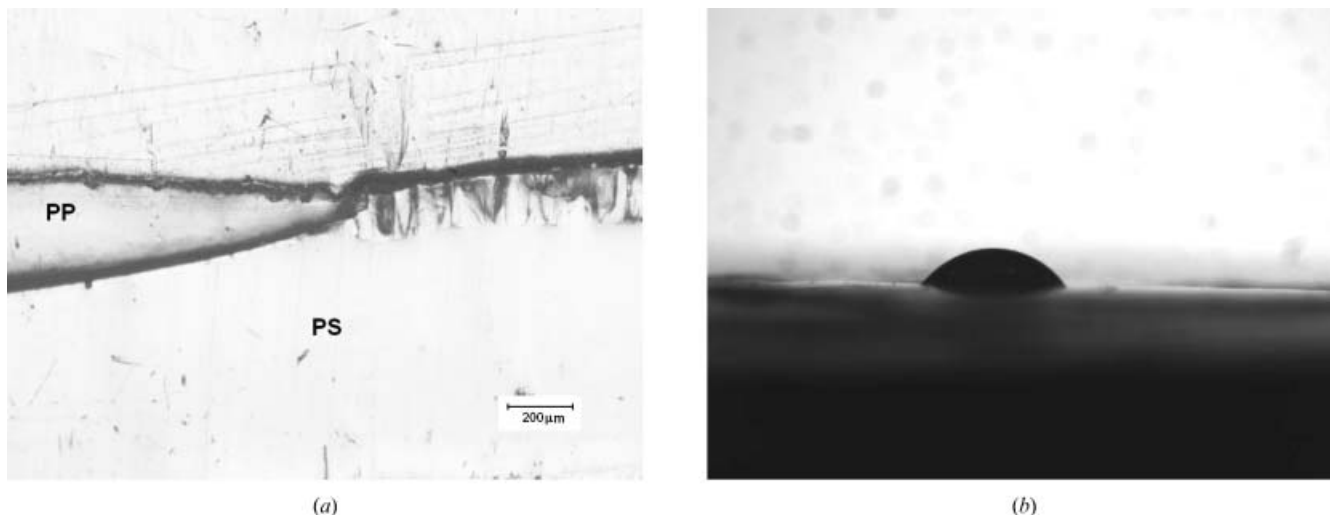


Figure 3. Sessile drops of: (a) PS on Vectra; (b) PP on PS.

PP/PS system. In a critical study, Kim and Jeong evaluated the contact angle method used to determine interfacial tension between polymers, showing that the method is subject to imprecision according to the plane and angle that the polymer drop is cut, and also if the upper and/or lower surfaces of the drop deviate from a spherical shape. This error analysis is based on the effects of cutting position and cutting angle as functions of geometrical relations obtained from the shape of the

Table 3. Contact angles for system PS/Vectra.

Temperature/°C	$\theta/^\circ$
180	54.3
	57.6
	54.9
	56.6
	52.4
	49.7
200	54.3
	51.0
	53.6
	49.7
	47.7
220	57.0
	53.9
	46.2
	55.6
	52.1
230	56.1
	41.3
	44.9
	43.3
	48.7
	50.0

drop. Following the derivation of Kim and Jeong, if a drop is formed by two spherical caps and cut perpendicularly exactly in its middle (optimal cutting condition), one can define three dimensionless

Table 4. Contact angles for the system PP/PS.

Temperature/°C	$\theta_1/^\circ$	$\theta_2/^\circ$
180	10	25
	8	25
	9	24
200	2	13
	2	20
	5	17
	5	20
220	5	20
	1	18
	1	18
	5	15
230	2	16
	1	19
	1	17
	1	14
	2	13
	2	12

Table 5. Average contact angles ($^\circ$) for systems PP/PS and PS/Vectra.

Temperature/°C	θ_1 -PP/PS	θ_2 -PP/PS	θ -PS/Vectra
180	9.0 ± 1.0	24.7 ± 0.6	54.3 ± 2.6
200	3.8 ± 1.6	18.0 ± 3.1	52.0 ± 3.3
220	2.0 ± 1.7	17.2 ± 1.6	47.5 ± 6.1
230	1.5 ± 0.6	14.0 ± 2.2	44.9 ± 3.6

parameters, α , β and κ , given by:

$$\alpha = \frac{h_1}{r_1}; \beta = \frac{h_2}{h_1}; \kappa = \frac{r_2}{r_1} \quad (3)$$

where h_1 , h_2 , r_1 and r_2 are defined in figure 4. The ‘true’ contact angles of the drop can then be obtained from the following relations:

$$\cos \theta_1 = 1 - \alpha \quad (4)$$

$$\cos \theta_2 = 1 - \frac{\alpha\beta}{\kappa} \quad (5)$$

For a drop cut in an arbitrary plane different from optimum condition, apparent contact angles θ_1' and θ_2' will be measured according to figure 5. In order to relate the apparent angles to the true contact angles, Kim and Jeong introduced two new geometrical dimensionless parameters, corresponding to the position ($\xi = x/s$) and angle (δ) of the cutting plane, as shown in the figure 6.

Using ξ and δ , Kim and Jeong found relations between the apparent contact angles and these dimensionless parameters:

$$\cos \theta_1' = \frac{(1 - \alpha) - \xi \cot \delta (2\alpha - \alpha^2)^{\frac{1}{2}}}{\left[1 + (2\alpha - \alpha^2)(\cot^2 \delta - \xi^2) - 2(2\alpha - \alpha^2)^{\frac{1}{2}}(1 - \alpha)\xi \cot \delta \right]^{\frac{1}{2}}} \quad (6)$$

$$\cos \theta_2' = \frac{(\kappa - \alpha\beta) - \xi \cot \delta (2\alpha - \alpha^2)^{\frac{1}{2}}}{\left[\kappa^2 + (2\alpha - \alpha^2)(\cot^2 \delta - \xi^2) - 2(2\alpha - \alpha^2)^{\frac{1}{2}}(\kappa - \alpha\beta)\xi \cot \delta \right]^{\frac{1}{2}}} \quad (7)$$

Note that, if $\xi = 0$ and $\delta = 90^\circ$ (optimal cutting conditions), the values of θ_1' and θ_2' become equal to the real contact angles, θ_1 and θ_2 .

In this work, the effect of the deviation from the optimum cutting conditions was evaluated for a typical drop of PP on PS prepared at 180°C . The geometric parameters of this drop are presented in table 6. The errors arisen from the cutting position deviations can be compared with those related to the cutting angle if the following relationship holds [21]:

$$\xi^2 = -\cot^2 \delta = X \quad (8)$$

If the cosines of the apparent contact angles calculated from the equations (6) and (7) are plotted as functions of the parameter X , the variations of the true contact angles with the deviations from the optimum cutting conditions can be visualized more easily. In this plot,

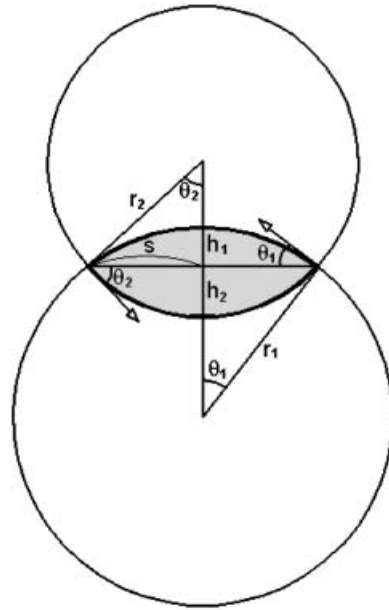


Figure 4. View of a drop at the optimum cutting plane; and definition of geometric parameters at the optimum condition (adapted from Kim and Jeong [21]).

the effect of cutting position (ξ) can be observed in the portions of the curves for positive values of X , and the effect of cutting angle (δ) can be evaluated in the portions of the curves for negative values of X . Figure 7 shows this plot for the drop under study obtained by varying X from -1 ($\delta = 45^\circ$) to 0.5 ($\xi = 0.7$, which corresponds, for example, in the case of a drop having a diameter of 5 mm, to cutting 1.75 mm away from the ideal plane). For these extreme values of δ and ξ it can be seen that the apparent contact angles deviate significantly from the real contact angle, measured at

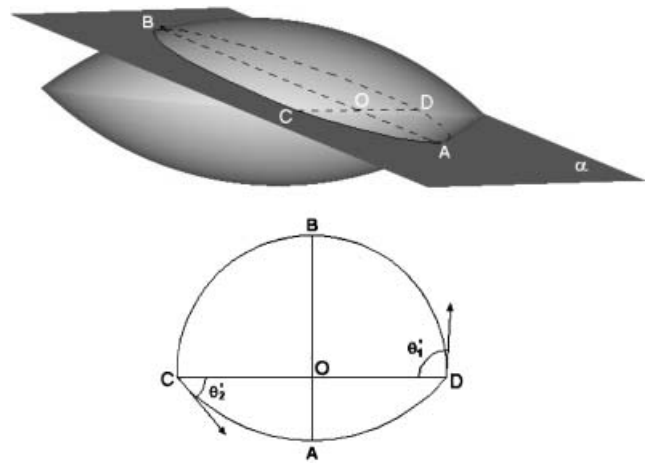


Figure 5. Arbitrary cutting plane α and intersection of this plane with the drop showing the apparent contact angles θ_1' and θ_2' (adapted from Kim and Jeong [21]).

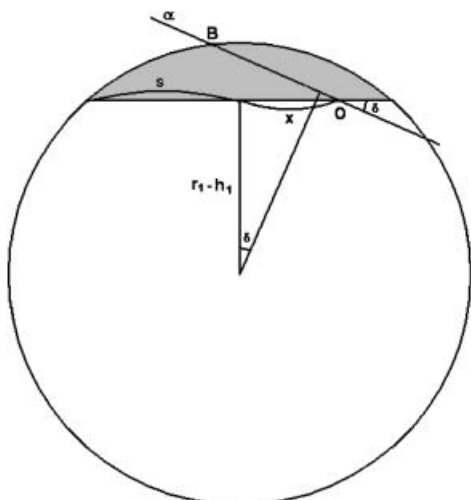


Figure 6. View of the upper part of a drop perpendicular to an arbitrary cutting plane α ; and definition of geometric parameters at arbitrary cutting conditions (adapted from Kim and Jeong [21]).

Table 6. Geometric parameters of a PP drop on a PS surface prepared at 180°C.

α	β	κ	$\cos \theta_1^a$	$\cos \theta_2^b$
0.0314	2.2088	0.4802	0.9686	0.8557

^aFrom equation (4).
^bFrom equation (5).

optimum cutting conditions ($X=0$), especially the value of θ_2 . But for smaller deviations of X it can be seen that the variation of the apparent contact angles is quite small. As an example, with a deviation of 20% of the cutting angle or the cutting position from the optimum cutting conditions (i.e. $\delta=72^\circ$ or $\xi=0.2$), the values of θ_1 and θ_2 deviate only approximately 1 degree. This

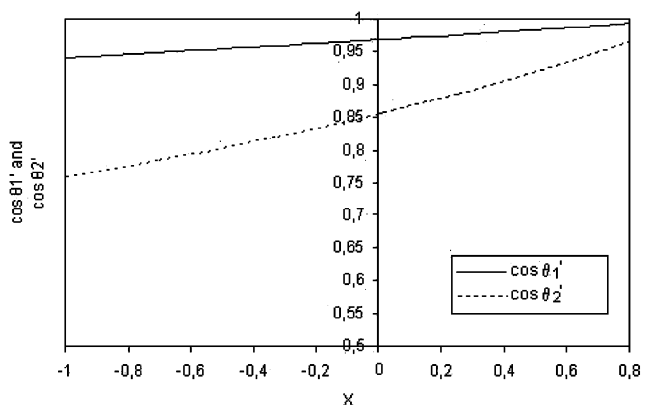


Figure 7. Plot of $\cos \theta_1'$ and $\cos \theta_2'$ versus X for a typical drop of PP on PS at 180°C.

variation is small because the contact angles formed by the drop are quite small. In the case of drops prepared at higher temperatures this effect is even smaller, because the contact angles decrease with increasing temperature. So in this work the errors introduced by variation of cutting angle and position can be neglected. Nevertheless, because the angles are small, there may have been an increase in uncertainty during the visual measuring, which could explain the scatter observed in table 3.

The scatter of contact angle values obtained for θ -PS/Vectra may be due to the inherent roughness of the Vectra surface. Although the Vectra samples were moulded by compression between two silicon wafers, a residual roughness of the samples was observed. This roughness can lead to a dispersion of the contact angle data [22]. To decrease this roughness it would have been better to have prepared the samples by a solution casting method on a very flat surface, such as a silicon wafer. However, this could not be done, because the Vectra polymer is almost insoluble, the best way found to achieve a flat enough surface was by pressing the molten polymer between two silicon wafers.

The values of surface tension of PS and PP presented in figure 2 and contact angle reported in table 5 were used together with equation (2) to evaluate the interfacial tension between PP and PS as a function of temperature. Figure 8 shows the interfacial tension between PP and PS as a function of temperature for temperatures ranging from 180 to 230°C. The circles represent the values obtained using the contact angle method and the squares using the pendant drop method. It can be seen that the values of interfacial tension between PP and PS obtained using both methods corroborate within experimental error. These results validate the use of the contact angle method to evaluate interfacial tension between Vectra and PS.

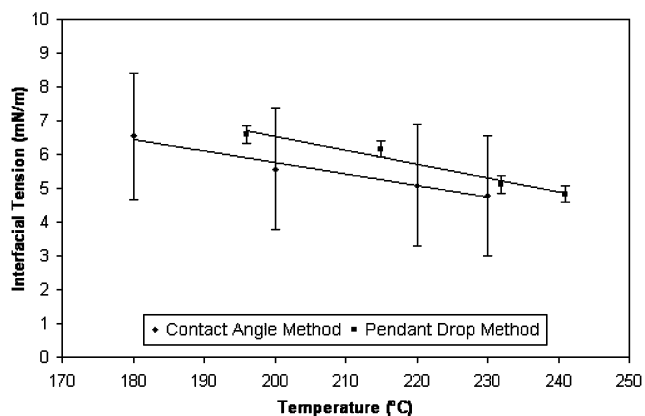


Figure 8. Interfacial tension of system PP and PS as a function of temperature.

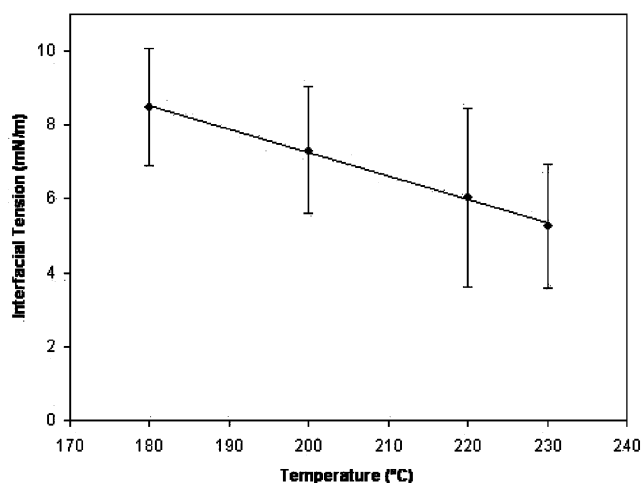


Figure 9. Interfacial tension of system PS and Vectra as a function of temperature.

The interfacial tension between PS and Vectra as a function of temperature was evaluated using the contact angle values reported in table 5 and values of surface tension of PS and Vectra shown in figure 8. Figure 9 shows the interfacial tension between PS and Vectra as a function of temperature. Table 7 reports the linear regression coefficients of the interfacial tension values of the two systems presented in figures 8 and 9.

The results shown in figure 9 indicate that within experimental error the interfacial tension between PS and Vectra appear to decrease linearly with increasing temperature, although the uncertainty in the data may be too large to warrant such a claim. However, the linearity is expected thermodynamically, as Vectra undergoes no thermal transition in the range of temperatures studied. Machiels *et al.* [8] obtained a value of 19 mN m^{-1} for the interfacial tension between PS and Vectra A950 at 300°C using the breaking thread method. The values obtained in this work are relatively low if compared with those of Machiels *et al.* This may be due to experimental difficulties and different assumptions made, regarding the rheological nature of the polymers, for the different methods used to evaluate

Table 7. Linear regression coefficients of $\gamma_{12}=a-bT$ for systems PP/PS and PS/Vectra.

System	a mN m^{-1}	b mN mK^{-1}	R^2
PP/PS (Contact angle method)	12.59	0.0342	0.9735
PP/PS (Pendant drop method)	14.87	0.0416	0.9622
PS/Vectra	20.00	0.0637	0.9972

the interfacial tension. The discrepancy may also arise from slight chemical structure differences between the LCPs used in the two studies. Another possible origin for this difference in results may be the value of solid surface tension of Vectra used in equation (1). This value was extrapolated from room temperature by adopting a value of $\partial\gamma/\partial T$ of -0.06 mN mK^{-1} which may not be correct, but literature data are too scarce for a comparison.

4. Conclusions

It has been shown that the contact angle method is reliable for evaluating interfacial tension between molten polymers, although the experimental error can be quite large. The interfacial tension evaluated between PS and PP as a function of temperature using the contact angle method corroborated results from the pendant drop method. Based on these results the interfacial tension between a liquid crystal polymer, namely Vectra A-910, and polystyrene was evaluated using the contact angle method, since no other method can be used for this polymer pair at the range of temperatures studied. The contact angles formed by the drop of PS on Vectra showed a large scatter, most likely due to the roughness of the Vectra samples. The interfacial tension between PS and Vectra showed a tendency to decrease linearly with temperature within the experimental error.

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