

Polymer 44 (2003) 3045-3052



www.elsevier.com/locate/polymer

# New procedure to increase the accuracy of interfacial tension measurements obtained by breaking thread method

Guillermo Palmer, Nicole R. Demarquette\*

Department of Metallurgical and Materials Engineering, University of São Paulo, Av. Prof. Mello Moraes, 2463, São Paulo, SP CEP 05508-900, Brazil

Received 4 September 2002; received in revised form 3 February 2003; accepted 5 February 2003

#### Abstract

The breaking thread method has been widely used to measure interfacial tension between molten polymers. However, various factors can introduce errors in the breaking thread measurements and is very difficult to obtain accurate values of interfacial tension. In this work a new procedure to enhance the accuracy of the breaking thread method is proposed. It consists of using Tomotika's original theory and Tjahjadi's et al. numerical simulation of the evaluation of a breaking thread simultaneously to identify fibers with residual stresses. These fibers should not be considered for breaking thread experiment. Also, a new experimental procedure for polymer pairs that cannot normally be tested using breaking thread method is presented. Using these two new procedures the interfacial tension between polypropylene and polystyrene and between polypropylene and polycarbonate was evaluated for temperatures ranging from 200 to 240 °C. It was shown that the accuracy of the method was increased by 28% when compared to the result obtained using one of the both theories, Tomotika or Tjahjadi et al, independently. The results of interfacial tension between polypropylene and polycarbonate corroborated the results obtained using other methods.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Breaking thread method; Interfacial tension; Polymers blends

# 1. Introduction

Interfacial tension in molten polymers has been studied both experimentally and theoretically, for the last decades due to it's importance in the field of polymer blends. It is one of the four factors that govern the morphology of binary blends [1], which in turn governs the final properties of product. Unfortunately, the experimental determination of interfacial tension in molten polymers is a difficult task owing to the high viscosity and rheological characteristics of those materials. A thorough review of the different techniques that can be used to measure interfacial tension between molten polymers can be found in Ref. [2]. One of the most popular for the last 20 years has been the breaking thread method [3-12]. It involves the observation of the evolution of the shape of a long fluid thread imbedded in another. Due to Brownian motion, small distortions of arbitrary wavelength are generated at the surface of the thread; this leads to a pressure difference between the inside

and the outside of the thread which induces more important deformations caused by the effect of the interfacial tension that tends to reduce the interfacial area. It is possible to infer interfacial tension between the polymers forming the thread and the matrix, from the study of the evolution of the disturbances and the zero shear viscosity of the polymers. However, the breaking thread method suffers from several drawbacks: during the preparation of the threads to be used in the breaking thread experiments residual stresses can be induced in the thread. Fibers with residual stresses will distort faster and this will lead to interfacial tension values much higher than the real one. Also, in order to determinate interfacial tension between two polymers using the breaking thread method, the fiber should be formed with the material that has the lowest viscosity [6,13,14] and at the same time the higher softening temperature (glass temperature for amorphous polymers or melting temperature for semicrystalline polymers). If the fiber is formed using the material with higher viscosity, phenomena such as end pinching and retraction will occur preventing the use of the method. Also, if the fiber is formed by the material with the lower softening temperature, distortions will start before the fiber

<sup>\*</sup> Corresponding author. E-mail address: nick@usp.br (N.R. Demarquette).

is completely imbedded in the matrix and air bubbles will form at the interface between both polymers [2,6,13,14]. Those two conditions can limit the use of the breaking thread method unless an experimental method is properly devised.

The interfacial tension can be inferred from the observation of a breaking thread using several theories such as Tomotika [3,4] which consists in evaluating the growth rate of the sinusoidal instabilities growing exponentially with time of a breaking thread and theory of Tjahjadi et al. [5] which consists of fitting the dynamic of amplitudes growth using curve-fitted polynomials, calculated from numerically generated results of the transient shape using boundary integral techniques. In this work, both theories are used simultaneously to enhance the accuracy of the method. Also a new experimental procedure for polymer pairs with comparable softening temperatures is presented.

The first part of the paper summarizes the theory used for the breaking thread method. In the second part the experimental procedures are described and the experimental results obtained for polypropylene/polystyrene and polypropylene/polycarbonate polymer pairs are presented, discussed and compared to the literature.

# 2. Theory

The breaking thread method involves the observation of the evolution of a fluid thread embedded in another fluid. Because of Brownian motion, when a thread of molten polymer with an aspect ratio higher than a critical value that depends on viscosity ratio [5], small distortions of arbitrary wavelength are generated at the surface of the thread. The thread then assumes the shape of sinusoid and breaks up into aligned spheres. Two theories, Tomotika [3,4] and Tjahjadi et al. [5], have been developed to infer interfacial tension between both polymers from the study of the evolution of the thread and the zero shear stress viscosity of the polymers. They are reviewed briefly below. Both the theories consider the polymers involved in the breaking thread measurements as Newtonian fluids. In the case of the polymers studied here it was checked that it was possible to use this hypothesis, calculating the value of interfacial tension for the polymer pairs involved in this work using Palierne's theory [15] which considers the viscoelasticity of the fluids. The values obtained in this work and reported below did not differ by more than 0.33% from the ones obtained using Palierne's theory.

## 2.1. Theory of Tomotika

Tomotika [3,4] presented a theory to determine the interfacial tension between a liquid cylinder embedded in a quiescent liquid matrix. Because of Brownian motion, small distortions of arbitrary wavelength,  $\Lambda$ , are generated at the surface of the thread. The amplitude of the distortions that

are larger than the circumference of the thread grow exponentially with time, according to:

$$\alpha = \frac{b - a}{4} = \alpha_0 \exp\{qt\} \tag{1}$$

where b and a are the bigger and the smaller diameters of the fiber, respectively (see Fig. 1);  $\alpha_0$  is the initial amplitude of the sinusoidal distortions; t is the time and q is the growth rate of the distortions.

The growth rate of the distortions, q, is a function of the interfacial tension,  $\gamma$ , the zero shear viscosity of the matrix,  $\eta_{\rm om}$ , the initial radius of the fiber,  $R_{\rm obt}$ , and of the dimensionless growth rate,  $\Omega(X,\lambda)$ , as shown in Eq. (2). The dimensionless growth rate is a function of the wave number, X (defined by Eq. (3)) and the viscosity ratio,  $\lambda$  (defined by Eq. (4))

$$q = \frac{\gamma \Omega(X, \lambda)}{2\eta_{\text{om}} R_{\text{obt}}} \tag{2}$$

$$X = \frac{2\pi R_{\text{obt}}}{\Lambda} \tag{3}$$

$$\lambda = \frac{\eta_{\text{of}}}{\eta_{\text{om}}} \tag{4}$$

where  $\Lambda$  is the wavelength of the distortions and  $\eta_{\rm of}$  is the zero shear viscosity of the fiber.

To obtain the interfacial tension,  $\ln(\alpha/R_{\rm obt})$  is plotted as a function of time resulting in a straight line. The growth rate is calculated from the slope of the graph and the interfacial tension is obtained from Eq. (2). To infer the interfacial tension between the polymers using Eq. (2), one must know the value of  $\Omega(X, \lambda)$  which can be obtained numerically. More details can be found in Machiels et al. [7] and Luciani et al. [8].

### 2.2. Theory of Tjahjadi et al

Tjahjadi et al. [5] presented another theory to determine the interfacial tension between two Newtonian fluids based

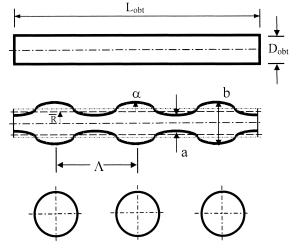


Fig. 1. Illustration of a fiber during the break-up process.

on the instabilities of a thread of a molten polymer imbedded into another. In the case of breaking thread experiments the polymers can be considered Newtonian because the shear rates involved during the breaking thread experiments are very low. This is not true, however, for fluids that exhibit shear thinning for low shear rates [16]. The method applies curve-fitted polynomials to describe the growth of the amplitude of the thread, using numerically generated results of the transient shapes obtained by boundary integral techniques. The dynamic of dimensionless maximum and minimum amplitudes,  $A_{\rm max}(\tau)/R_{\rm obt}$  and  $A_{\rm min}(\tau)/R_{\rm obt}$ , as a function of the viscosity ratio,  $\lambda$ , and dimensionless time were given by:

$$\frac{A_{\text{max}}(\tau)}{R_{\text{obt}}} = \sum_{n=0}^{3} k'_n(\lambda)\tau^n \tag{5}$$

$$\frac{A_{\min}(\tau)}{R_{\text{obt}}} = \sum_{n=0}^{8} k_n''(\lambda) \tau^n \tag{6}$$

where  $A_{\rm max}$  and  $A_{\rm min}$  are maximum and minimum amplitudes of the fiber at time  $\tau$  ( $\mu$ m);  $\lambda$  is the viscosity ratio defined in Eq. (4).  $R_{\rm obt}$  is the undeformed radius of the fiber at t=0 and  $\tau$  is a dimensionless time defined by:

$$t = t/t_{\rm c} \tag{7}$$

where t is the experimental real time and  $t_c$  is a characteristic time for the interfacial-tension-motions in the experiment given by:

$$t_{\rm c} = \frac{R_{\rm obt} \eta_{\rm om}}{\gamma} \tag{8}$$

The coefficients  $k'_0 - k'_3$  and  $k''_0 - k''_8$  were presented by Tjahjadi et al. [5] and tabulated for viscosity ratios ranging from 0.01 to 10.

More details about the theory can be found in the original work of Tjahjadi et al. [5]

In this work, both the theories by Tomotika and Tjahjadi et al. were tested and evaluated to infer interfacial tension from the study of the dynamic of a breaking thread.

#### 3. Materials

Table 1 lists the characteristics of the materials used in

Table 1 Materials used in this work

Polymer MFI (g/10 min)  $\eta_0$  (Pa s)  $T_g$  (°C)  $T_{\rm m}$  (°C) Supplier Specification 200 °C 240 °C 220 °C  $PP_1$ 20 1100 870 780 -5163 Polibrasil VS6100  $PP_2$ 5.5 4000 Polibrasil TM6100 8300 6400 163 2.5 9900 BASF PS 103 5300 2600 145H PC 20 43,400 11,300 3500 151 Bayer 2458

this study. Two types of PP were used in this work, PP<sub>1</sub> was used to evaluate the interfacial tension between PP/PS and both PP<sub>1</sub> and PP<sub>2</sub> were used to measure interfacial tension between PP/PC. This was done to study the effect of rheological properties of the polymers on the breaking thread process.

#### 3.1. Sample preparation

In this work, based on the softening temperatures, PS and PC were chosen to make the films (matrix) and PP to produce fibers. The fibers were obtained by melt spinning of molten pellets from a hot plate. Fibers diameters varied from 30 to 110 µm. The fibers were annealed during 12 h at 150 °C under vacuum to avoid residual stresses. The fibers used were cut into pieces of 0.1 cm prior to annealing. The aspect ratio AR =  $L_{\rm obf}/D_{\rm obf}$  (where  $L_{\rm obf}$  and  $D_{\rm obf}$  are the length and diameter of the fiber for t = 0 s, respectively) was chosen so that it would be higher than a critical value that depends on the viscosity ratio  $\lambda = \eta_{\rm of}/\eta_{\rm om}$  (where  $\eta_{\rm of}$ is the zero shear viscosity of the fiber and  $\eta_{\rm om}$  is the zero shear viscosity of the matrix) [5]. During the annealing process, the fibers had their extremities fixed to avoid significant distortions of the diameter. The films (matrix) used in the experiments and the disks used for rheological measurements were obtained by compression molding.

The control of thickness of the films (matrix) is very important when using the breaking thread method. This thickness was optimized (250  $\mu$ m) to minimize eventual problems with air bubbles and to promote a melting process fast enough to avoid the fibers distortion to start before complete melting of the films. The width and length of the films were 1.5 cm.

# 3.2. Rheological measurements

Rheological characterization of the samples was carried out using a stress controlled rheometer (model SR-5000 from Rheometric Scientific®) under a dry nitrogen atmosphere. A parallel plate configuration was used with a gap of 0.67 mm and plate diameter of 25.0 mm. Strain and stress sweeps were performed to define the region of linear viscoelasticity of the polymers. Dynamic frequency sweeps were performed with frequency ranging from 0.01 to

500 rad/s. The zero shear viscosity  $(\eta_0)$  of polymers necessary for the interfacial tension calculation was inferred by fitting Carreau's Model [17] to plots of the complex viscosity  $(\eta^*)$  against frequency. The values are presented in Table 1.

# 3.3. Interfacial tension experimental procedure

The experiments were carried out placing the fibers between two films. The 'sandwich' formed was placed between two glass sheets and heated in a hot stage (Mettler FP-90). The temperature was raised at a rate of 20 °C/s to 150 °C. The system was maintained at 150 °C to allow all the air bubbles to escape. Then, the temperature was raised to the temperature at which the experiment was performed (200, 220, and 240 °C). Observations were made using an optical microscope at a magnification of 50 × or 100 × depending on the radius of the fiber. Photos of the break-up process were taken using a CCD camera. The images were then analyzed using a commercial digital image analysis software package. Photographs from a typical experiment are shown in Fig. 2. The registered images correspond to the central region of the fibers, to avoid the influence of mechanisms other than capillary instabilities of Rayleigh [13,14].

#### 4. Results and discussion

Fig. 3 shows the curves of zero shear viscosity of the polymers studied in this work as a function of temperature. It can be seen that for the whole range of temperatures studied, the zero shear viscosity of PP<sub>1</sub> is lower than the zero shear viscosity of PS and of the zero shear viscosity of PC. In the case of PP<sub>2</sub> and PC polymer pair the zero shear viscosity of PP<sub>2</sub> is lower than the one of PC only for temperatures lower than 230 °C. In order to determine the

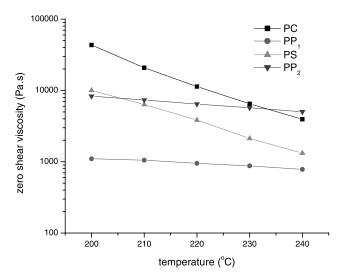


Fig. 3. Zero shear viscosity of the polymers used in this work.

interfacial tension between two polymers using the breaking thread method, the fiber should be formed with the material that has the lower viscosity [13,14], and at the same time the higher softening temperature. If the fiber is formed using the material with higher zero shear viscosity, phenomenon such as end pinching and retraction could occur preventing the use of the method. Therefore for PP<sub>2</sub>/PC polymer pair at a temperature of 240 °C a special experimental procedure had to be developed. It will be described below.

The values of interfacial tension for  $PP_1$  in PS at temperature of 200 °C for 20 different experiments of breaking thread are summarized in Table 2. It can be seen that the values of interfacial tension range from 4 and 12 mN/m. Analyzing the data of samples 7 and 15, samples with same initial fiber diameter, it can be seen that the time for complete break-up of the fiber of sample 7 is much lower than the one of sample 15. To evaluate the difference between the two experiments, the theoretical time for complete break-up,  $tb_{\rm theo}$ , was calculated for a fiber of  $PP_1$ 

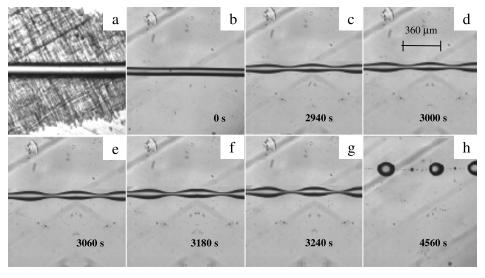


Fig. 2. Optical micrographs of a PP fiber imbedded in a PS matrix at 200 °C.

Table 2 Interfacial tension for PP<sub>1</sub>/PS at 200 °C, with  $\lambda = 0.11$ , determined by theories of Tomotika [3,4] and Tjahjadi et al. [5]

Samples	Measurements			Tomotika's theory		Tjahjadi's theory		
	$tb_{\rm exp}$ (s)	$tb_{\rm theo}$ (s)	D <sub>0</sub> (μm)	$\Omega(X,\lambda)$	γ (mN/m)	$\Delta \tau \left( A_{\mathrm{max}} \right)$	$\Delta \tau \left( A_{\min} \right)$	γ (mN/m)
1	6123	5959	62.423	0.205	5.29	0.33	0.34	5.33
2	3506	5093	66.535	0.192	7.09	1.29	1.24	6.91
3	5307	5647	60.122	0.179	6.13	0.69	0.82	6.93
4	5495	5524	63.141	0.206	5.74	3.35	3.14	5.29
5	3673	3707	38.123	0.173	5.87	9.03	8.71	5.77
6	1005	3394	57.822	0.185	9.45	4.27	13.22	9.40
7	1968	3096	64.703	0.180	12.05	6.07	5.70	11.77
8	1169	3409	58.558	0.206	8.58	0.62	1.27	9.55
9	5098	5177	61.024	0.204	5.98	8.42	8.31	5.95
10	5019	5028	43.028	0.141	6.04	1.25	1.27	6.13
11	2355	4487	64.122	0.205	7.23	1.38	0.68	7.69
12	4219	3206	68.213	0.205	10.81	8.41	4.12	8.28
13	6457	6173	62.706	0.205	5.12	1.41	1.45	5.53
14	3518	3723	36.917	0.167	5.82	2.63	2.61	5.67
15	5364	5595	64.633	0.190	6.32	2.29	2.32	6.07
16	2322	2587	37.125	0.139	10.13	2.45	1.07	8.64
17	2219	2606	59.124	0.199	11.73	8.41	2.52	6.18
18	6098	6167	62.003	0.169	6.14	1.41	1.45	5.53
19	3518	3676	32.621	0.200	4.31	4.06	2.58	4.65
20	3356	5619	67.581	0.127	9.89	2.31	2.22	5.91

 $D_0$  is the initial diameter of the fiber;  $\lambda$  is the viscosity ratio;  $\Omega(X,\lambda)$  is the dimensionless growth rate;  $\gamma$  is the interfacial tension;  $tb_{\rm exp}$  and  $tb_{\rm theo}$  are the experimental and theoretical times for complete break-up of the fiber;  $\Delta \tau (A_{\rm max})$  and  $\Delta \tau (A_{\rm min})$  are the dimensionless time differences for maximum and minimum amplitude of the fiber, respectively.

imbedded in PS at a temperature of 200 °C using the expression developed by Elemans et al, [14] given by:

$$tb_{\text{theo}} = \frac{\eta_{\text{om}} R_{\text{obt}}}{\Omega_{\text{max}} \gamma} \ln \left( \frac{1.39 \gamma (R_{\text{obt}})^2}{kT} \right)$$
(9)

where  $\eta_{\rm om}$  is the zero shear viscosity of the matrix,  $R_{\rm obt}$  is the initial radius of the fiber,  $\Omega_{\rm max}$  is the dimensionless growth rate, k is the Boltzmann constant (1.3807 × 10<sup>23</sup> J/K), T is the absolute temperature (in K) and  $\gamma$  is the interfacial tension between two polymers.

The values of experimental and theoretical times for complete break-up for 20 experiments of breaking thread are summarized in Table 2. The value of interfacial tension used in this calculation was  $\gamma = 5.52$  mN/m determined by pendant drop method [9]. Comparing the experimental to the theoretical values of time for complete break-up a difference of more than 2000 s can be observed for samples 2, 6–8, 11, and 20. This difference is probably due to residual stresses in the fiber. For this reason, samples 2, 6, 7, 8, 11, and 20 should be discarded.

The value of interfacial tension obtained by breaking thread method for PP<sub>1</sub> in PS at 200 °C after discarding those samples was 6.82 and 6.14 mN/m according to theories of Tomotika and Tjahjadi et al. respectively. These results are higher than the ones obtained using the pendant drop method [9]. The theory of Tjahjadi et al. allows the evaluation of the maximum and minimum distortions of the fiber independently. It can be seen from Table 2 that for samples 6, 8, 11, 12, 16, 17, and 19 the dimensionless time

difference,  $\Delta \tau$ , for the maximum and minimum amplitudes differs by more than 100% for each case. For these samples the maximum and minimum amplitudes of the fiber do not behave in a homogeneous way along the fiber, causing a distortion of the value of the interfacial tension. This discrepancy in the behavior of the instabilities suggests the presence of other mechanisms not considered in breaking thread theories. Therefore, these samples should be discarded. When discarding these samples the value of interfacial tension obtained using the breaking thread method using Tomotika and Tjahjadi et al. theories were  $5.85 \pm 0.38$  mN/m and  $5.82 \pm 0.35$  mN/m, respectively. These values corroborate the one obtained by pendant drop method [9] within experimental error.

Table 3 lists the values of interfacial tension obtained for PP<sub>1</sub>/PC and PP<sub>2</sub>/PC polymer pairs for temperatures ranging from 200 to 240 °C using the procedure reported above. It can be seen that for 200 and 220 °C the values of interfacial tension obtained using both theories corroborate, within experimental error, for both polymer pairs. Also, the experimental results corroborate the values obtained with harmonic and geometric mean equations [18]. However, the value of interfacial tension at a temperature of 240 °C obtained for PP<sub>1</sub> in PC and PP<sub>2</sub> in PC differ by more than 100% for all the theories. This discrepancy may be due to the viscosity ratio,  $\eta_{\text{PP2}}/\eta_{\text{PC}}$  (where  $\eta_{\text{PP2}}$  is the zero shear viscosity of the PP<sub>2</sub> and  $\eta_{\text{PP1}}$  is the zero shear viscosity of the PC), that is higher than 1.

Fig. 4(a) shows a fiber of PP<sub>2</sub> imbedded in PC at a

Table 3 Average values of interfacial tension for PP/PC polymer pair

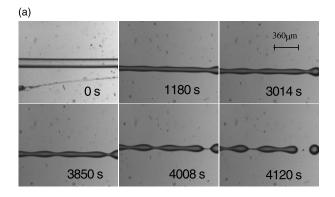
Materials	<i>T</i> (°C)	$\gamma e$ deviation (mN/m)	Breaking t	Mean equation		
			Tomotika	Tjahjadi et al.	Н	G
PP <sub>1</sub> in PC	200	γ deviation	13.01	12.37	equation  i et al. H G  12.09 11.  10.12 9.  - 8.02 7.  12.09 11.  10.12 9.	11.84
-		•	0.54	equat  notika Tjahjadi et al. H  11.37	_	_
	220	$\gamma_{12}$ deviation	10.34	10.56	10.12	9.84
		,	0.53	0.39	_	_
	240	γ deviation	8.79	8.63	8.02	7.66
			0.59	0.42	-	-
PP <sub>2</sub> in PC	200	γ deviation	12.83	12.45	12.09	11.84
			0.61	0.39	_	_
	220	γ deviation	10.53	10.72	10.12	9.84
			0.48	0.43	_	_
	240	γ deviation	15.3	17.4	8.02	7.66
			0.75	0.71	-	-
PC in PP <sub>2</sub>	240	γ deviation	8.55	8.50	8.02	7.66
_			0.43	0.39	-	_

T: temperature;  $\gamma$ : interfacial tension; H: harmonic mean equation; G: geometric mean equation.

temperature of 240 °C. In this case, the softening temperature of the matrix is smaller than the softening temperature of the fiber, which facilitates the imbedding process, however, the viscosity ratio ( $\lambda = \eta_f/\eta_m$ ) is higher that 1, and mechanism known as end pinching and retraction can be observed. These mechanisms produce irregular distortions not considered in breaking thread theories. For this reason the value of interfacial tension inferred from this experiment should not be considered. It was therefore attempted to use PP as a matrix and PC as a fiber. Fig. 4(b)

shows a fiber of PC imbedded in PP2 at a temperature of 240 °C. Problems with the imbedding process can be observed: air bubbles are happed at the interface between PP and PC. In order to cope up with this problem a special experimental procedure was developed. Fig. 5 shows the thermal treatment undergone by the matrix fiber assembly as well as the evolution of the thread as a function of time. It can be seen that this treatment results in a typical evolution of the fiber. The value of interfacial tension obtained performing this thermal treatment for PP<sub>2</sub>/PC polymer pair was  $8.5 \pm 0.4$  mN/m for both theories. This value corroborates the value obtained with geometric and harmonic mean equations. These considerations could explain the high values found by Chapleau et al. [14] when measuring interfacial tension between PP and PC at temperatures of 225 and 245 °C using the breaking thread method. They found a value of 17.4 and 15.3 mN/m, respectively, which did not corroborate with the ones obtained using geometric and harmonic mean equations [18]. These discrepancies could be explained by the fact that the experiment by Chapleau et al. [10] had a viscosity ratio ( $\lambda = \eta_f/\eta_m$ ) higher

Fig. 6 shows the interfacial tension between PP/PS and PC/polypropylene (PP<sub>1</sub> and PP<sub>2</sub>) as a function of temperature. The values of interfacial tension were obtained by averaging the values of interfacial tension obtained from Tomotika and Tjahjadi's et al. theories and are listed in Tables 3 and 4. The different symbols represent the experimental data for different polymer pairs and the straight line represents the best fit obtained by linear regression. The results of the best fitting are listed in Table 5. It can be seen that for the three polymer pairs studied in



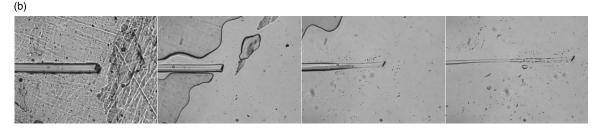


Fig. 4. (a) Optical micrographs of a PP<sub>2</sub> fiber imbedded in a PC matrix at 240 °C with  $\lambda = 1.16$ . (b) Optical micrographs of a PC fiber imbedded in a PP<sub>2</sub> matrix at 240 °C with  $\lambda = 0.86$ .

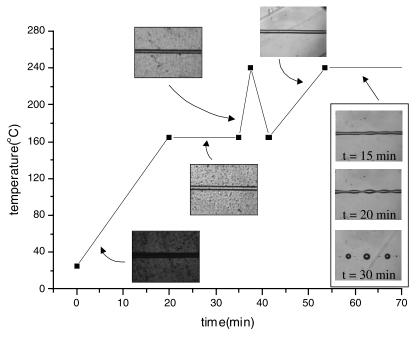


Fig. 5. Sequence of temperature and rate heating for PC in PP<sub>2</sub>.

this work the interfacial tension decreases with increasing temperature which is expected thermodynamically. The order of magnitude of  $-\partial \gamma/\partial T$  found in this work corroborate the ones found in the literature [10,19].

# 5. Conclusions

In this work the interfacial tension between polypropylene and polystyrene and between polypropylene and polycarbonate for temperatures ranging from 200 to 240 °C was evaluated using the breaking thread method. A new experimental procedure to enhance the accuracy of the breaking thread method was presented. It consists of using simultaneously the theories of Tomotika and Tjahjadi et al. to discard experiments for which the fibers have residual stresses. The procedure consists of; first comparing the experimental and theoretical times for complete break up of the fiber and discarding the experiments for which the difference between these two

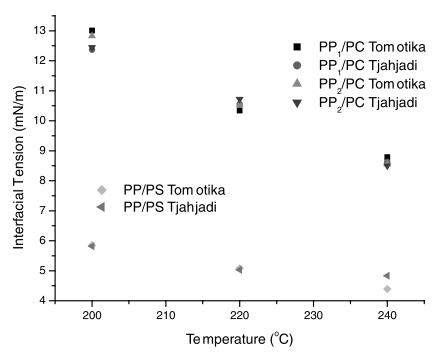


Fig. 6. Interfacial tension between polypropylene and polystyrene and between polypropylene and polycarbonate.

Table 4 Average values of interfacial tension for PP/PS polymer pair

Materials	T (°C)	$\gamma e$ deviation (mN/m)	Breaking thread		Pendant drop	Mean equation	
			Tomotika	Tjahjadi et al.	Demarquette et al. [9]	Н	G
PP <sub>1</sub> in PS	200	γ deviation	5.85	5.82	5.52	5.02	4.84
			0.38	0.35	0.25	_	_
	220	γ deviation	5.08	5.03	_	4.91	4.57
			0.61	0.54	_	_	_
	240	γ deviation	4.67	4.39	4.83	4.54	4.37
			0.55	0.39	0.25	_	_

T: temperature;  $\gamma$ : interfacial tension; H: harmonic mean equation; G: geometric mean equation.

times is higher than 30%. In a second step, the dimensionless time differences for the maximum and minimum amplitude of the fiber calculated following Tjahjadi et al's theory should be compared. The experiments for which these two values differ by more than 30% should be discarded. The accuracy of the breaking thread method can be further increased by decreasing the tolerance for the difference between the times calculated. However, one should remember that the calculated value of time for complete break up depends heavily on the value of interfacial tension used in the calculation. The value normally used is inferred from geometric and harmonic mean equations which can lead to substantial error [20].

For both polymer pairs studied the standard deviation of the values obtained with the theory of Tjahjadi et al. was smaller than standard deviation obtained with the theory of Tomotika. However, the determination of the interfacial tension for the theory of Tjahjadi et al. is more complex.

A new experimental procedure for polymer pairs that cannot normally be tested using breaking thread method (Polymer with higher softening temperature and higher viscosity.) was presented. The experimental results showed that it was more convenient to work with polymer pair for which the fiber has a lower softening temperature than for which the fiber has a higher viscosity. The imbedding of the fiber can be achieved by a special thermal treatment that should be tailored for each polymer pair.

Table 5 Linear regression coefficients of  $\gamma = a - bT$  (200  $\leq T \leq$  240)

Polymer pair	Method	а	b	$r^2$
PP/PS	Tomotika	11.690	0.0295	0.9699
11/15	Tjahjadi	12.945	0.0358	0.9963
	Average	12.318	0.0326	0.9874
PP <sub>1</sub> /PC	Tomotika	33.923	0.1055	0.9771
PP <sub>1</sub> /PC	Tjahjadi	31.090	0.0935	0.9997
	Average	12.945 0.0 12.318 0.0 33.923 0.1 31.090 0.0 32.507 0.0 34.177 0.1 32.282 0.0	0.0995	0.9948
PP <sub>2</sub> /PC	Tomotika	34.177	0.1070	0.9981
2	Tjahjadi	32.282	0.0988	0.9949
	Average	33.229	0.1029	0.9999

It was shown that the interfacial tension between polypropylene and polystyrene e and between polypropylene and polycarbonate decreases linearly with the increase in temperature.

## Acknowledgements

The authors would like to thank the Polibrasil SA, BASF and Bayer for supplying the materials and FAPESP Brazilian funding agency for financial support (FAPESP 97/06071-2).

# References

- Utracki LA. Encyclopaedic dictionary of commercial polymer blends. Toronto, Canada: Chemtec Publishing; 1996.
- [2] Demarquette NR. Int Mater Rev. Accepted for publication.
- [3] Tomotika S. Proc R Soc 1935;A150:322–37.
- [4] Tomotika S. Proc Roy Soc 1936;A153:302-18.
- [5] Tjahjadi M, Ottino JM, Stone HA. AIChE J 1994;40(3):385-94.
- [6] Peixiang X, Bousmina M, Rodrigue D, Kamal MR. Macromolecules 2000;33:8020–34.
- [7] Machiels AGC, Van Dam J, Posthuma de Boer A, Norder B. Polym Engng Sci 1997;37(9):1512–25.
- [8] Luciani A, Champagne MF, Utracki LA. Polym Networks Blends 1996;6(2):51–62.
- [9] Demarquette NR, Souza AMC, Palmer G, Macaúbas PHP. Polym Engng Sci. 2003;43(3):670–83.
- [10] Chapleau N, Favis BD, Carreau PJ. Polymer 2000;41:6695-8.
- [11] Everaert V, Groeninckx G, Pionteck J, Favis BD, Aerts L, Moldenaers P, Mewis J. Polymer 2000;41:1011–25.
- [12] Son Y. Polymer 2001;42:1287-91.
- [13] Stone HA, Leal LG. J Fluid Mech 1989;198:399-427.
- [14] Elemans PHM, Hansen JHM, Meijer HEH. J Rheol 1990;34(8): 1311–25.
- [15] Palierne JF, Lequeux F. J Non-Newtonian Fluid Mech 1991;40(3): 289–306.
- [16] Machiels AGC, Busser RJ, Van Dam J, Posthuma de Boer A. Polym Engng Sci 1998;38(9):1536–48.
- [17] Carreau PJ, De Kee D, Chhabra R. Rheology of polymeric systems principles and applications. Munich: Carl Hanser; 1997.
- [18] Wu S. Polymer interfacial and adhesion. New York: Dekker; 1982.
- [19] Kamal MR, Lai-Fook R, Demarquette NR. Polym Engng Sci 1994; 34(24):1834–9.
- [20] Shimizu RN, Demarquette NR. J Appl Polym Sci 2000;76:1831–45.