

Polymer Communication

Measuring the interfacial tension of polyamide/polyethylene and polycarbonate/polypropylene blends: effect of temperature

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Abstract

In this study, the influence of temperature on the interfacial tension for three polymer pairs (polycarbonate/polypropylene; polyamide/polyethylene-1; polyamide/polyethylene-2) is investigated. The interfacial tension is measured using the breaking thread method and the temperature coefficients are reported for each polymer pair. It is demonstrated that in all three cases, the temperature dependence is higher than predictions based on the Good and Girifalco equation differentiated with respect to temperature. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The interfacial tension is the most basic parameter which characterizes the interface between polymers. Recently, renewed interest in the measurement of the interfacial tension has been occurring due to improvements in measuring techniques such as the pendant drop and breaking thread methods and values of the interfacial tension between various homopolymer pairs are becoming more and more available [1–5]. However, little experimental data for the interfacial tension dependence on temperature has been reported.

In this study, the influence of temperature on the interfacial tension, σ , between three polymer pairs is investigated. Temperature coefficients, $-d\sigma/dT$, are reported for a polyamide in two high density polyethylenes and a polycarbonate in a polypropylene. The interfacial tension is measured using the breaking thread method, which is based on the observation of the disintegration of long cylinders imbedded in a matrix via a phenomenon known as capillary instabilities. The analysis, developed by Tomotika [6], relates the growth rate (q) of the sinusoidal distortion growing exponentially with time of a breaking fiber. Although it is based on liquids exhibiting Newtonian behavior, this analysis is adequate for viscoelastic polymers if the break-up process occurs at very low rates. This tech-

nique has been used for measuring the interfacial tension between many molten homopolymer pairs and has proven to be useful for evaluating the interfacial tension reduction due to the addition of compatibilizing agents [2,3,5,7–10].

2. Experimental

2.1. Materials

The properties of the materials used are reported in Table 1. In order to minimize degradation, 0.2 wt.% of an antioxidant (Irganox 1010) was added to the polyethylenes. Prior to any manipulation, all materials containing hydrophilic resins were dried under vacuum overnight.

2.2. Sample preparation

For all systems, the polymer which has the highest glass transition or melting temperature (PC or PA) is used as the thread.

A thin filament of one of the components is sandwiched between two films of the matrix. Threads of the resins are drawn from a few pellets melted on a hot plate and cut into 10 mm long pieces. Typical thread diameters ranged from 20 to 60 μm . Thin films (approximately 300 μm thick) of the PP or PE matrices are melt pressed. Further details are given in previous papers [7,9,10].

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Table 1
Properties of the components studied

Component	Supplier	Molecular weight (kg/kmol)
Polypropylene PP	PVF222 Himont	$M_n = 53,000$, $M_w = 447,000$
Polycarbonate PC	Lexan A-130 General Electric	$M_n = 10,600$, $M_w = 26,200$
High density polyethylene PE-1	Dow Chemical	$M_n = 20,200$, $M_w = 81,300$
High density polyethylene PE-2	Dow Chemical	$M_n = 24,000$, $M_w = 79,000$
Polyamide-6 PA	Zytell 211 DuPont	$M_n = 25,000$, $M_w = 44,000$

2.3. Rheological analysis

The theory of Tomotika requires accurate values of the zero-shear viscosities of the components. All samples underwent mixing procedures prior to any rheological measurements, which were performed on a Bohlin CSM rheometer in oscillatory mode with parallel plates of 25 mm diameter. Dry nitrogen was sparged around the plates during the measurements. Typical gaps ranged from 1.2 to 1.8 mm. All the polymers studied exhibited a Newtonian plateau and the loss angle was always higher than 87° . The zero-shear viscosities, evaluated using a Carreau–Yasuda model [11], of the different matrices and threads at three temperatures are reported in the form of Arrhenius plots in Figs. 1 and 2.

2.4. Capillary instability observations

The capillary instabilities were observed with a Nikon microscope equipped with a Mettler FP82 HT hot stage. Digitized images of the developing oscillations were captured. An image processing system (Visilog 4.1.3) was used to measure the amplitude (α) and wavelength (λ) of the growing distortions. The amplitude was

calculated by measuring the evolution of the minimum and maximum diameters of one oscillation. Each value of interfacial tension is obtained from an average of at least five experiments. In each experiment, the sample is first slowly heated to the melting temperature of the matrix in order to avoid air bubble formation at the interface. The temperature is then increased to just below the glass transition or melting temperature of the thread and annealed for 5 min. Finally, the sample is rapidly heated to the test temperature. Further experimental and theoretical details concerning the breaking thread technique are given in Ref. [7].

3. Results and discussion

The growth rate of the sinusoidal distortion, q , was obtained from the slope of semi-log plots of the amplitude α vs. time. Since the magnitude of the amplitude is difficult to measure visually in the early stages of the breaking process, only images captured in the middle of the experiment are digitized and analyzed.

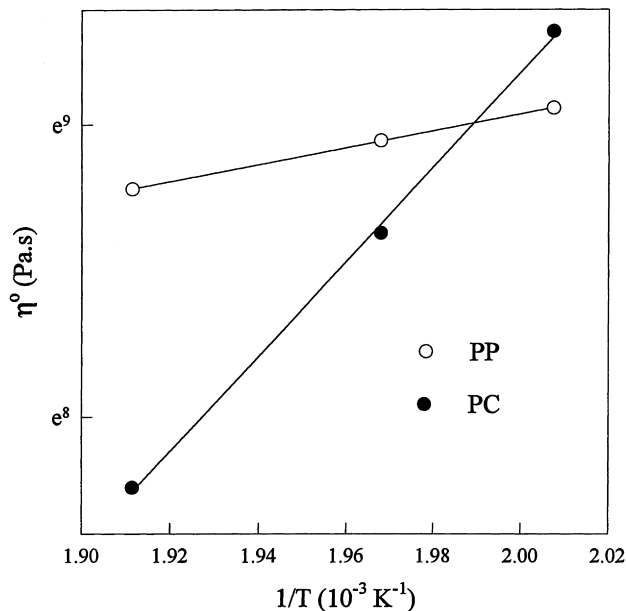


Fig. 1. Arrhenius plots of the zero-shear viscosities as a function of temperature for PC and PP.

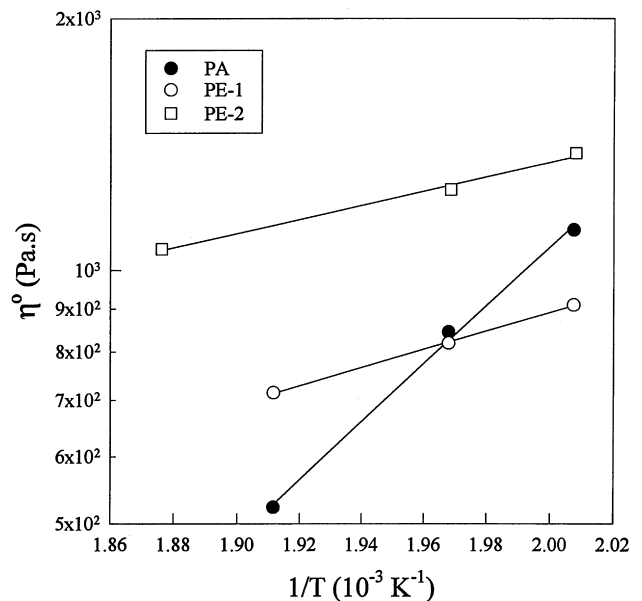


Fig. 2. Arrhenius plots of the zero-shear viscosities as a function of temperature for PA, PE-1 and PE-2.

Table 2
Interfacial tension as a function of temperature for all the systems studied. Temperature coefficients, obtained by linear regression, are also given.

Thread/matrix	<i>T</i> (°C)	σ (mN/m)	$-\frac{d\sigma}{dT}$ (mN/m °C)
PC/PP	225	17.4	0.09
	235	15.8	
	245	15.3	
	250	14.6	
	265	13.8	
PA/PE-1	225	16.3	0.12
	235	14.6	
	240	14.0	
PA/PE-2	250	12.0	0.08
	225	18.4	
	235	18.3	
	245	17.0	
	260	15.8	

3.1. Uncompatibilized systems

The exponential behavior of α vs. time which is predicted by the Tomotika theory is observed for PC imbedded in a PP matrix. Similar behavior for the PA in PE systems is also obtained. Table 2 gives the interfacial tension as a function of temperature for the uncompatibilized systems. These data are shown graphically in Fig. 3. The interfacial tension between PC and PP varies from 17.3 mN/m at 225°C to 13.8 mN/m at 265°C. The interfacial tension calculated using the harmonic mean equation yields a value of $\sigma_{PC/PP} = 9.5$ mN/m at 250°C [12]. In a series of studies on interfacial tension from this laboratory a good correlation

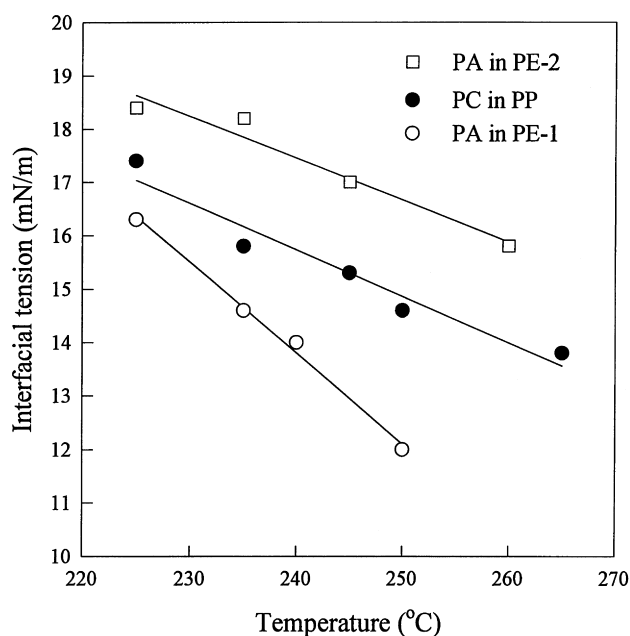


Fig. 3. Interfacial tension as a function of temperature for the homopolymers studied.

of the breaking thread method has been found with other techniques of measurement (pendant drop [13], sessile drop [7], and emulsion model approach [14]). At the same time a number of studies have reported that the harmonic mean value tends to underestimate the real value of the interfacial tension [7,9,10]. This also appears to be confirmed in this study. Recently Pham and Carriere [15], using the imbedded fiber retraction method, have reported on the temperature dependence of interfacial tension for PC, PE blends. They report surprisingly low values for σ ranging from about 2.8 dyn/cm at 210°C to 2.1 dyn/cm at 240°C (note that 1 dyn/cm = 1mN/m).

The values of interfacial tension shown in this work for the PA in PE systems are comparable to the experimental data reported by other authors for similar systems [2,3,5]. In previous work [9] it was shown that the harmonic mean equation predicts $\sigma_{PA/PE} = 12.6$ mN/m at 250°C. The differences in interfacial tension when using the two PE matrices (14.6 mN/m °C for PE-1 and 18.3 mN/m °C for PE-2) are significant. The molecular properties of the polyethylenes are similar (see Table 1) but PE-1 has a higher polydispersity than PE-2. It has been suggested for polydisperse systems that the smaller molecules can migrate to the interface and act as surfactants by lowering the interfacial tension. Experimental data by Kamal et al. [16] supported this hypothesis when studying polystyrene/polypropylene systems at high temperature. The data in this work shows the same trend. Furthermore, it must be remembered that the materials used in this study are commercial resins. A paper by Luciani et al. [3] has shown that the addition of a very small amount (0.5 wt.%) of an additive to films used in a breaking thread experiment increased the interfacial tension by a factor of 1.3. This stresses the specific nature of the measured interfacial tension between commercial polymers.

For the three systems the interfacial tension decreases with temperature, as expected. The slopes of each curve shown in Fig. 3 were calculated by linear regression and the temperature coefficients ($-\frac{d\sigma}{dT}$) are given in Table 2. The temperature coefficient values are lower than those typically observed for low molecular weight liquids. For polymers, the coefficients are expected to be lower because of conformational restrictions at the interface, due to the high molecular weights. The values of the temperature coefficients in this work are however higher than those predicted by theory and other studies on polymeric systems. For example, when the Good and Girifalco [17] equation:

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2\phi(\sigma_1\sigma_2)^{1/2}$$

is differentiated as a function of temperature:

$$\frac{d\sigma_{12}}{dT} = \frac{d\sigma_1}{dT} + \frac{d\sigma_2}{dT} - \phi \left[\left(\frac{\sigma_1}{\sigma_2} \right)^{1/2} \frac{d\sigma_2}{dT} + \left(\frac{\sigma_2}{\sigma_1} \right)^{1/2} \frac{d\sigma_1}{dT} \right]$$

the values of $-\frac{d\sigma}{dT}$ (with the values of the surface tensions (σ_1 and σ_2) and interaction parameters (ϕ) taken from Wu [12]) are 0.06 and 0.03 mN/m °C for the PC/PP and PA/PE

systems, respectively. Our values of 0.09 for PC in PP, 0.12 for PA in PE-1 and 0.08 mN/m °C for PA in PE-2 are higher.

The variation of interfacial tension with temperature has been reported previously in the literature. All the experimental results given below were obtained using a pendant drop apparatus and, in all cases, a linear decrease of the interfacial tension with temperature was observed. Wu [18] has evaluated the temperature coefficients for polyvinylacetate/polyethylene and polyvinylacetate/polyisobutylene systems and the calculated values were 0.027 and 0.02 mN/m °C. Roe [19] studied polymer pairs consisting of a polyethylene and five polar polymers. His values were all below 0.017 mN/m °C. The temperature coefficients were even lower when evaluating the interfacial tension between polar polymer pairs (below 0.009 mN/m °C). Anastasiadis et al. [20], in a study on temperature and molecular weight dependence on interfacial tension, also reported a linear decrease of the interfacial tension with temperature for polystyrene drops in a hydrogenated 1,2-polybutadiene matrix. The temperature coefficients decreased from 0.0148 to 0.00882 mN/m °C when the molecular weight (M_n) of the polystyrene was increased from 2200 to 10,200 kg/kmol. In another study on temperature and molecular weight effects, Kamal et al. [16] obtained temperature coefficients decreasing from 0.045 to 0.037 mN/m °C for monodisperse polystyrene drops of various molecular weights (increasing from 4755 to 380,000 kg/kmol) in a polypropylene. When using a polydisperse polystyrene (polydispersity of 2.8), the temperature coefficient increased to 0.072 mN/m °C. This latter result now falls into the range of our values of 0.09 mN/m °C for PC in PP, 0.12 mN/m °C for PA/PE-1 and 0.08 mN/m °C for PA/PE-2 systems. The latter two systems have polydispersities of 4 and 3, respectively. It is interesting to note that when increasing the polydispersity from about 3 to 4 for the PA/PE blends there is a corresponding increase in the temperature dependence of the interfacial tension from 0.08 mN/m °C to 0.12 mN/m °C. It is possible that polydispersity is responsible for the high temperature coefficients. Using the breaking thread method for measuring the interfacial tension between many molten polymer pairs, Luciani et al. [3] calculated a temperature gradient of 0.045 mN/m °C for polyamide fibers imbedded in a low density polyethylene.

4. Concluding remarks

The interfacial tensions between a polyamide (PA) in two high density polyethylenes (PE-1 and PE-2) and between a polycarbonate (PC) in a polypropylene (PP) have been measured using the breaking thread method at different temperatures. In all cases, the interfacial tension decreases with temperature, as expected. The values of the temperature coefficients, $-d\sigma/dT$, for the homopolymer systems are 0.09, 0.12 and 0.08 mN/m °C for the PC/PP, PA/PE-1 and PA/PE-2 systems, respectively. The values of $-d\sigma/dT$ reported in this study are higher than predictions based on the Good and Girifalco equation differentiated with respect to temperature.

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