

Interfacial Tension of Poly(*p*-phenylene sulfide) with Other Polymer Melts

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SYNOPSIS

The interfacial tension of poly(*p*-phenylene sulfide) (PPS) with various thermoplastics of different composition and polarity has been carried out using the breaking thread and pendant drop methods. The value of the polyethylene (PE)/PPS interfacial tension is found to be intermediate between PE/polysulfone and PE/polycarbonate. The highest interfacial tension for PPS found in the systems studied was with polyamide-6 followed by PE. The lowest values were with polysulfone followed by polystyrene. The effects of small additions of polysulfone and polystyrene in PPS on interfacial tension is studied with various thermoplastics. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(*p*-phenylene sulfide) (PPS) is an important engineering thermoplastic. It was first commercialized by the Phillips Petroleum Co. in the late 1960s.¹ There were only limited studies in the 1970s.¹⁻⁵ It received greatly enhanced interest in the 1980s because of its outstanding high-temperature and solvent-resistant characteristics. Many companies, especially in Japan, developed new PPS production technologies including Toray, Kureha, Tonen, Idemitsu, and Tosoh. Toray and Phillips formed a joint venture. Kureha has licensed Celanese and Hoechst-Celanese to produce PPS according to their technology. In our laboratories, we have carried out extensive studies of processing PPS including formation of biaxially oriented film,^{6,7} melt spinning of fibers,⁸ and injection molding.⁹

The necessity of finding new applications for PPS led to the study of its blends. Studies on blends in the patent literature¹⁰⁻¹³ date to the late 1970s and early 1980s. Published studies begin with the work of Nadkarni and colleagues.¹⁴⁻¹⁶ Studies of blends of PPS with polyetherimide, polyamides, and polysul-

fone have been described in papers from our laboratories.^{17,18}

To understand the characteristics of binary blends, it seems logical to investigate the interaction of the PPS melt phase with other melts. The primary interface property that characterizes the interface between two polymer melts is the interfacial tension.

BACKGROUND ON INTERFACIAL TENSIONS OF THERMOPLASTICS

The concept of surface tension is quite old and is generally attributed to Seanon in the mid-18th century. Young and Laplace independently in 1804-1806 developed much of theory of surface tension. As long ago as 1878, Maxwell¹⁹ published an extensive review on this subject with a long historical survey. Maxwell was well aware of interfacial tension between liquids as opposed to surface tension. The concept of interfacial tension between different liquids is clearly found in the earlier work of Quincke and Plateau in the last century. Quincke²⁰ in 1870 published measurements of interfacial tensions between water and mercury as well as each of these liquids with carbon disulfide, chloroform, alcohol, and turpentine. In the late 19th century, many investigators including Rayleigh^{21,22} and Reynolds²³ made basic studies of the spreading of liquids onto

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Table I Polymers Used in This Study

Polymer	Designation	Sources
Poly(<i>p</i> -phenylene sulfide)	PPS	Phillips Petroleum
Polystyrene	PS	Dow Chemical Styron 619
Low-density polyethylene	LDPE	Quantum Chemical Petrothene NA-212
Polypropylene	PP	Fina Oil Fina 6283
Polyamide-6	PA6	Allied Chemical Capron 8200
Polysulfone	PSF	Union Carbide Udel P-1700
Polycarbonate	PC	Mobay Chemical Makrolon 2603
Poly(ethylene terephthalate)	PET	Kodak Kodapak PET7352

each other. In the 1930s, Tomotika^{24,25} simulated the hydrodynamic instabilities occurring for liquid filaments immersed in a second liquid, noting the key role of interfacial tension.

Measurements of interfacial tensions for pairs of molten polymers began in 1964 with the work of Chappellear²⁶ using broken thread measurements. In 1965, Sakai²⁷ reported using a sessile drop method. From 1969, the key work of S. Wu²⁸⁻³⁰ of DuPont and R. J. Roe³¹ of Bell Laboratories were published. These early investigations used the pendent drop technique of Andreas et al.³² In the 1980s, this technique gained considerable attention in the literature.³³⁻³⁵ Other techniques such as the spinning drop,³⁶⁻³⁸ breaking thread,^{39,40} and embedded fiber retraction technique^{41,42} have been described. Research in our own laboratory has, to date, emphasized the pendent drop technique.⁴³

It is our purpose in the present article to present an investigation of interfacial tensions of poly(*p*-phenylene sulfide) (PPS) with various important commercial polymers. It is our hope in this study that this will lead to a better understanding of its characteristics in blends with other polymers. We will use both "pendent drop" and "breaking thread" techniques in these studies.

EXPERIMENTAL

Materials

PPS and seven different polymers were used in this investigation. These were (i) low-density polyeth-

ylene (LDPE), (ii) polypropylene (PP), (iii) polystyrene (PS), (iv) polycarbonate (PC), (v) poly(ethylene terephthalate) (PET), (vi) polyamide-6 (nylon-6) (PA6), and (vii) polysulfone (PSF). Their sources are listed in Table I.

The density of the various polymer melts at 290°C was determined in a capillary rheometer (Instron) by measuring the weight needed to fill a pressurized machine cavity at various pressures. This was extrapolation to zero pressure. The results are summarized in Table II.

The zero shear rate viscosity of the various polymers at 290°C were determined with a Rheometrics RMS-800 in a parallel plate mode. The results are listed in Table III.

Pendent Drop Experiment

The pendent drop apparatus consists of a light source filter, pendent drop cell, and a camera as de-

Table II Polymer Melt Density at 290°C

Polymer	Melt Density at 290°C (g/cm ³)
PPS	1.177
PS	0.891
LDPE	0.735
PP	0.725
PA6	0.958
PSF	1.134
PET	1.159
PC	1.086

Table III Zero Shear Viscosity at 290°C

Polymer	Zero Shear Viscosity at 290°C (Pa-s)
PPS	460
PS	680
LDPE	1500
PP	1100
PA6	235
PSF	7700
PET	200
PC	580

scribed in a previous article.⁴³ The lower density compression-molded polymer of was first introduced into the cell. At a certain equilibrium temperature, extruded filaments of higher density were introduced into the polymer melt of lower density through a capillary. Photographs of the drop profile were taken as a function of time. N₂ gas was introduced to avoid possible degradation of polymer melts. The drop profile shape was followed until equilibrium was achieved.

The interfacial tension, κ , was determined by the method of Andreas et al.³² using

$$\kappa = \frac{g \Delta \rho (d_e)^2}{H} \quad (1)$$

where g is the acceleration of gravity; $\Delta \rho$, the density difference between the two phases; d_e , the equatorial diameter; and H , a function of the ratio d_s/d_e , where d_s is the horizontal diameter measured at a distance up from the bottom of the drop.

Breaking Thread Experiment

Fine threads of PPS were melt spun from a Instron capillary rheometer. The diameters were controlled

down to 16 μm . Thin sheets of other polymers with dimensions of $10 \times 10 \times 0.5$ mm were prepared by a compression-molding press. The PPS thread was dried for 24 h and then placed between two sheets of the second polymer. This composite was brought to the desired temperature with a hot stage under an Leitz Laborex optical microscope. The distortion of the thread was photographed at regular intervals of time.

This method, based on the theory of Tomotika²⁴ on the capillary breaking of a fluid thread, was first used by Chappellear²⁶ in an attempt to measure the interfacial tension of polymer melts. A liquid cylinder of radius R_0 is generally subject to disturbances that were represented by small sinusoidal distortions of arbitrary wavelengths λ . The amplitude of the disturbance α grows exponentially with time t :

$$\alpha = \alpha_0 e^{qt} \quad (2)$$

where the growth rate q is given by

$$q = \frac{\kappa \Omega(\lambda, p)}{\eta_m R_0} \quad (3)$$

with κ , the interfacial tension; η_d , the shear viscosity of the thread phase; η_m , the viscosity of the matrix phase, and $\Omega(\lambda, p)$, a tabulated function.²⁴ The viscosity ratio (η_d/η_m) is represented by p .

RESULTS

In Table IV, we summarize the interfacial tensions of PE with a wide range of polymers including PPS. This allows us to see how PPS stands in terms of relative polarity with other thermoplastics. The value of κ was 7.9 dynes/cm by the pendent drop method and 7.2 dynes/cm by the breaking thread method. These values were intermediate between the systems of PE/PSF and PE/PC.

Table IV Interfacial Tension of Polyethylene with Other Polymer Melts

Polymer	Temperature (°C)	Pendent Drop κ (dyne/cm)	Breaking Thread κ (dyne/cm)
Polyethylene	290	0	0
Polypropylene	290	—	—
Polystyrene	290	4.0	5.0
Polysulfone	290	7.0	6.5
Poly(<i>p</i> -phenylene sulfide)	290	7.9	7.2
Poly(ethylene terephthalate)	290	9.4	9.2
Polycarbonate	290	12.5	13.0
Polyamide-6	290	12.8	13.2

Table V Interfacial Tension of Poly(*p*-phenylene sulfide) with Other Polymer Melts

Polymer	Temperature (°C)	κ (dyne/cm)	Method
Polyethylene	290	7.9	Pendent drop
Polypropylene	290	5.8	Pendent drop
Polystyrene	290	2.7	Pendent drop
Polysulfone	290	1.6	Breaking thread
Poly(<i>p</i> -phenylene sulfide)	290	0	—
Polycarbonate	290	3.5	Breaking thread
Poly(ethylene terephthalate)	290	5.1	Breaking thread
Polyamide-6	290	9.9	Breaking thread

In Table V, we look at the interfacial tension of binary combinations of PPS with other thermoplastics. The minimum value is PPS/PSF with 1.6 dynes/cm. The maximum is PPS/PA6, which has a value of 9.9 dynes/cm.

DISCUSSION

Position of PPS in PE-based Experiments

In the experiments determining the interfacial tension of PE with other polymer melt systems, the data were ordered as

$$\text{PE/PA6} > \text{PE/PET} > \text{PE/PC} > \text{PE/PPS} \\ > \text{PE/PSF} > \text{PE/PS} \quad (4)$$

Interfacial tensions are often associated with polarity differences between immiscible liquids. The relative position of the PE/PPS system would seem to indicate the polarity difference in PE/PPS is less than in PE/N6, PE/PET, and PE/PC but more than in PE/PS and PE/PSF.

The order of the PPS interfacial tensions with other polymers ranks as

$$\text{PPS/PA6} > \text{PPS/PE} > \text{PPS/PP} \\ \approx \text{PPS/PET} > \text{PPS/PC} \\ > \text{PPS/PS} > \text{PPS/PSF}(5)$$

This is not in disagreement with what is suggested by the inequality of eq. (4). It suggests the crude approximation of the Antonow⁴⁴ rule that the interfacial tension between the liquids is roughly the differences in their surface tensions. Much better methods of estimating interfacial tensions were given by Wu.⁴⁵

Introduction of Additives

There is a long literature that small amounts of suitable additives can reduce surface and interfacial tensions.^{36,42} Interfacial tensions of various systems where one component contains such as an additive of 5% PSF or PS in PPS are summarized in Table

Table VI Interfacial Tension of Poly(*p*-phenylene sulfide) with Other Polymer Melts in Ternary System

Fiber	Matrix	Temperature (°C)	Pendent Drop κ (dyne/cm)	Breaking Thread κ (dyne/cm)
PPS/PS	PE	290	6.8	6.0
	PP	290	5.0	4.2
	PC	290	—	9.0
	N6	290	—	11.0
PPS/PSF	PE	290	7.2	6.7
	PP	290	5.2	4.7
	PC	290	—	4.2
	N6	290	—	9.8

VI. For PE and PP, these yielded slightly decreased interfacial tension compared with their binary systems. However, these reductions are not as substantial as those found in other studies using compatibilizing agents.^{36,42} For PC and PA6, we found the interfacial tensions to be increased relative to pure PPS.

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