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Measurement of interfacial tension between polyamide-6 and poly(styrene-*co*-acrylonitrile) by breaking thread method

Y. Son*

R&D Center, Cheil Industries Inc., 332-2, Gochun-dong, Euiwang-shi, Kyunggi-do 437-010, South Korea

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Abstract

The measurement of the interfacial tension by the breaking thread method is known to be a proper method for high viscosity materials such as polymer melt. The interfacial tensions between polyamide-6 (PA-6) and a series of poly(styrene-*co*-acrylonitrile) (SAN) having AN contents varying between 0 and 41 wt% were obtained at 230°C by the breaking thread method. The interfacial tension has a maximum value at AN content of zero in the range of this study. It decreases rapidly at low AN content as AN content increases, and has minimum at ~14% of AN content followed by increasing up to ~28% AN. The interfacial tension increases slightly above ~28% AN. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Interfacial tension; Breaking thread method; Polyamide-6

1. Introduction

The final properties of polymer blend depend critically on the morphology of the immiscible domains that develop during blending and processing [1–3]. The final size and shape of the dispersed phase in a polymer blend depend on the properties of the component as well as processing conditions [4,5]. Several parameters can influence the final morphology of polymer blend such as: viscosity ratio, composition, processing method, and types of flow. In addition to the above, the role of interfacial property is critical. The basic parameter, which characterizes the interface, is the interfacial tension. So far, many studies on the interfacial tension of various homopolymer pairs, using different testing methods, have been reported [6–15]. However, the studies on copolymer/homopolymer pairs are comparably rare.

One of the most popular polymer blend which is being produced commercially is poly(acrylonitrile–butadiene–styrene) (ABS). Due to many advantages of polymer blend, ABS is also blended with another polymers such as polycarbonate, polyamide, polybutyleneterephthalate. Since poly(styrene-*co*-acrylonitrile) (SAN) is a matrix phase in ABS, it is important to get the value for interfacial tension between SAN and its counter parts as a function of AN contents in SAN in order to choose an optimal SAN grade in the study of ABS based blends.

PC/ABS is the most popular blend among ABS based blends. Watkins and Hobbs [11] measured the interfacial tension of PC/SAN. They found that the interfacial tension depends on the AN content in SAN, and has minimum value at about 15 wt% AN in SAN.

Polyamide-6/ABS is also commercial product about which many studies have been carried out [16–22]. Most studies were focused on the reactive compatibilization and processing–morphology–properties relationship. Surprisingly, there is no data reported on the interfacial tension between SAN and polyamide despite of its importance.

In this study, author reported the interfacial tensions between polyamide-6 (PA-6) and SAN having various AN content by the breaking thread method. These data will be helpful information to the researchers who study PA-6/ABS blend.

2. Experimental

2.1. Materials

The characteristics of the materials used are listed in Table 1. PA-6 is a commercial product (trade name: Kolon KN171, $Mn = 30,000$). Several kinds of SAN having various AN content were used in this study. Some

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* Present address: Institute of Materials Science, University of Connecticut, 97 North Eagleville Road, Storrs, CT 06269, USA.

E-mail address: sonyg@mail.ims.uconn.edu (Y. Son).

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Table 1
The characteristics of the materials used and interfacial tension between PA-6 obtained in this study

Materials	Commercial name	Molecular weight (Mn)	Zero shear viscosity (Pa s)	AN content (wt.%)	Interfacial tension (mN/m)	Std. deviation (mN/m)
PS	Cheil HF2660	120,000	1080	0	7.63	0.41
SAN6	Synthesized	80,000	164	6	4.21	0.44
SAN13	Synthesized	100,000 (Mw)	157	13	2.70	0.44
SAN19	Synthesized	60,000 (Mw)	84	19	3.34	0.23
SAN24	Cheil AP-F	53,000	450	24	4.38	0.40
SAN28	Cheil HR5330	56,000	1640	28.5	4.55	0.39
SAN32	Cheil CR5381	56,000	2390	32.5	4.42	0.14
SAN35	Cheil AP65	90,000 (Mw)	720	35	4.79	0.34
SAN41	Cheil AS4N	63,000	3150	41	4.55	0.13
Nylon6	Kolon KN171	30,000	740	–	–	–

of them were supplied by Cheil Industries, and the others were synthesized by a following radical polymerization.

Styrene and acrylonitrile were obtained from Samsung General Chemicals and DongSuh Petrochemicals, respectively, and used without further purification. A 1 L glass flask fitted with a mechanical stirrer, a thermometer and an condenser was charged with 200 g of monomer mixture and 400 ml of aqueous dispersions with 1 g of potassium rosin soap as emulsifier. The temperature was then raised to 70°C and the initiator, potassium persulfate (0.5 g), dissolved in 20 ml of water was introduced to the reactor slowly, which started the copolymerization. After 8 h of reaction, the reaction was terminated by an addition of 10 wt% aluminum sulfate solution. Coagulated products were washed, filtered and dried for a day.

2.2. Rheological measurement

The zero-shear viscosity is critical to get a correct interfacial tension in breaking thread method. They were obtained measuring the shear viscosity at different shear rate ($10^{-2} \sim 5\ \mathrm{s}^{-1}$) in the steady mode. Every polymer used in this study shows a newtonian regime at the shear rate $10^{-2} \sim 10^{-1}\ \mathrm{s}^{-1}$. The rheometer used was a Rheometric Dynamic Spectroscopy, RMS-800. Parallel plate configuration (diameter = 25 mm) was used with a gap of about 1.5 mm. The temperature for measurement was 230°C.

2.3. Measurement of interfacial tension

Films of SAN of 1 mm thickness were pressed between two metal plates on a Carver laboratory press at 180°C. The PA-6 fibers were obtained by drawing on a capillary rheometer at 230°C. The fiber diameters ranged from 20 to 80 μm. The fibers were cut with 20 mm length and annealed at 80°C for about 24 h. The breaking thread method was used to measure the interfacial tension between PA-6 and SAN at 230°C. A mettler hot-stage model FP82 HT connected to a FP 90 central processor and to a Olimphus transmission optical microscope were used. The method consists of inserting a thread of PA-6 between two films of SAN. This sample is enclosed between two glass slides and then placed in the hot stage under the microscope. At first, the temperature of the hot stage was elevated and maintained at 200°C for 10 min in order to ensure the perfect imbedding without undesired deformation of PA-6 fiber ($T_m = 216$°C). The temperature was then increased to 230°C. To make measurements, digital images from the microscope were captured periodically by a computer equipped with a Coreco Oculus image analysis system. An example is shown in Fig. 1. At least seven series of measurements were carried out. Among them, those with best agreement between theoretical dimensionless wave number (X_m) and experimental dimensionless wave number were chosen. Details about the calculation of interfacial tension and theoretical procedures are reported in the literature [14,15].

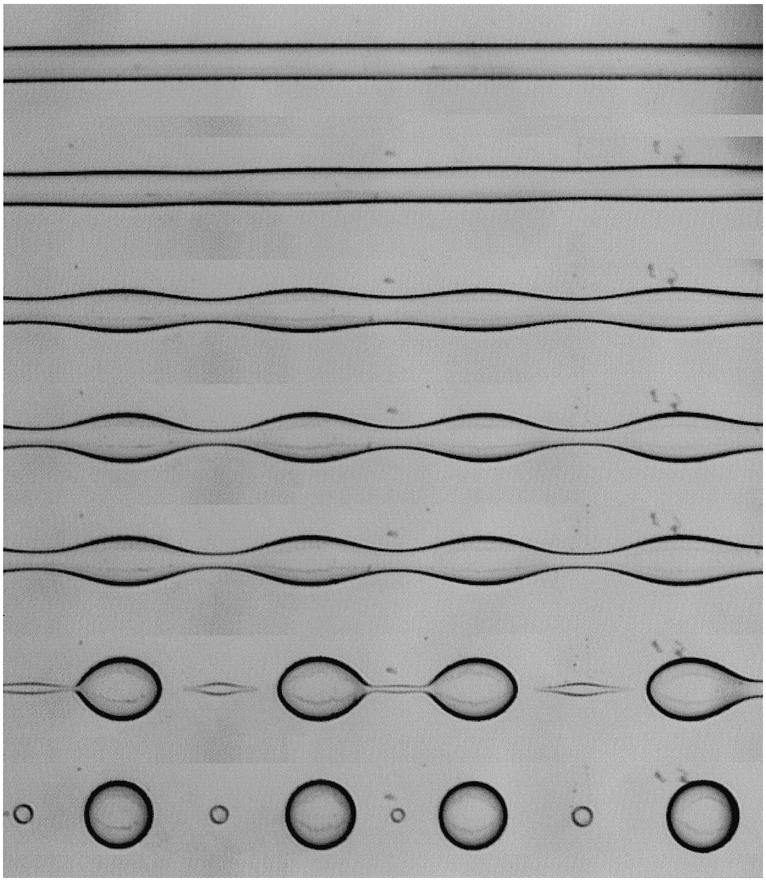

Fig. 1. Sinusoidal distortions on a PA-6 thread, with diameter 54 μm, embedded in a polystyrene matrix. The measurement was performed at 230°C; the times for subsequent photographs are: 0; 183; 300; 340; 396; 494 s and infinite.

3. Results and discussion

According to the theory describing the disintegration of a cylinder thread immerged in another fluid, developed by Tomotika, the distortion grows exponentially with time:

$$\alpha = \alpha_0 \exp(qt) \tag{1}$$

where α_0 is the initial amplitude and the growth rate of this distortion, q, is given by:

$$q = \frac{\sigma\Omega(x_m, \lambda)}{2\eta_m R_0} \tag{2}$$

where σ is the interfacial tension, η_m is the viscosity of the matrix, λ is viscosity ratio and R_0 is the initial thread radius. The function, $\Omega(x_m,\lambda)$, can be obtained from Tomotika's original paper [23] or the following equation. This equation was obtained by curve-fitting the values reported Tomotika's original paper and is valid for $0.01 < \lambda < 10$.

$$\Omega(x_m, \lambda) = \exp(a_0 + a_1 \log(\lambda) + a_2[\log(\lambda)]^2 + a_3[\log(\lambda)]^3 + a_4[\log(\lambda)]^4) \tag{3}$$

where $a_0 = -2.588$, $a_1 = -1.154$, $a_2 = 0.03987$, $a_3 = 0.0889$ and $a_4 = 0.01154$. One can obtain the interfacial tension from the slope by plotting $2\eta_m R_0 \ln(\alpha)/\Omega$ versus time.

Fig. 2 shows typical results of $2\eta_m R_0 \ln(\alpha)/\Omega$ versus time for the PA-6 and PS pairs. The slope of this plot is the interfacial tension. No significant variation in the interfacial tension with initial thread diameter is observed. The interfacial tension between PA-6 and PS obtained from this study was 7.63 mN/m. The values for the PA-6/PS pair which have been reported previously are 20 mN/m at 230°C [14] and 7.3 mN/m at 240°C [15]. Considering the temperature dependency of interfacial tension, the interfacial tension from this study is very close to that of Cho's group. As discussed by Cho et al., our value seems to be closer to the exact value.

Interfacial tensions between PA-6 and SAN are plotted as a function of wt% AN in the SAN in Fig. 3. The interfacial tension and its standard deviation were also shown in Table 1. Each of the data points represents a series of measurements taken on more than three separate threads. The interfacial tension has a maximum value at zero of AN content (polystyrene) in the range of this study. It decreases rapidly at low AN content as AN content increases, and has a minimum at ~14% AN content followed by increasing up to ~28% AN. The interfacial tension increases slightly

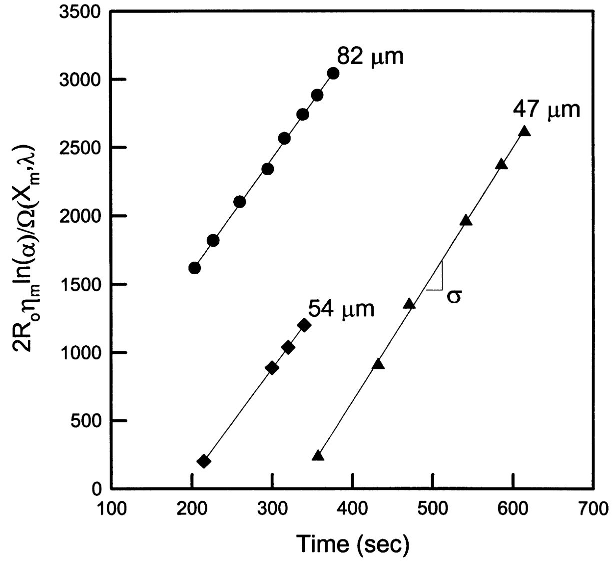

Fig. 2. Plot of $2\eta_m R_0 \ln(\alpha)/\Omega$ versus time. The numbers shown in the graph are initial thread diameters.

above ~28% AN. Interfacial tensions between PC and SAN as a function of AN content obtained by Watkins and Hobbs also show a minimum value at ~15% AN [11]. Takeda et al. [24] examined the morphology of blends of SAN having various AN contents up to 65 wt% in a matrix of 75% PA-6. They found that the size of SAN domain depends significantly on AN content and the average domain size decreases continuously as AN content increases. They used SANs having similar viscosities. That means the viscosity ratio does not affect the domain size significantly in their blends and the domain size is directly proportional to the interfacial tension unless the elasticity ratio affects the domain size. Their result is not consistent with this study. Probably, the elasticity affected the domain size in their blend. More extensive work is needed to clear this issue.

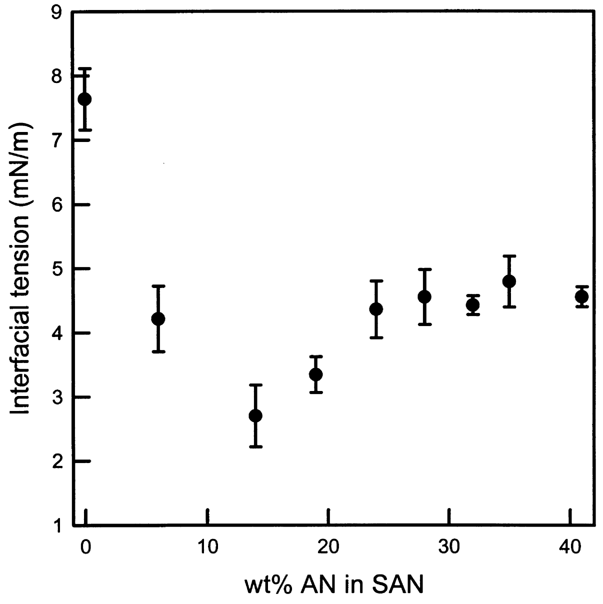

Fig. 3. Interfacial tension between PA-6 and SAN as a function of wt% AN in SAN.

According to the fractional polarity theory, the interfacial tension between immiscible polymer melts is well approximated by harmonic mean equation [25]:

$$\sigma = \gamma_1 + \gamma_2 - 4\left(\frac{\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p}\right) \tag{4}$$

where γ_1 and γ_2 are the surface tension of the two polymers and superscripts d and p refer to the dispersion and polar components of the surface tension, respectively. The polar component of the surface tension is defined in terms of the polarity, x_p, as $x_p\gamma$ and the dispersion component is $(1 - x_p)\gamma$. For PS [25], polarity $x_p = 0.168$, $-d\gamma/dT = 0.072$ mN m^{-1} °C^{-1} and $\gamma^{20°C} = 40.7$ mN/m. The surface tension of PS at 230°C was estimated to be 25.6 mN/m. For PA-6 [25], $\gamma^{260°C} = 36.1$ mN/m. The temperature dependency of the surface tension and the polarity for PA-6 were not found in the literature. It is assumed that the temperature dependency of PA-6 is close to that of PA-6,6 ($-d\gamma/dT = 0.065$ mN m^{-1} °C^{-1}) [25] due to the similar chemical structures of both polymer. The surface tension of PA-6 at 230°C was estimated to be 38.4 mN/m using these values. The polarity of PA-6 was not found in the literatures, but the polarity of PA-6 can be obtained from Eq. (4) and interfacial tension between polyethylene and PA-6 since the polarity of PE is zero. For PE [25], polarity $x_p = 0$, $-d\gamma/dT = 0.057$ mN m^{-1} °C^{-1} and $\gamma^{20°C} = 35.7$ mN/m. The reported interfacial tension between PE and PA-6 is 10.7 mN/m at 250°C [9]. The polarity of PA-6 was calculated to be 0.28. The surface tension of polyacrylonitrile (PAN) was found to be 44 at 20°C [26]. The temperature dependency of the surface tension for PAN was approximated to be 0.05 mN m^{-1} °C^{-1} [25]. The polarity of PAN was not found in the literature, though it is expected to be high value (>0.25) considering the chemical structure.

A crude estimation of the interfacial tension between PA and SAN for various polarity of PAN was carried out using Eq. (4) and assuming that the SAN are random and their surface tensions and polarities vary linearly with molar composition [25]. The result is shown in Fig. 4. Agreement is poor for any polarity of polyacrylonitrile. Not only absolute values but also the curve shape is different with that from experiment. Probably, higher value of the surface tension for PAN is more realistic. The interfacial tension between PA-6 and PS was estimated to be 3.6 mN/m by the fractional polarity theory. Although this theory has certain error, it can predict approximate value. Therefore, it is inferred that the interfacial tension between PS and PA-6 from this study is more reliable than that of Elemens [14].

4. Conclusions

The interfacial tensions between PA-6 and a series of

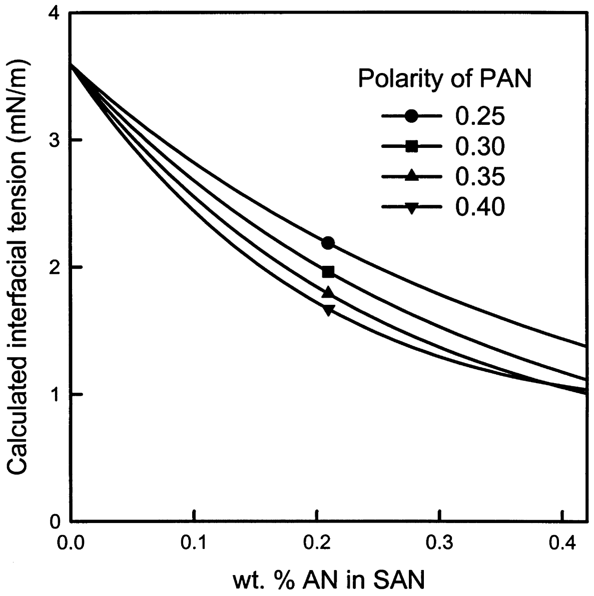

Fig. 4. Calculated interfacial tension between PA-6 and SAN from the fractional polarity theory for various polarity value of PAN.

SAN were obtained by the breaking thread method. The measured value for PA-6/PS was 7.63 mN/m with a standard deviation of 0.41. This value was higher than that calculated from the fractional polarity theory. The interfacial tension decreases rapidly at low AN content as AN content increases, and has a minimum at ~14% AN content followed by increasing up to ~28% AN. The interfacial tension increases slightly above ~28% AN.

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