# Determination of interfacial tensions between BPA polycarbonate and styrene–acrylonitrile copolymers from capillary thread instability measurements

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The interfacial tensions between BPA polycarbonate (PC) and a series of styrene-acrylonitrile (SAN) blends having S/AN ratios varying between 100/0 and 60/40 (wt%) have been determined by measuring capillary thread breakup rates at 200°C. A distinct minimum in the interfacial tension is observed close to the SAN composition reported to show maximum miscibility with PC. For the case of PC/PS, the measured values are compared with those calculated from published studies on PS/poly methyl methacrylate (PMMA) and PC/PMMA.

**(Keywords: interfacial tension; polycarbonate; SAN copolymers)**

## *Introduction*

Blends of BPA polycarbonate (PC) and acrylonitrile–butadiene–styrene (ABS) copolymers form an important class of engineering polymers in which compatibilization is achieved as the result of partial mixing between PC and free poly(styrene-*co*-acrylonitrile) (SAN) in the ABS. Since these blends are not stabilized by the incorporation of a copolymer, their morphologies tend to be strongly affected by the concentrations and relative viscosities of the two phases, their interfacial tension and melt processing conditions[1,2]. While adequate properties are normally achieved during short moulding cycles, tensile and impact strengths can be compromised at longer times and higher temperatures as the result of microstructural coarsening[3,4]. Moreover, in some circumstances (e.g. in mouldings containing knit lines), consistently low strengths and elongations are often observed which are unequivocally related to flow-induced stratification of the two phases.

Many PC/ABS compositions of commercial interest consist of a continuous phase of PC and a dispersed phase of ABS/SAN. In these blends, the generation and breakup of the low viscosity ABS domains during extrusion and moulding has been found to be dominated by the formation and disintegration of elongated melt threads produced by shear and extensional flows[1,2]. A generalized mathematical treatment of this process has been developed by Tomotika[5], who showed that the breakup rate is dependent on the thread diameter, the viscosity ratio of the two resins and their interfacial tension.

Tomotika's results have a very direct impact on the study of polymer melt blends. First, they define a relationship between two important variables affecting overall morphology — interfacial tension and melt viscosity. Secondly, because the breakup rates scale with filament diameter, they allow the process to be conveniently simulated by embedding drawn fibres of one resin in another and heating the composite structure above the softening point ($T_m$ or $T_g$) of both resins. This technique has been used to advantage to measure the interfacial tensions of a number of pairs of polymers[6–11].

In this paper, we describe the use of capillary instability measurements to determine the interfacial tensions between PC and SAN resins having various S/AN ratios. The results are discussed in terms of the known miscibility behaviour of PC and SAN and available interfacial tension data.

## *Background*

In Tomotika's original analysis[5], a sinusoidal distortion is imposed along a cylindrical thread as shown in *Figure 1*, where $R$ is the average thread radius, $\alpha$ is the distortion amplitude, $\lambda$ is the distortion wavelength, $z$ is a coordinate along the thread and

$$R(z) = R + \alpha \sin\left(\frac{2\pi z}{\lambda}\right) \tag{1}$$

If volume is conserved, the average radius is given in terms of the initial thread radius, $R_0$, and $\alpha$ as:

$$R^2 = R_0^2 - \frac{\alpha^2}{2} \tag{2}$$

Only those distortions with a wavelength greater than the initial circumference produce the decreases in interfacial area required for spontaneous growth. According to the theory, those distortions will grow exponentially with time according to the relationship:

$$\alpha = \alpha_0 \exp(qt) \tag{3}$$

where $\alpha_0$ is the distortion at $t = t_0$ and $q$ is the growth rate given as:

$$q = \frac{\sigma \Omega(\lambda, p)}{2\eta_c R_0} \tag{4}$$

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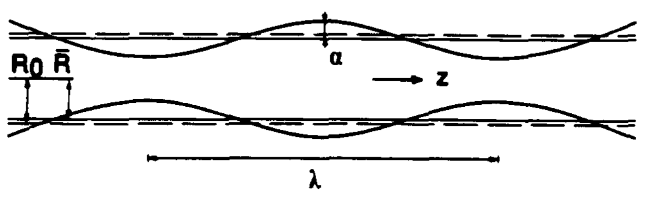

**Figure 1** Schematic diagram showing parameters associated with developing instability

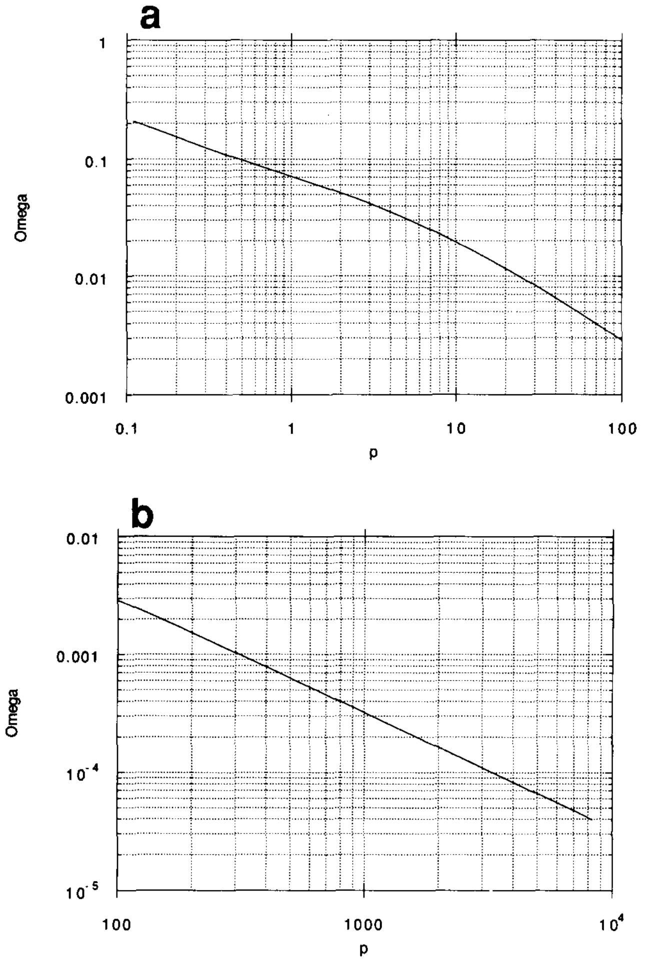

**Figure 2** Plot of $\Omega$ *versus* $p$ for $p$ values in the range of: (a) $10^{-1}$–$10^{-2}$; (b) $10^2$–$10^4$

where $\sigma$ is the interfacial tension, $\eta_c$ is the matrix viscosity and $p$ is the viscosity ratio ($\eta_{\text{dispersed}}/\eta_{\text{continuous}}$).

$\Omega(\lambda, p)$, which is a complex function of the viscosity ratio and wavelength, can be calculated from Tomotika's original equations. It has the unusual property that it reaches a maximum value for a particular wave number which depends on $p$. Values for $\Omega(\lambda, p)$ are plotted as a function of $p$ for $p = 10^{-1}$–$10^2$ and $10^2$–$10^4$ in *Figures 2a* and *b*, respectively.

## *Experimental*

*Samples.* The PC resin used was supplied as Lexan®* polycarbonate resin grade 115 by the GE Plastics Division in Mt. Vernon, IN. The SAN resins were synthesized at the GE facility in Parkersburg, WV by means of emulsion polymerization. N.m.r. analyses showed that the S/AN sequence distributions were reasonably approximated by the penultimate model proposed by Hill *et al.*[12]. A series of narrow molecular weight distribution polystyrene resins was obtained from the Pressure Chemical Co. All samples were free of pigments and other additives and used without further purification.

*Molecular weight and melt viscosity measurements.* Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and polydispersities for each of the resins were determined by gel permeation chromatography (g.p.c.) using polystyrene calibration standards and $CHCl_3$ as the elution solvent. The respective values are shown in *Table 1*.

Melt viscosity/shear rate curves for all of the resins were generated on a Rheometrics mechanical spectrometer. The experiments were run in an oscillatory mode over a shear rate range of $10^{-1}$–$10^3\ s^{-1}$ at 200°C. The data are reproduced in *Figures 3* and *4*. The curves were sufficiently flat in the low shear rate region so that $p$ and $\Omega$ could be determined directly from the values obtained at $10^{-1}\ s^{-1}$.

*Capillary instability measurements.* Films of the SAN resins were pressed from pre-dried powders between Ferrotype plates on a Carver Laboratory Press at ~210°C. Threads of PC were drawn from small pools of pre-dried resin melted on a hot plate. Thread diameters ranged from 25 to 70 $\mu$m. All films and threads were stored in a desiccator throughout the course of the experiments.

Short sections of thread (~10 mm) were sandwiched between two films of the SAN and consolidated between a heated glass slide and cover slip. The samples were subsequently transferred to a Zeiss Universal microscope equipped with a Mettler FP-2 hot stage and annealed at 180°C for 30 min prior to observing the capillary breakup process at 200°C.

**Table 1** Molecular weight data

| Resin | $\bar{M}_w$ ($\times 10^3$) | $\bar{M}_n$ ($\times 10^3$) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|
| S/AN | | | |
| 96.2/3.8 | 102.5 | 48.7 | 2.1 |
| 91.7/8.3 | 208.0 | 80.7 | 2.6 |
| 87.0/13.0 | 109.1 | 52.2 | 2.1 |
| 84.8/15.2 | 110.4 | 53.9 | 2.0 |
| 70.9/29.1 | 114.9 | 55.9 | 2.1 |
| 64.8/35.2 | 76.3 | 37.6 | 2.0 |
| 61.5/38.5 | 78.7 | 39.0 | 2.0 |
| PS | | | |
| 1 | 90.1 | 86.7 | 1.0 |
| 2 | 152.0 | 145.0 | 1.0 |
| 3 | 207.7 | 198.2 | 1.0 |
| PC 115 | 30.4 | – | – |

**Table 2** PC/PS interfacial tension data

| $\bar{M}_w$ PS ($\times 10^3$) | $\sigma^{200°C}_{PC/PS}$ (dyn cm$^{-1}$) |
|---|---|
| 90.1 | 3.4 |
| 152.0 | 3.5 |
| 207.7 | 3.7 |

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* Lexan is a registered trademark of the General Electric Company

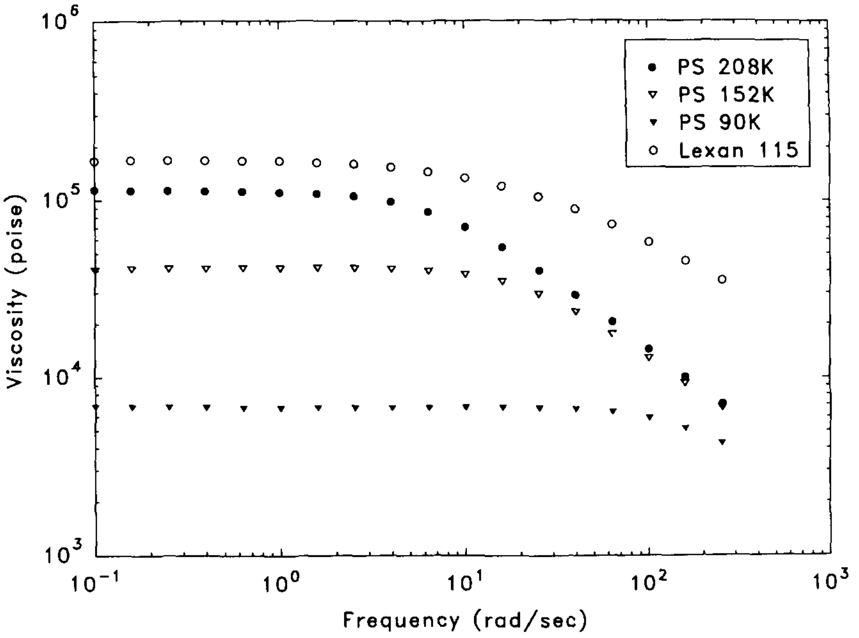

**Figure 3** Viscosity/shear rate curves for PC and PS at 200°C

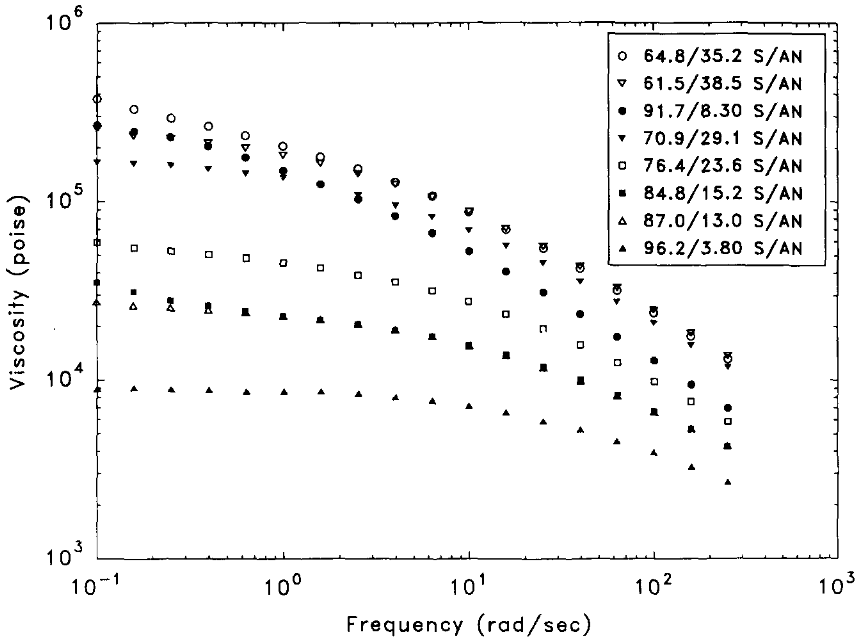

**Figure 4** Viscosity/shear rate curves for SAN resins having different S/AN ratios at 200°C

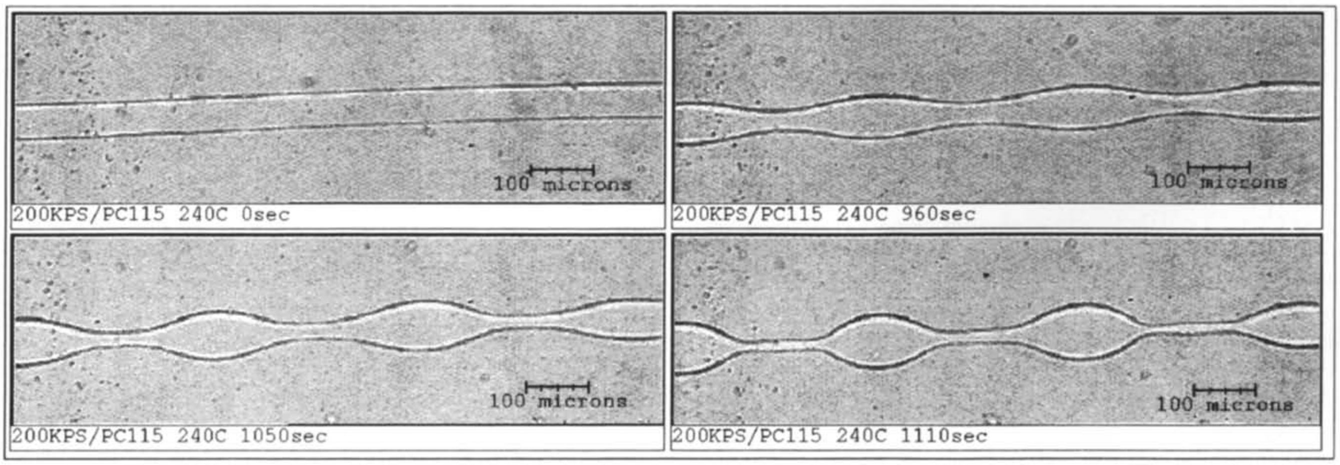

**Figure 5** Typical series of breaking thread images collected from a PGT IMIX image processing system

As the sinusoidal oscillations developed, digitized images were periodically captured on a PGT IMIX image processing system. An example is shown in *Figure 5*. For each SAN resin, a minimum of three threads were observed. In some cases, more than one distortion was monitored per thread. Measurements of the maximum and minimum diameters ($D_{max}$ and $D_{min}$) of the growing distortions were used to obtain values for $\alpha$ using the relationship:

$$\alpha = \frac{(D_{max} - D_{min})}{4} \tag{5}$$

Values for $q$ were obtained from least squares plots of $\ln(\alpha/R_0)$ *versus* time according to equation (3). Interfacial tension values were subsequently calculated from $q$ *versus* $1/R_0$ plots using equation (4).

## *Results and discussion*

Interfacial tension values for PC *versus* PS are listed as a function of PS molecular weight in *Table 2* and those for PC *versus* SAN are plotted as a function of wt% AN in the SAN in *Figure 6*. Each of the data points represents a series of measurements taken on three to five separate threads. Reproducibility was $\pm 0.5\,\mathrm{dyn\,cm^{-1}}$. No significant variation in $\sigma$ with PS molecular weight is observed. The plot of $\sigma$ *versus* % AN is asymmetrical with a pronounced minimum at ~15% AN. This minimum occurs at a slightly lower AN level than that giving the highest level of PC/SAN miscibility[13].

To our knowledge, interfacial tension values for PC and PS and SAN copolymers have not been previously reported. Likewise, published values for the surface tensions of PC melts are lacking. Carriere *et al.* have employed an embedded fibre retraction technique to determine the interfacial tensions between PS/poly(methyl methacrylate) (PMMA) and PC/PMMA[14,15]. From their data it is possible to estimate the interfacial tension between PC and PS for comparison with our results.

Wu has shown that the interfacial tension between immiscible polymer melts is well approximated by the harmonic mean expression:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4\left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}\right) \tag{6}$$

where $\gamma_1$ and $\gamma_2$ are the surface tensions of the two polymers and $\gamma_1^p$, $\gamma_2^p$ and $\gamma_1^d$, $\gamma_2^d$ are their respective polar and dispersive contributions[16]. $\gamma^p$ is defined in terms of the polarity, $x^p$, as $x^p\gamma$. If the surface tensions of one of the two components is known, the surface tension of the other can be calculated from this relationship from measured values of the interfacial tension.

For PS, $x^p = 0.168$, $-\mathrm{d}\gamma/\mathrm{d}T = 0.072\,\mathrm{dyn\,cm^{-1}\,{}^\circ C^{-1}}$ and $\gamma^{20^\circ C} = 40\,\mathrm{dyn\,cm^{-1}}$ (refs 17 and 18). For PMMA, $x^p = 0.280$ and $-\mathrm{d}\gamma/\mathrm{d}T = 0.076\,\mathrm{dyn\,cm^{-1}\,{}^\circ C^{-1}}$ (ref. 18). The reported[14] interfacial tension for PS/PMMA at 190°C is $1.1 \pm 0.2\,\mathrm{dyn\,cm^{-1}}$. Using Wu's value[19] for the temperature dependence of the interfacial tension of PS/PMMA, $-\mathrm{d}\gamma/\mathrm{d}T = 0.013\,\mathrm{dyn\,cm^{-1}\,{}^\circ C^{-1}}$, the interfacial tension for PS/PMMA is estimated to be $\sim 0.98\,\mathrm{dyn\,cm^{-1}}$ at 200°C. Substituting these values in equation (6), the surface tension for PMMA is calculated to be $27.5\,\mathrm{dyn\,cm^{-1}}$ at 200°C and $41.2\,\mathrm{dyn\,cm^{-1}}$ at 20°C. This latter value is in excellent agreement with the surface tension of $41.1\,\mathrm{dyn\,cm^{-1}}$ determined experimentally for low molecular weight PMMA at 20°C[19].

In order to estimate the surface tension of PC at 200°C, the foregoing calculations can now be repeated for PC/PMMA. The measured interfacial tension for this pair is $1.44 \pm 0.16\,\mathrm{dyn\,cm^{-1}}$ at 240°C[14]. Correcting for temperature, $\gamma_{PC/PMMA} = 1.96\,\mathrm{dyn\,cm^{-1}}$ at 200°C. Assuming $x_{PC}^p = 0.267$ (ref. 19) and $\gamma_{PMMA}^{200^\circ C} = 27.5\,\mathrm{dyn\,cm^{-1}}$ and using equation (6), the surface tension for PC is calculated to be $38.9\,\mathrm{dyn\,cm^{-1}}$ at 200°C. Combining this result with the published surface tension data for PS, $\gamma_{PS/PC}$ is estimated to be $3.0\,\mathrm{dyn\,cm^{-1}}$. This result is slightly less than the value of $3.5\,\mathrm{dyn\,cm^{-1}}$ determined in the present study.

An approximation of the PC/SAN interfacial tension curve is frustrated by the lack of surface tension data for either polyacrylonitrile or SAN and the uncertainties associated with S or AN blocking in the copolymer and variations in PC/SAN miscibility. A crude estimation is possible using the surface tension for polyacrylonitrile calculated from parachor values ($48\,\mathrm{dyn\,cm^{-1}}$)[20,21] and assuming that the SAN copolymers are random and their surface tensions and polarities vary linearly with molar composition[22]. The result, using equation (6), is shown by the broken line in *Figure 6*. Agreement is poor, especially at high AN levels, suggesting both that the model is over simplified and that a higher value for $\gamma_{AN}$ may be more realistic. More extensive study is needed to resolve this issue.

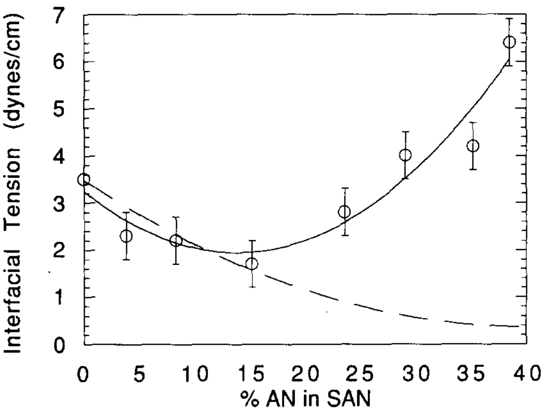

**Figure 6** Plot of measured interfacial tension between PC and SAN as a function of wt% AN in SAN. The broken line is calculated from parachor values for polyacrylonitrile as described in the text

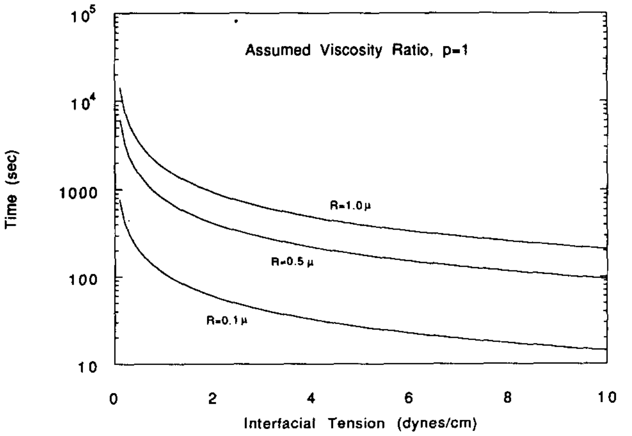

**Figure 7** Plots of theoretical breakup times as a function of interfacial tension and thread radius of SAN threads in PC with $\eta_c = 100\,000$ and $p = 1$

Because of the importance of thread breakup in producing and maintaining well-dispersed PC/SAN blends, it is useful to estimate breakup times for SAN filaments having diameters comparable to those produced during extrusion and moulding. Based on fluctuation theory, Elemans *et al.*[10] have shown that this time can be expressed in terms of the previously defined variables as:

$$t_b = \frac{\eta_c R_0}{\Omega(\lambda, p)\sigma} \ln\left(\frac{1.39\sigma R_0^2}{kT}\right) \tag{7}$$

Breakup times for SAN filaments in PC at 200°C calculated using this equation are plotted as a function of interfacial tension and filament radius for $\eta_c = 100\,000$ and $p = 1$ in *Figure 7*. The strong dependence of $t_b$ on $R_0$ is evident. It is noteworthy that even threads having very small diameters can persist for a minute or more when the PC/SAN interfacial tension is near its minimum value. These times are comparable to those encountered during many injection moulding cycles. Thus, it is not surprising that large numbers of unbroken or partially broken SAN threads have been observed in PC/SAN mouldings in which PC is the continuous phase[1,2]. More complete breakup is expected at higher temperatures and lower viscosity ratios.

## *Conclusions*

Interfacial tension values for PC against PS and a series of SAN copolymers have been determined using the breaking thread method. Reproducibility was $\pm 0.5\,\mathrm{dyn\,cm^{-1}}$. The measured value for $\gamma_{\mathrm{PC/PS}}$ ($3.5\,\mathrm{dyn\,cm^{-1}}$) is $\sim 0.5\,\mathrm{dyn\,cm^{-1}}$ higher than that calculated from data on PC/PMMA and PS/PMMA systems. The interfacial tension between PC and SAN falls slightly and then rises with increasing AN concentration. A minimum interfacial tension is observed close to the SAN composition giving the highest PC/SAN miscibility.

When the viscosities of PC and SAN are similar and their interfacial tension is at its minimum value, threads with radii as small as 0.1 mm may persist for a minute or more before disintegrating. As a result, elongated filaments are expected to be formed and retained in sections of mouldings where shear or extensional flows are high. Published morphological studies are consistent with this expectation[1,2].

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