

Control of morphology and interfacial tension of PC/SAN blends with compatibilizer

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Abstract

Block copolymers of PC-b-PMMA (polycarbonate-b-polymethylmethacrylate) and PC-b-SAN (polycarbonate-b-(styrene-*c*-acrylonitrile)), were examined as compatibilizers for blends of PC with SAN copolymer. The average diameter of the dispersed particles was measured with an image analyzer, and the interfacial properties of the blends were analyzed with an imbedded fiber retraction (IFR) technique. The average diameter of dispersed particles and interfacial tension of the PC/SAN blends reached a minimum value when the SAN copolymer contained about 24 wt% AN. Interfacial tension and particle size were further reduced by adding compatibilizer to the PC/SAN blends. PC-b-PMMA was more effective than PC-b-SAN as a compatibilizer in reducing the average diameter of the dispersed particles and interfacial tension of PC/SAN blend. A direct proportionality between the particle diameter and interfacial tension was also observed. The interfacial properties of the PC/SAN blends were optimized by adding a block copolymer and using an SAN copolymer that had minimum interaction energy with PC.

Keywords : PC/SAN blend, compatibility, size of dispersed particles, interfacial tension

1. Introduction

Polymer blends are of great interest. By blending one may be able to achieve useful combinations of the advantage of each material into a single product. In addition, one can expect a continuous range of properties simply by variation of blend composition. Binary polymer mixture obtained from the melt processing always exhibited phase separated structure when its interaction energy that is related to interfacial tension is positive at the processing temperature and pressure. The application of blends having phase separated structure often limited because of their poor interfacial properties (Wool, 1989). It is crucial to employ a proper compatibilizer for improving interfacial adhesion of polymer blends. A proper compatibilizer placed at the interface reduces interfacial tension that plays an important role in the development and stabilization of blend morphologies. One of the main goals for compatibilization is not to render the blend homogeneous but rather to control the degree of heterogeneity, and as usually to reduce the size of the dispersed particles found in it. The

multidimensional nature of the retraction in the presence of shear and elongational ambient flows does not allow for an analytical relationship between interfacial tension and morphology. Since an analysis of relation between interfacial tension and the size of dispersed particles under real process conditions is very difficult, the basic physical mechanisms should be analyzed under controlled conditions enabling the developing of solutions.

In the current work, the changes in the interfacial tension of the PC/SAN blends containing a proper compatibilizer were examined with the imbedded fiber retraction (IFR) technique (Carriere, 1989; Cohen, 1989; Carriere, 1991) and then the size changes of dispersed particles under a given set of processing conditions were explored as a function of interfacial tension. Blends of PC with ABS materials have been commercially available for many years (Freitag, 1988; Paul, 1988). The useful properties can be generated without compatibilizer because the PC-SAN interaction is apparently sufficiently favorable to form an interface strong enough that the blends can develop useful mechanical properties (Kim, 1992; Callaghan, 1993). However, the application of blends having phase separate structure often limited because of flow-induced stratification and their poor adhesion at weld (Wool, 1989). It is cru-

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Table 1. Polymers used in this study

Polymers	Copolymer composition (wt%)	Molecular weight	$\overline{M}_w/\overline{M}_n$	$\eta_f/\eta_m^a)$	Sources
PC	-	$\overline{M}_w = 38,600$	1.61	1	Dow Chemical Calibre 300-5
SAN 15	14.7% AN	$\overline{M}_w = 182,000$	2.19	4.103	Asahi Chemical
SAN 20	19.7% AN	$\overline{M}_w = 150,200$	1.95	3.764	Asahi Chemical
SAN 24	24.0% AN	$\overline{M}_w = 140,900$	1.92	3.405	LG Chemical SAN 80
SAN 28	28.0% AN	$\overline{M}_w = 146,600$	1.77	3.058	LG Chemical SAN 90
SAN 32	32.5% AN	$\overline{M}_w = 170,600$	1.84	2.876	LG Chemical SAN 95
SAN 40	40% AN	-	-	3.488	Jeil Chemical

^{a)} η_f/η_m is the ratio of zero-shear viscosity of PC to that of SAN copolymer. Note that zero-shear viscosity of PC at 240°C is 6550 Pa.s.

cial to employ a proper compatibilizer for improving interfacial adhesion of PC/ABS blends. Based on the interaction information related to the various binary pairs (Kim, 1992), block copolymers such as PC-b-PMMA and PC-b-SAN, were prepared to explore as interfacial agents of PC/SAN blends.

2. Experimental

2.1. Materials

Polymers used in the experiments and their pertinent information were listed in Table 1. Some are commercially available while others are experimental materials. PC-b-PMMA and PC-b-SAN copolymers were specially synthesized for the current work.

P-isopropenylphenol that contains vinyl moiety at the chain end was prepared by the thermal cracking of bisphenol-A. A mixture containing the required amount of purified bisphenol-A and NaOH was heated in a round-bottomed flask at 250°C for an hour under the reduced pressure of 2-5 torr. P-isopropenylphenol separated from the resulting product was further purified using n-hexane reprecipitation. The p-isopropenylphenol terminated polycarbonates were synthesized by the interfacial polymerization technique. Bisphenol-A and Na₂S₂O₄ placed in the flask were dissolved in the aqueous solution of NaOH. A solution of p-isopropenylphenol and triphosgene in dichloromethane was added and then reacted at 30°C for 2 hours. The reaction was continued for 4 more hours after adding triethylamine as a phase transfer catalyst.

Synthesis of the final block copolymer was performed in solution. The vinyl-terminated polycarbonate dissolved in chloroform was reacted at 70°C for 21 hours by adding MMA or S/AN dissolved in toluene and AIBN as the initiator. The precipitated polymer in isopropyl alcohol was vacuum filtered, air dried overnight and dried in a vacuum

oven at 80°C for 24 hours. Molecular weights of block copolymers were determined by GPC using polystyrene standard. Acrylonitrile content in SAN was determined by elemental analysis. Acrylonitrile content of SAN in PC-b-SAN was fixed to 24 wt%. The similar procedure for the synthesis of PC-b-PS copolymer has been reported previously [Matsumoto (1988)].

2.2. Experimental procedure

Blends of PC with SAN copolymer were prepared by melt mixing or by solution casting. Mixtures of PC/SAN were mixed in a torque rheometer (Haake Rheomix) for 15 min. at 60 rev/min and 240°C. Blend films were also prepared by solution casting from dichloromethane in a petri dish. The solvent was allowed to evaporate slowly at room temperature, and the formed films were dried in a vacuum oven at 90°C for a week.

The number average diameter of the dispersed particles in the blend was measured with a digital image analyzer [Bummi Universe Co. I-Top]. Specimens prepared by melt mixing were mounted on a hot stage [Linkam THMS 600] equipped with a temperature controller [Linkam TMS 92]. The samples were heated rapidly to 240°C and then changes in the size of the dispersed particles were monitored for a day. Changes in the average diameter were not observed for a day. Because of this, samples annealed at 240°C for 5 min. were used to measure the average diameter. Each of the data points represents a series of measurements taken on ten separate photographs.

Interfacial tension between PC and SAN, or that between PC and SAN containing various amount of compatibilizer was measured with an imbedded-fiber retraction technique. Fibers of PC were produced with an Instron fiber spinning apparatus. SAN copolymer sheets with 1.5 mm thickness were prepared by the compression molding at 220°C. PC fibers and SAN plates were dried under vacuum oven at

Table 2. Block copolymers synthesized in this study

polymer	Molecular weight of vinyl terminated PC ^{a)}	molecular weight of PC-b-PMMA
PC-b-PMMA	$\overline{M}_n = 15,100$	$\overline{M}_n = 23,100$
	$\overline{M}_w = 35,000$	$\overline{M}_w = 62,000$
PC-b-SAN ^{b)}	$\overline{M}_n = 15,100$	$\overline{M}_n = 34,300$
	$\overline{M}_w = 35,000$	$\overline{M}_w = 72,200$

^{a)}Molecular weight of block copolymers were determined by GPC using polystyrene standards.

^{b)}AN content of SAN determined by elemental analysis was 24 wt%.

170°C and 110°C, respectively for 24 hours to ensure that no elastic effects related to the fiber orientation. PC fibers were then placed between two plates of SAN copolymer. The samples were subsequently transferred to a microscope equipped with a hot stage and a temperature controller. The samples were annealed at 180°C for 1 hour prior to observing the fiber retraction process with image analyzer at 240°C. The zero shear viscosities (η_0) of PC and SAN copolymer were measured by using a Rheometrics dynamic spectrometer (RDS-II, Rheometrics Inc.) over the shear rate range from 10^{-1} to 10^3 rads^{-1} under a nitrogen atmosphere at 240°C. Values for η_0 obtained from the low-frequency plateau viscosities were listed in Table 1.

3. Results and discussion

3.1. Changes in the size of the dispersed particles

The main measure of the degree of compatibility in a blend is the size scale of domains under a given set of conditions. One of the main goals for compatibilization is not to render the blend homogeneous but rather to control the degree of heterogeneity, and as usually to reduce the size of the dispersed particles found in it. The crucial step in the determination of how well a particular compatibilizer is working is to characterize its effects on the size of the dispersed particles in the blend. The changes in the average diameter of the dispersed particles were measured with image analyzer at a fixed condition.

It is well recognized that the interactions between PC and SAN copolymers containing various amounts of AN are not favorable enough to produce complete miscibility, although the evidence for varying extents of miscibility has been reported (Keitz, 1984; Guest, 1989; Quintens, 1991; Cheng, 1993; Lee, 2001). The minor component in the immiscible blend forms droplets, i.e., domains dispersed in the continuous phase mainly composed of major component of blend. Blend samples prepared by melt mixing were microtomed and then transferred to a hot stage in which temperature was maintained 240°C. An image analyzer was used to measure the average diameter of the dis-

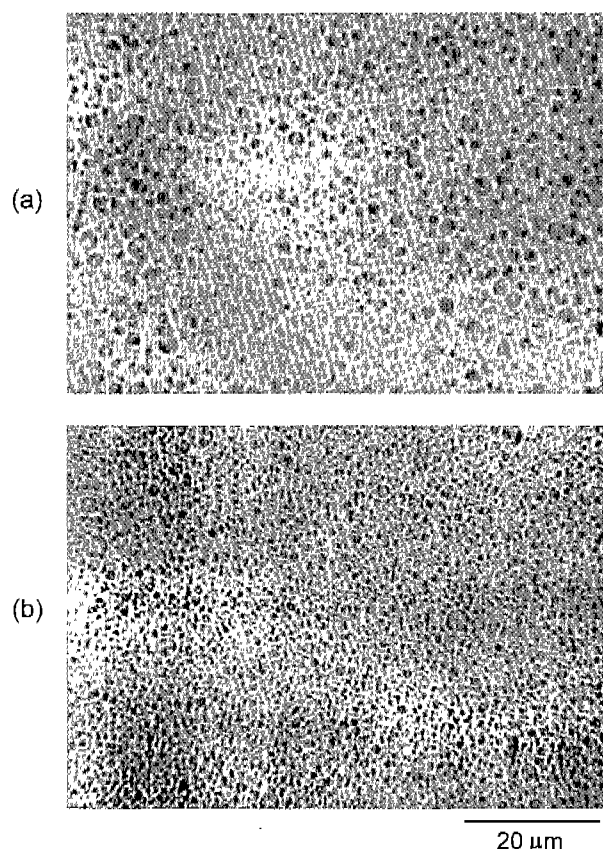


Fig. 1. Microphotograph of PC/SAN 24=8/2 blend observed with an image analyzer: (a) without compatibilizer, (b) with 5 phr PC-b-PMMA.

persed particles as a function of annealing time, composition, and AN content of SAN copolymers at 240°C.

Changes in the average particle size with time were not observed for initial 24 hrs. Because of this, blends were only annealed for 5 min to obtain the average diameter of the dispersed particles. Fig. 1(a) shows microphotograph that observed with an image analyzer for the blend of PC with SAN 24. The average diameter of the dispersed particles estimated from the microphotographs as a function of AN content of SAN copolymers at three different compositions were shown in Fig. 2. Among the various PC/SAN blends, PC/SAN 24 blend showed minimum value in the average diameter at each composition. These results suggest that high molecular weight blends of PC and SAN copolymer are immiscible but the optimum level of AN content of the copolymer for the miscibility with PC is about 24 wt%. These results are consistent with the previous results related to the thermodynamic interaction energy between PC and SAN that reaches a minimum when the AN content of copolymer is about 24 wt% (Kim, 1992; Callaghan, 1993). The average diameter of the dispersed particles in blends (PC/SAN = 8/2) was varied from $3.0 \mu\text{m}$ to $2.1 \mu\text{m}$ by controlling AN content of SAN

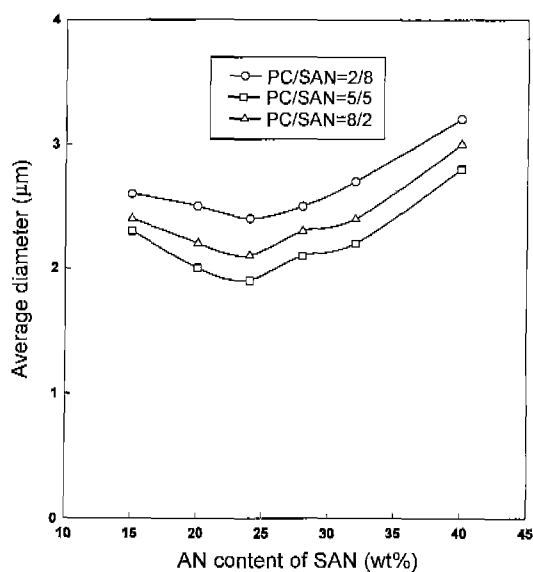


Fig. 2. Dependence of particle size on the AN content for PC/SAN blends.

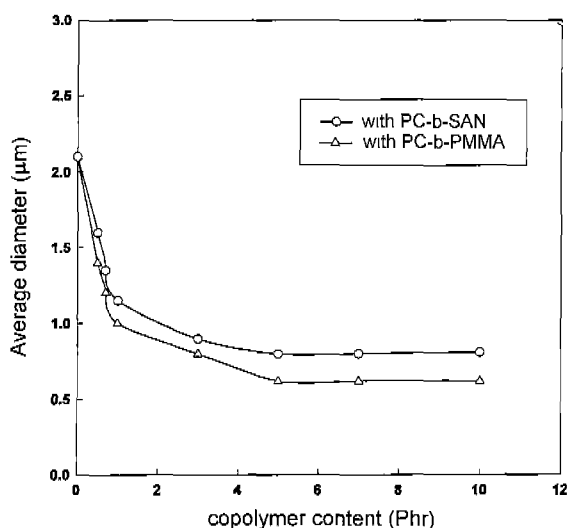


Fig. 3. The particle size for PC/SAN 24=8/2 blends as a function of compatibilizer content.

copolymer from 15.7 wt% to 40 wt%. To broaden the commercial applications of PC/ABS blend by enhancing interfacial adhesion, PC-b-PMMA or PC-b-SAN copolymer was employed as a compatibilizer of PC blend with SAN.

The changes in the average diameter of the dispersed particles in the PC/SAN 24 (=8/2) blend were shown in Fig. 3 as a function of the block copolymers content. The average diameter was decreased for the blends of containing block copolymer from 0 to about 5.0 phr and then leveled off at a fixed size. PC-b-PMMA was more effective in reducing the average diameter of the dispersed particles in the PC/SAN blends. The similar trend was observed regardless compatibilizer at the other compositions. Because

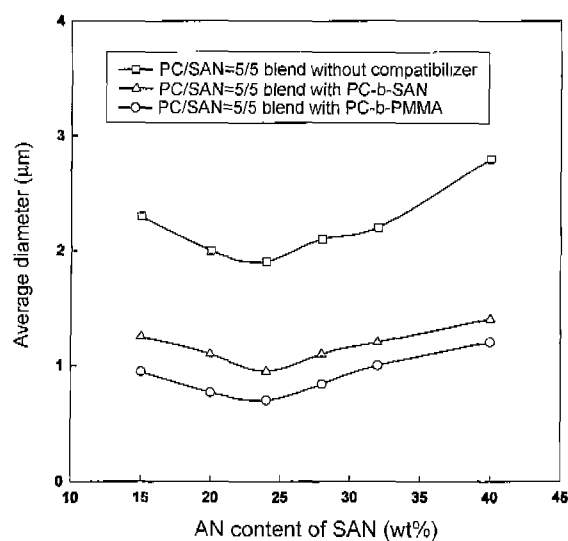


Fig. 4. The effects of compatibilizer on the particle size for PC/SAN=5/5 blends.

of these, the average domain sizes reported hereafter were those for the blends containing 5 phr block copolymer. The microphotograph shown in Fig. 1(b) represents the morphology of PC/SAN24 (=8/2) blend containing 5 phr PC-b-PMMA. The average diameter of the dispersed particles calculated from the microphotographs was exhibited in Fig. 4. The average diameter was dramatically reduced regardless blend compositions and AN content of SAN copolymers. Particularly, the average diameter of the dispersed particles in the PC/SAN 24 (=5/5) blends was further reduced up to 0.7 μm by adding PC-b-PMMA copolymer. These results indicated that compatibility of PC/SAN blends might be enhanced by adding a proper compatibilizer. It is well known that window of miscibility for PMMA with SAN copolymers extends from 9.5 to 32.5 wt% AN (Suess, 1987; Fowler, 1987). Compatibilization of PC/SAN 40 blend with PC-b-PMMA copolymer might stem from that PMMA block in compatibilizer stretches to the SAN 40 rich phase instead of PC rich phase even though SAN 40 copolymer is not miscible with PMMA.

3.2. Interfacial characteristics of PC/SAN blends

The interfacial tension is an important factor in determining the morphology of the immiscible blend. The imbedded fiber retraction (IFR) technique was developed as a dynamic method for measuring the interfacial tension between molten, high molecular weight polymers (Carriere, 1989; Cohen, 1989; Carriere, 1991). The standard equilibrium methods have limitation in measuring interfacial between high-viscous polymers due to the factors such as prohibitively long equilibrium time and thermal degradation of polymers. The IFR technique involves the microscopic tracking of the shape evolution of a short imbedded fiber and uses interfacial tension as a driving

force for the retraction process. As given in equation (1), the slope of the function related retraction shape of imbedded fiber, $\lambda [f(R/R_o) - f(R_e/R_o)]$, against the retraction time yields the interfacial tension.

$$\lambda [f(R/R_o) - f(R_e/R_o)] = t\gamma \tag{1}$$

Where R is the effective radius of the retraction fiber, R_e is its value at time $t = 0$, R_o is the radius of a sphere with a value equal to the volume of the fiber, and γ is interfacial tension. The function $f(R/R_o)$ and λ in equation (1) were given by

$$f(x) = \frac{3}{2} \ln \left(\frac{\sqrt{1+x+x^2}}{1-x} \right) + \frac{3^{1.5}}{2} \arctan \left(\sqrt{3} \frac{x}{2+x} \right) - \frac{x}{2} - \frac{4}{x^2} \tag{2}$$

$$\lambda = (\eta_m + 1.7\eta_f)R/2.7 \tag{3}$$

Where x is equal to R/R_o or R_e/R_o , and η_m and η_f are the zero-shear bulk viscosity of the matrix and fiber, respectively. As predicted in the equation (1), the experimental data shown in Fig. 5 did yield straight line. Fig. 6 shows the Interfacial tension, γ , between PC and various SAN copolymers as a function of AN content. A minimum value in the interfacial tension was observed at around 24 wt% AN. The changes in the values of the interfacial tension also consistent with the experimental results related to the average diameter of the dispersed particles and interaction energies. To explore the effect of the addition of the PC-b-PMMA or PC-b-SAN copolymer, SAN matrices containing various amount of block copolymer were prepared. The changes in the interfacial tension of PC/SAN 24 blend as a function of the block copolymer content were given in Fig. 7. The interfacial tension decreased very rapidly for block copolymer content ranging from 0 to 10 wt% and then leveled off to a saturation value of 0.77 dyne/cm as the

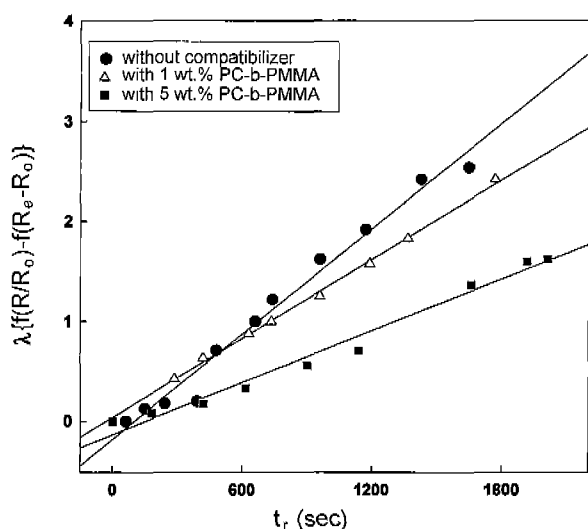


Fig. 5. Plot of the function $\lambda [f(R/R_o) - f(R_e/R_o)]$ vs the retraction time for a PC fiber.

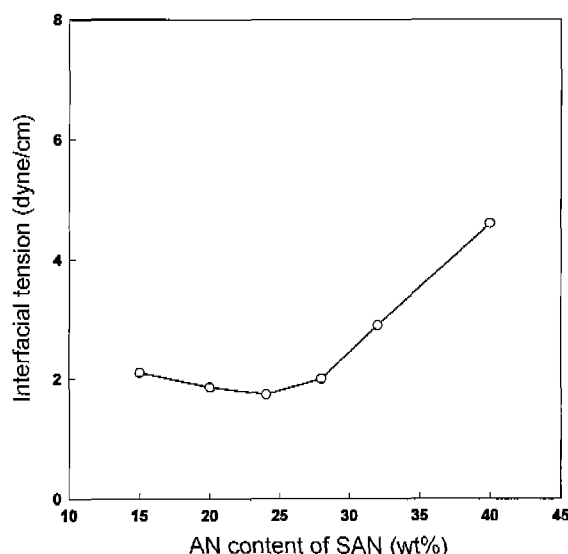


Fig. 6. Interfacial tensions between PC and SAN copolymer as a function AN content of SAN copolymers.

PC-PMMA content increased. The average diameters of the dispersed particles obtained here are plotted versus the estimates of interfacial tension from the IFR analysis shown in Fig. 8. The data are well described by a direct proportionality between average diameter and interfacial tension. Thus, the morphological observations are consistent in a quantitative sense with these estimates of PC-SAN interfacial tension.

4. Summary

Block copolymers, i.e., PC-b-PMMA and PC-b-SAN

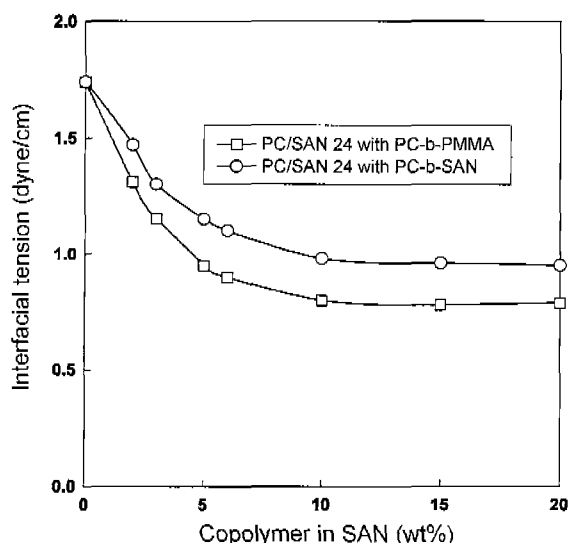


Fig. 7. Changes of interfacial tension with compatibilizer content in SAN 24 matrix.

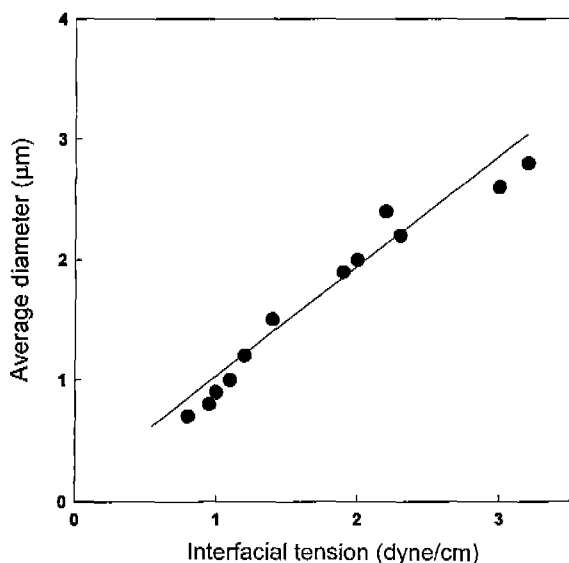


Fig. 8. Correlation of particle size achieved by melt mixing with examined PC/SAN interfacial tension.

were examined as a compatibilizer of PC/SAN blends. They were produced from the MMA or S/AN monomer and the vinyl terminated polycarbonate prepared by interfacially reacting bisphenol-A with triphosgene and p-isopropenylphenol. The number average diameter of the dispersed particles and their interfacial properties were explored. The average diameter of the dispersed particles and Interfacial tension measured as a function of AN content of SAN copolymers reaches a minimum value when the SAN copolymer contains 24 wt% AN. The results related to the particle size and interfacial tension consistent with the previous observation related to the thermodynamic interaction between PC and SAN that reaches a minimum when the AN content of copolymer is about 24 wt%. Interfacial tension and the average diameter of the dispersed particles were further reduced by adding copolymer to the PC/SAN blends. A direct proportionality between the particle diameter and interfacial tension was also observed. The commercial PC/ABS products having optimum interfacial properties might be obtained by adding proper interfacial agent as well as by controlling AN content of SAN copolymer.

Acknowledgement

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