

The Effect of Chemical Composition on the Miscibility of Styrene/Acrylonitrile/Fumaronitrile Terpolymers with Styrene/Acrylonitrile Copolymers

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SYNOPSIS

Blends were prepared of styrene-acrylonitrile-fumaronitrile (SANFN) terpolymers with styrene-acrylonitrile (SAN) copolymers and of SANFN terpolymers with SANFN terpolymers of different compositions. Miscibility was determined by differential scanning calorimetry. For three SANFN terpolymer compositions containing 11–17% fumaronitrile, a range of miscible SAN copolymers was defined. The miscibility can be predicted by using a Flory-Huggins-type mean-field approach.

INTRODUCTION

The phase behavior of blends of random copolymers has been described using a mean-field binary interaction model.^{1–3} This approach essentially involves assigning segmental interaction parameters to each mer unit and considers both inter- and intramolecular interactions. This has led to the concept that repulsions between monomers within a copolymer molecule may be more important in promoting miscibility than are specific attractions between polymers. A recent review discusses the balance between unfavorable physical forces and favorable specific interactions to predict miscibility.⁴

One example explained by this mean-field approach is a blend of poly(butadiene-*co*-styrene) with poly(vinyl chloride-*co*-vinyl acetate).⁵ There are certain copolymer compositions that are miscible; however, none of the binary combinations of the four homopolymers are miscible. A number of other systems are explained with this miscibility model.^{6–14} Recently, this treatment has been extended to blends of random terpolymers with homopolymers and with random copolymers,^{12,14} and a generalized formula has been presented.⁷

Fumaronitrile is a monomer that radically copolymerizes with a number of other vinyl mono-

mers.^{15–19} This work describes the miscibility of styrene-acrylonitrile-fumaronitrile (SANFN) terpolymers with styrene-acrylonitrile (SAN) copolymers. The experimental results are compared to miscibility predictions based on average solubility parameters of the whole polymers and on interaction parameters between each polymer segment. The miscibility of SANFN terpolymers with various compositions is also described.

The case of a binary blend of random copolymers such as $(A_x B_{1-x})_{n_1} / (C_y D_{1-y})_{n_2}$ can be treated as follows:

The free energy (ΔG) of mixing is given by

$$\Delta G/RT = (\Phi_1/n_1) \ln \Phi_1 + (\Phi_2/n_2) \ln \Phi_2 + \Phi_1 \Phi_2 \chi_{\text{blend}} \quad (1)$$

where Φ is the volume fraction, n is the degree of polymerization, and R and T have their usual meaning.

The interaction parameter for the blend, χ_{blend} , in this example is

$$\chi_{\text{blend}} = xy\chi_{AC} + x(1-y)\chi_{AD} + y(1-x)\chi_{BC} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad (2)$$

where the χ values are the interaction parameters

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between each segment and x and y are the mol fractions of monomers in the copolymers.

Equation (3) was formulated to calculate the interaction parameter for the blend (χ_{blend}) of two terpolymers ($(A_w B_x C_{1-w-x})_{n1} / (A_y B_z C_{1-y-z})_{n2}$). In this case, A designates styrene; B, acrylonitrile; and C, fumaronitrile. If $w + x = 1$ or $y + z = 1$, this describes a blend of a styrene/acrylonitrile/fumaronitrile terpolymer with a styrene/acrylonitrile copolymer:

$$\begin{aligned} \chi_{\text{blend}} = & wz\chi_{AB} + w(1-y-z)\chi_{AC} + xy\chi_{AB} \\ & + x(1-y-z)\chi_{BC} + y(1-w-x)\chi_{AC} \\ & + z(1-w-z)\chi_{BC} - wx\chi_{AB} \\ & - w(1-w-x)\chi_{AC} - x(1-w-x)\chi_{BC} - yz\chi_{AB} \\ & - y(1-y-z)\chi_{AC} - z(1-y-z)\chi_{BC} \quad (3) \end{aligned}$$

Miscibility is predicted when

$$\chi_{\text{blend}} - \chi_{\text{critical}} \leq 0 \quad (4)$$

where

$$\chi_{\text{critical}} = 0.5(n_1^{-1/2} + n_2^{-1/2})^2 \quad (5)$$

The segmental interaction parameters, χ_{AB} , χ_{AC} , etc., were calculated from the solubility parameters:

$$\chi_{AB} = (V/RT)(\delta_A - \delta_B)^2 \quad (6)$$

Solubility parameters and molar volumes were calculated using group contribution techniques.²⁰

The criterion used for determining miscibility was glass transition temperature (T_g), measured by differential scanning calorimetry (DSC). The level of molecular mixing required to yield a single T_g is not clearly defined, but T_g detects the motions of 10–50 repeat units; hence, this method should detect inhomogeneities of the order of 100 Å.²¹

Table I SANFN Terpolymers Used in This Study

S/AN/FN (wt %)	M_n	M_w	M_w/M_n	T_g (°C)
71/18/11	43,100	101,000	2.35	136
70/13/17	56,400	120,000	2.12	147
64/20/16	48,500	92,000	1.90	141

Table II SAN Copolymers Used in This Study

S/AN (wt %)	M_n	M_w	M_w/M_n	T_g (°C)
94/6	112,000	346,000	2.95	110
75/25	70,100	150,000	2.14	112
70/30	45,600	87,900	1.93	114
66/34	57,800	117,000	2.02	110
60/40	67,700	131,000	1.94	114
58/42	66,000	129,000	1.94	117
55/45	55,000	106,000	1.92	116
49/51	43,600	74,400	1.71	114

Since the glass transitions of the SAN and SANFN polymers are separated by 25–35°C, differentiating miscible, partially miscible, and immiscible pairs was possible. Immiscible pairs are defined as blends that exhibit the two glass transitions of the pure-blend components, partially miscible pairs have two distinct transitions at temperatures between the glass transitions of the pure-blend components,²² and miscible pairs have a single T_g with a value between that of the two-blend components. Pairs of materials that exhibited shoulders or one very broad transition were also considered to be partially miscible.

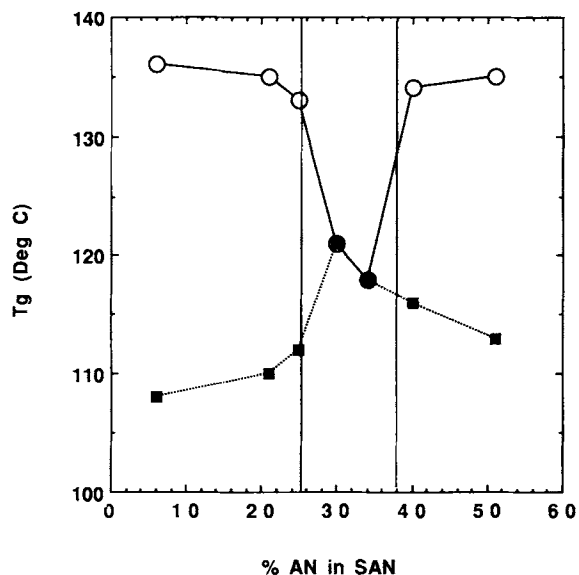


Figure 1 T_g vs. percent AN in SAN for blends with SANFN 71/18/11. The open circle and the filled square represent the T_g of the S/AN/FN terpolymer and the S/AN copolymer, respectively, in the blends. The coincident symbols represent the T_g of the miscible blend, and the window of miscibility is indicated by the two vertical lines.

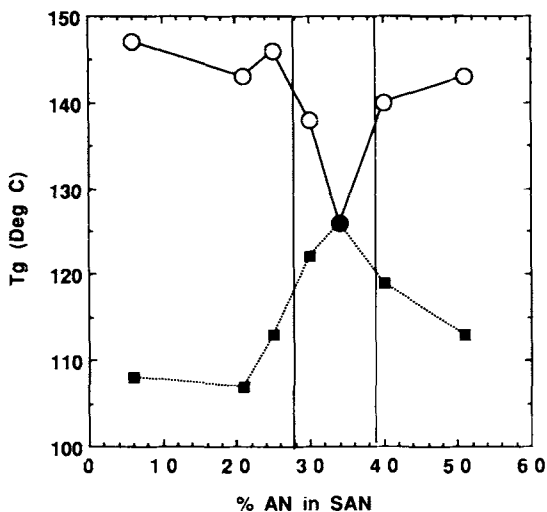


Figure 2 T_g vs. percent AN in SAN for blends with SANFN 70/13/17. See Figure 1 for explanation of symbols.

EXPERIMENTAL

All polymers were produced at The Dow Chemical Company on either production or 1 lb/h miniplant scale. Fumaronitrile (> 99% purity) was obtained from Takeda Chemicals Industry. The terpolymers had S/AN/FN compositions of 71/18/11, 70/13/17, and 64/20/16 wt %. The molecular weights and glass transitions are summarized in Table I. The styrene/acrylonitrile copolymers had acrylonitrile contents of 6, 25, 30, 34, 40, 42, 45, and 51% by weight. These resins are characterized in Table II.

Molecular weights were determined on a system composed of a Waters Associates 510 pump, 490 multiwavelength detector set at 254 nm, Wisp 710B injector system, and Nelson Analytical software. Two Polymer Labs 10 micron mixed-bed columns were used with tetrahydrofuran as the eluent (1 cc/min). The column was calibrated with polystyrene standards.

Composition of the fumaronitrile-containing polymers was determined by ^{13}C -NMR at 75.5 MHz on a Nicolet NT300 spectrometer. The relative areas of the resonances for the two fumaronitrile nitrile carbons (at 117.0 ppm), the one acrylonitrile nitrile carbon (at 120.9 ppm), and the five styrene aromatic ring carbons (at 128.7 and 127.0 ppm) were used. An estimate of the relative compositional error at the 95% confidence level is $\pm 10\%$.

Blends were prepared by solution blending in methylene chloride followed by slow evaporation at ambient temperature and complete drying for 5 min in a 180°C vacuum oven at 5 mmHg. Glass transi-

tions were measured on the dried films by DSC on a DuPont 1090 system at a heating rate of 20°C/min at the midpoint of the second-order transition. The reproducibility of the glass transition temperature by this measurement is $\pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

SANFN/SAN

The extent of miscibility for three different SANFN terpolymers with SAN copolymers is summarized in Figures 1–3, in which the positions of the one or two glass transitions observed in each SANFN–SAN blend are plotted against percent acrylonitrile in the SAN component. The open circles represent the glass transitions of the SANFN terpolymers in immiscible or partially miscible blends and the filled squares represent the glass transitions of the SAN copolymers in immiscible blends. The coincident symbols represent the single glass transitions for miscible blends where the glass transitions of the components have converged. The partially miscible zone is the composition range where the component glass transitions are converging and is indicated by the two solid vertical lines.

The size of the composition windows in which SAN and SANFN polymers are miscible are comparable for the two 70% styrene, 30% (acrylonitrile + fumaronitrile) terpolymers examined (Figs. 1 and 2). The miscible SAN composition ranges are approximately 10% wide in acrylonitrile. The change

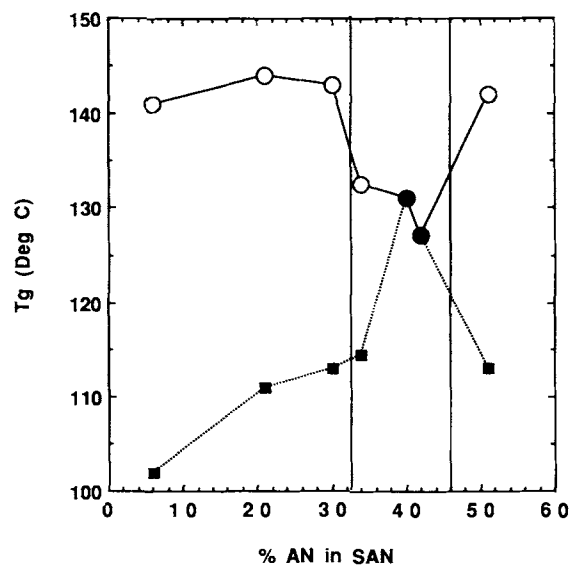


Figure 3 T_g vs. percent AN in SAN for blends with SANFN 64/20/16. See Figure 1 for explanation of symbols.

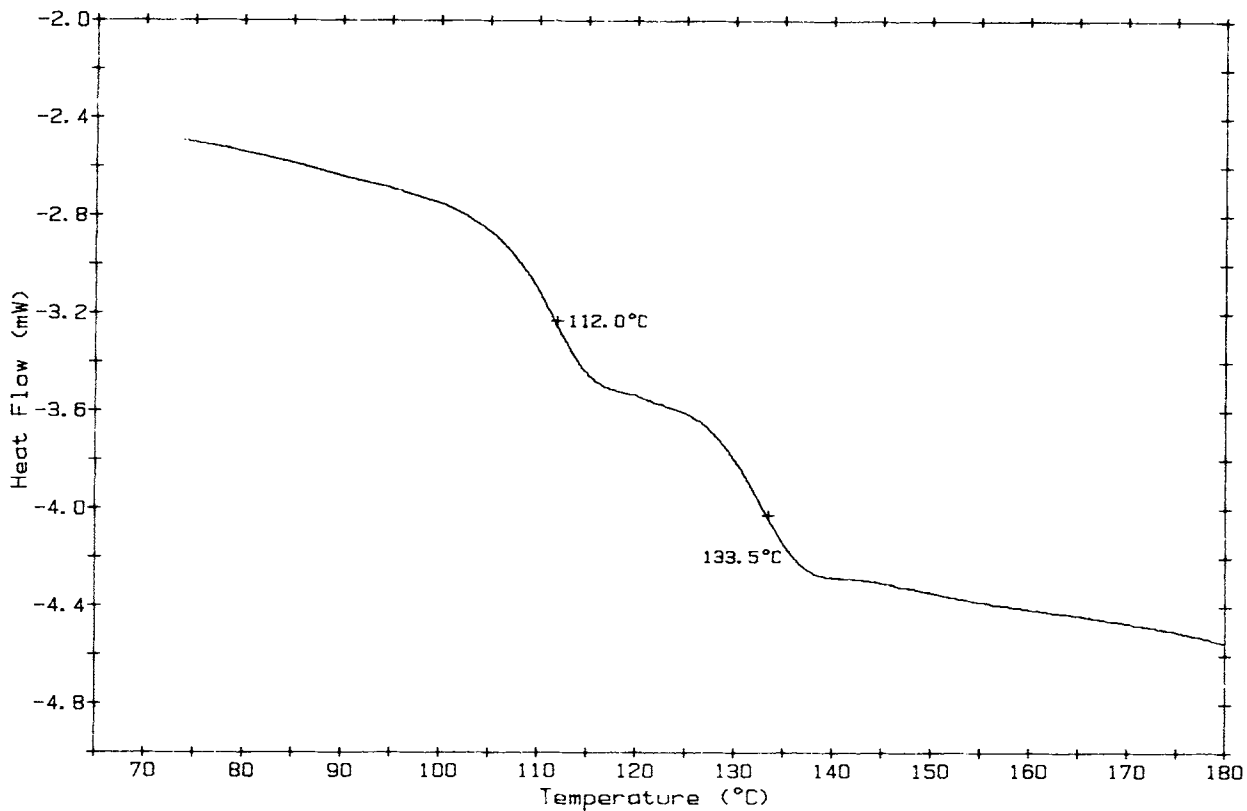


Figure 4 DSC thermogram for the immiscible blend S/AN/FN = 71/18/11 with S/AN = 75/25.

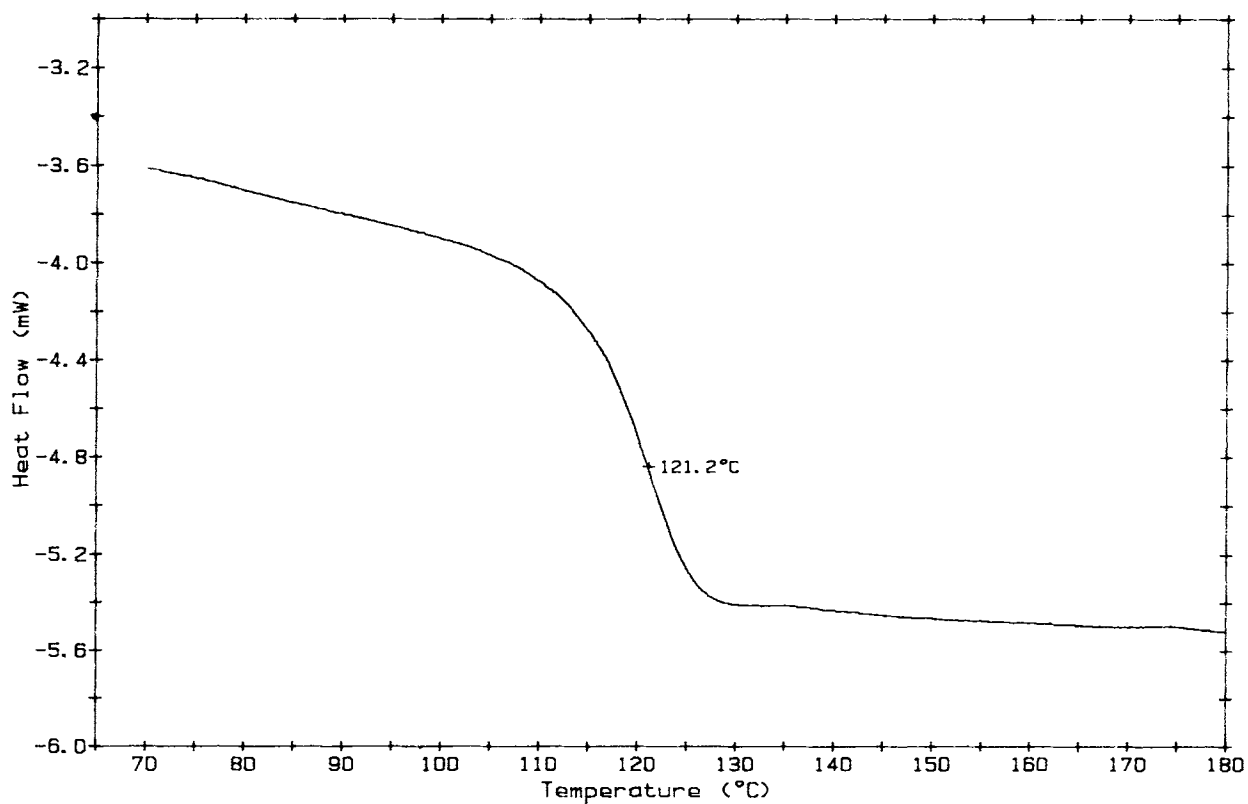


Figure 5 DSC thermogram for the miscible blend S/AN/FN = 71/18/11 with S/AN = 70/30.

from 18/11 to 13/17 acrylonitrile/fumaronitrile in the resins does move the window to higher acrylonitrile levels.

The third SANFN terpolymer examined is higher in nitrile content and contains only 64% styrene. This material requires about 40% acrylonitrile in the SAN for miscibility.

Figures 4 and 5 show thermograms from two blends to illustrate the data obtained by DSC. Figure 4 shows data for an immiscible blend, S/AN/FN = 71/18/11 with S/AN = 75/25. Two distinct transitions are seen at about the same temperatures as for the pure components of the blend. A blend of the same terpolymer, S/AN/FN = 71/18/11, with a copolymer containing 5% more acrylonitrile, S/AN = 70/30 is miscible, exhibiting a single glass transition (Fig. 5).

Plotted in Figure 6 are $\chi_{\text{blend}} - \chi_{\text{critical}}$ as calculated from eqs. (3)–(5). For the calculated $\chi_{\text{blend}} - \chi_{\text{critical}}$ vs. percent acrylonitrile in the SAN copolymer, all curves show a minimum in the region of miscibility.

The solubility parameters of the copolymers and terpolymers were calculated as outlined by Krause.⁴ First, the solubility parameters of the homopolymers were calculated from the group molar attraction constants.²⁰ The solubility parameters of the copolymers and terpolymers can be calculated by

$$\delta_c = \sum \delta_i \Phi_i \quad (7)$$

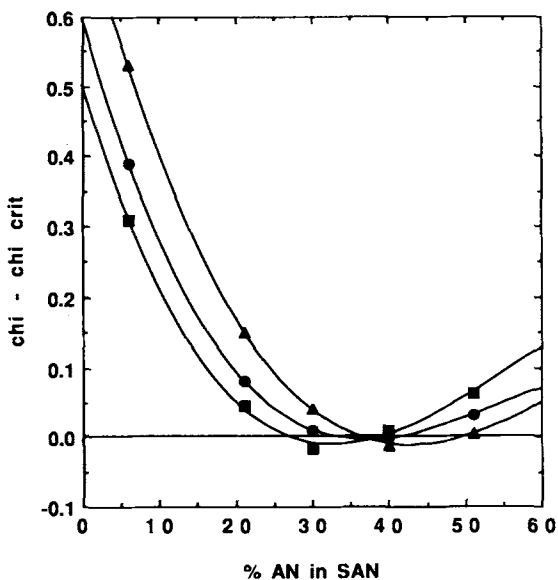


Figure 6 Calculated interaction parameter vs. percent AN in SAN for blends of SANFN and SAN: (square) S/AN/FN = 71/18/11; (circle) S/AN/FN = 70/13/17; (triangle) S/AN/FN = 64/20/16.

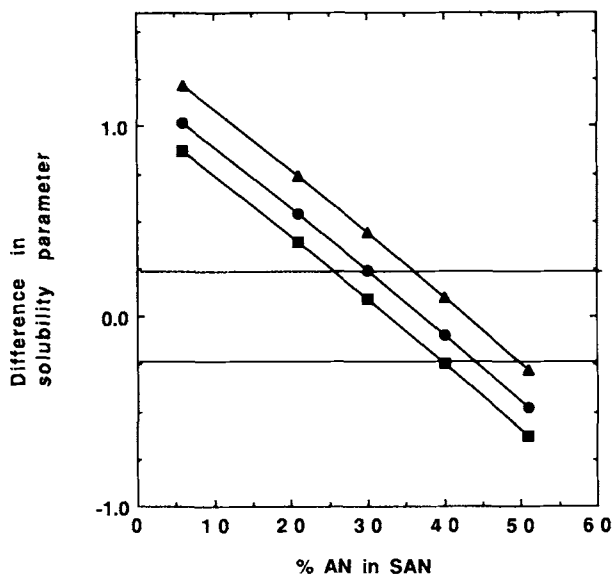


Figure 7 Calculated difference in solubility parameter vs. percent AN in SAN for blends of SANFN and SAN: (square) S/AN/FN = 71/18/11; (circle) S/AN/FN = 70/13/17; (triangle) S/AN/FN = 64/20/16.

where δ_i and Φ_i are the solubility parameters and volume fractions of each polymer component in the copolymer.

The density of terpolymers can be calculated by

$$\rho = M/V = (x_A M_A + x_B M_B + x_C M_C) / (x_A V_A + x_B V_B + x_C V_C) \quad (8)$$

where x is the mol fraction of each component, M is the molecular weight of each component, and V is the molar volume of each component.

Predicting SANFN–SAN miscibility simply on the basis of solubility parameter differences ($\Delta\delta$) was successful. This can be seen most easily in Figure 7 where the difference in solubility parameters between the terpolymer and copolymer is plotted vs. percent acrylonitrile in the SAN copolymer, and the miscible ranges are delineated. The observed miscible regions bounded by the two horizontal lines correspond to a solubility parameter difference of zero, specifically, 0 ± 0.25 .

SANFN/SANFN

For SANFN–SANFN blends, the correlation between the interaction parameter approach and the experimental results here is also generally satisfying

Table III T_g ($^{\circ}\text{C}$) of 50/50 SANFN/SANFN Blends by DSC

S/AN/FN	S/AN/FN			
	71/18/11 (10.26)	70/17/13 (10.33)	70/13/17 (10.41)	64/20/16 (10.61)
71/18/11 (10.26) ^a	136 [0.00] ^b <-0.0040> ^c			
70/17/13 (10.33)	136 [0.07] <-0.0009>	136 [0.00] <-0.0040>		
70/13/17 (10.41)	142 [0.15] <-0.0028>	136 [0.08] <-0.0027>	147 [0.00] <-0.0040>	
64/20/16 (10.61)	137 + shoulder [0.35] <0.024>	134 (broad) [0.28] <0.0054>	144 [0.20] <0.014>	141 [0.00] <-0.0040>

^a () = solubility parameter, δ .

^b [] = solubility parameter difference, $\delta_{\text{SANFN}} - \delta_{\text{SANFN}}$.

^c < > = $\chi_{\text{blend}} - \chi_{\text{critical}}$.

(Table III). Immiscibility is seen at $\chi_{\text{blend}} - \chi_{\text{critical}} = +0.024$, partial miscibility is seen for $\chi_{\text{blend}} - \chi_{\text{critical}} = +0.005$, and miscibility is seen for $\chi_{\text{blend}} - \chi_{\text{critical}}$ values of -0.004 , -0.003 , and -0.001 . The only inconsistency is for the blend of SANFN terpolymers with compositions 64/20/16 and 70/13/17, which has a large positive $\chi_{\text{blend}} - \chi_{\text{critical}}$ (0.014), yet is miscible. We have no explanation for this observation.

CONCLUDING REMARKS

1. For three SANFN terpolymer compositions containing 11–17% fumaronitrile ($T_g = 136$ – 147°C), a range of miscible SAN copolymers was defined:

S/AN/FN	% Acrylonitrile in SAN for Miscibility
71/18/11	32 \pm 5
70/13/17	35 \pm 5
64/20/16	40 \pm 5

2. A useful approach for predicting SAN–SANFN miscibility is the Flory–Huggins-type mean-field method where the interaction parameters of all polymer segments are considered.

Surprisingly, comparing the solubility parameters of the entire polymers was also an accurate predictor. Miscibility was observed when the difference in solubility parameters was less than 0.25.

3. The interaction parameter approach and solubility parameters were useful for determining SANFN–SANFN miscibility. When $\Delta\delta \leq 0.20$, there is complete miscibility (single T_g). When $\Delta\delta = 0.28$, there is partial miscibility (single broad T_g). When $\Delta\delta = 0.35$, there is complete immiscibility (double T_g).

REFERENCES

1. G. ten Brinke, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **16**, 1827 (1983).
2. D. R. Paul and J. W. Barlow, *Polymer*, **25**, 487 (1984).
3. R. P. Kambour, J. T. Bendler, and R. C. Bopp, *Macromolecules*, **16**, 753 (1983).
4. M. M. Coleman, C. J. Serman, D. E. Bhagwagar, and P. C. Painter, *Polymer*, **31**, 1187 (1990).
5. S. Krause, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, Vol. 1, Chap. 2.
6. W. Huh and F. E. Karasz, *Polym. Mater. Sci. Eng.*, **60**, 792 (1989).
7. T. Shiomi, M. Suzuki, M. Tohyama, and K. Imai, *Macromolecules*, **22**, 3578 (1989).

8. F. E. Karasz, and W. J. MacKnight, *ACS Adv. Chem.*, **211**, 67 (1986).
9. T. Shiomi, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **19**, 2274 (1986).
10. M. E. Fowler, J. W. Barlow, and D. R. Paul, *Polymer*, **28**, 1177 (1978).
11. A. C. Fernandes, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **32**, 5357 (1986).
12. T. S. Ellis, *Macromolecules*, **22**, 742 (1989).
13. J. M. G. Cowie and D. Lath, *Makromol. Chem. Macromol. Symp.*, **16**, 103 (1988).
14. M. Nishimoto, H. Keskkula, and D. R. Paul, *Polymer*, **30**, 1279 (1989).
15. R. G. Fordyce and G. E. Ham, *J. Am. Chem. Soc.*, **73**, 1186 (1951).
16. G. E. Ham, *J. Polym. Sci.*, **45**, 177 (1960).
17. G. F. D'Alelio, U.S. Pat. 2,531,409 (1950).
18. R. B. Seymour, U.S. Pat. 2,439,226 (1948).
19. D. T. Mowry, U.S. Pat. 2,417,607 (1947).
20. D. W. Van Krevelen, *Properties of Polymers: Correlations with Chemical Structure*, Elsevier, Amsterdam, 1972.
21. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979, p. 20.
22. M. E. Fowler, D. R. Paul, L. A. Cohen, and W. T. Freed, *J. Appl. Polym. Sci.*, **37**, 513 (1989).

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