

Miscibility of Poly(vinyl acetate) and Vinyl Acetate–Ethylene Copolymers with Styrene–Acrylic Acid and Acrylate–Acrylic Acid Copolymers

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SYNOPSIS

Poly(vinyl acetate) and vinyl acetate–ethylene (VAE) copolymers compose one of the more important polymeric materials, widely employed in coating and adhesive applications. A new class of miscible polymer blends involving poly(vinyl acetate) and VAE with styrene–acrylic acid and acrylate–acrylic acid copolymers has been found. Experimental windows of miscibility as a function of the ethylene content for VAE copolymers and the acrylic acid content of the acrylate–acrylic acid copolymers are observed (acrylate = methyl acrylate, ethyl acrylate, *n*-butyl acrylate, and 2-ethylhexyl acrylate). Employing well-established analog heat of mixing measurements, predicted windows of miscibility were compared with experimental results. Fair qualitative agreement was observed and supported the hypothesis that specific rejection arguments can be employed to explain the observed miscibility. Failure to quantitatively predict miscibility based on the analog heat of mixing measurements may be due to the higher association tendencies of the model compounds relative to acrylic acid units in the high molecular weight polymers. No miscible combinations were found for methyl methacrylate–acrylic acid copolymers or acrylate–methacrylic acid copolymers in admixture with poly(vinyl acetate) or the VAE copolymers, thus indicating the sensitivity of phase behavior to minor structural changes. VAE (30 wt % ethylene) copolymers were also noted to be miscible with several polymers previously noted to be miscible with poly(vinyl acetate), namely, poly(vinylidene fluoride), poly(ethylene oxide), and nitrocellulose. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl acetate) and vinyl acetate copolymers are among the more important commodity polymers utilized in the large coating and adhesive markets. As such, polymer blends comprising vinyl acetate-based polymers are of significant interest. As vinyl acetate-based polymers have been available for over 60 years, a large number of blend combinations have been reported in the open and patent literature. The study presented here discusses a new class of polymer blends miscible with poly(vinyl acetate) (PVAc) and vinyl acetate–ethylene (VAE) (≥ 70 wt % VAc) copolymers, namely, acrylate–acrylic acid and styrene–acrylic acid copolymers.

A review of PVAc and vinyl acetate (VA) copolymers¹ published in 1979 listed only a few polymers noted to be miscible. These included PVAc miscibility with poly(vinyl nitrate),² nitrocellulose,³ poly(methyl acrylate),⁴ and poly(vinylidene fluoride).^{5,6} VAE (65–70% VAc) was also noted to be miscible with poly(vinyl chloride).⁷ Additional references involving PVAc or VAE blends will be briefly discussed.

Poly(methyl acrylate) blends with PVAc have been the subject of several papers. Kern and Slocombe reported this blend to be miscible.⁸ Hughes and Britt⁴ studied the PVAc–poly(methyl acrylate) blend prepared via three different mixing techniques: (1) mixing preformed emulsions, (2) solution blending followed by solvent devolatilization, and (3) emulsion polymerization of one polymer in the presence of the other preformed polymer. Only the

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solution-cast film was noted to be miscible. Nandi et al.⁹ noted that PVAc and poly(methyl acrylate) were miscible at all combinations. They noted that (based on inverse gas chromatography studies) no specific interactions were present. Depending on the solvents utilized, it was noted that cast films could yield two-phase behavior. Fuchs¹⁰ noted phase separation of this blend when cast from toluene. Li et al.¹¹ noted that interpenetrating polymer networks of PVAc and poly(methyl acrylate) are phase-separated at low crosslink density but yield a single T_g as the crosslink density of the IPN constituents is increased.

Hsieh and Wong¹² studied the effect of charged groups in polystyrene and PVAc ionic blends. PVAc and polystyrene were noted to be immiscible. Styrene-vinylpyridine copolymers were noted to be miscible with vinyl acetate-acrylic acid copolymers. It is interesting to note that this article did not investigate blends of styrene-acrylic acid (SAA) with PVAc and thus failed to recognize the miscibility of PVAc with SAA (≥ 18 wt % AA) as noted in our studies reported later in this article.

The miscibility of PVAc with poly(ethylene oxide) (PEO) was noted by Cimmino et al.,¹³ resulting in a depression in the spherulitic growth rate for PEO with addition of PVAc. The melt rheology of PEO/PVAc blends was reported by Martuscelli et al.¹⁴ Jinghua et al.¹⁵ also noted the miscibility of PEO and PVAc, with heat of mixing results showing molecular weight dependence with negative values observed at $< 45,400 M_n$ for PVAc.

Poly(vinyl propionate) and poly(ethyl acrylate) blends were noted by Bhattacharyya et al.¹⁶ to exhibit miscibility. Poly(vinyl propionate) was noted to be immiscible with poly(methyl acrylate). Note that PVAc is miscible with poly(methyl acrylate) and immiscible with poly(ethyl acrylate).

Pearce et al.¹⁷ observed single T_g 's for blends of PVAc and a modified polystyrene containing vinylphenyl hexafluorodimethylcarbinol groups. Polystyrene was noted to be immiscible with PVAc. Hydrogen bonding was shown to be the reason for miscibility for the modified polystyrene as the hexafluorodimethylcarbinol groups (proton donor) interact with the carbonyl (proton acceptor) of the PVAc.

Coleman et al.^{18,19} noted poly(4-vinylphenol) to be miscible with PVAc and VAE (70 wt % VAc) over the entire composition range. Hydrogen bonding of the phenol hydroxyl with acetate carbonyl was shown to be the specific interaction responsible for miscibility.

Greco and Martuscelli noted that poly[D(-)-3-hydroxybutyrate] (PHB) was miscible with PVAc.²⁰ PHB-PVAc blends exhibit a single T_g along with a significant depression of the melting point for PHB. PHB has been introduced commercially as a biodegradable packaging material.

Coleman et al.²¹ reported that the hydrolyzed copolymer (essentially equimolar) of tetrafluoroethylene (TFE) and VA (thus a TFE-vinyl alcohol alternating copolymer [FVOH]) is miscible with PVAc at all concentrations. Miscibility for VAE at all concentrations of the blend is limited to 20% ethylene. At 30% ethylene, miscibility is limited to less than 55 wt % FVOH. The association model developed by Coleman and co-workers²² adequately predicted the miscibility window for FVOH with VAE copolymers.

Poly(vinyl methyl ether) was shown by Dutta et al.²³ to be miscible with poly(vinyl propionate) and poly(vinyl butyrate) but immiscible with PVAc. Inverse gas chromatography data using hydrogenated monomers as probes correctly predicted the observed miscibility results.

Miscibility of PVAc and poly(ethylene-*o*-phthalate) has been noted.²⁴ A lower critical solution temperature at 130°C was noted at the 50/50 composition. The interaction of the PVAc carbonyl with the poly(ethylene-*o*-phthalate)phenylene moiety was hypothesized as the specific interaction yielding miscibility for this polymer blend.

PVAc is not miscible with poly(vinyl chloride) (PVC); however, VAE copolymers exhibit miscibility in the range of 60–85 wt % VA. The miscibility of VAE with PVC has been widely studied.^{7,25–27} A review of this blend by Cruz-Ramos and Paul²⁸ noted miscibility in the range of 60–85 wt % VA for the copolymer based on literature data and interaction energy densities determined from heat of mixing analog compound studies. While the VAE copolymer in the composition range of miscibility with PVC offers a potential low-cost permanent plasticizer for PVC, the low T_g VAE “gumstock” material is not amenable to typical PVC compounding procedures and thus has not been successfully commercialized except in a few specific cases. The resolution of this problem has been addressed commercially by DuPont with the introduction in the mid 1970s of an ethylene/vinyl acetate/carbon monoxide (E/VA/CO) terpolymer under the tradename Elvaloy.

The miscibility of the E/VA/CO terpolymers as well as E/EA/CO (EA = ethyl acrylate) terpolymers with PVC was described by Robeson and McGrath.²⁹ The incorporation of CO in the terpoly-

mer allows for much higher ethylene contents than does EVA while still retaining miscibility with PVC. At ethylene contents > 65 wt %, low levels of polyethylene sequence crystallization results, leading to a "solid" permanent plasticizer for PVC, thus eliminating the "gumstock" problems of VAE.

As noted, a significant number of studies have been reported showing a broad range of miscible polymer blends comprising PVAc or VAE as one of the components. This article describes a new series of miscible blends involving PVAc and VAE with AA-containing copolymers (namely, SAA and acrylate-AA copolymers).

EXPERIMENTAL

The polymers employed in this study involved VAE copolymers, acrylate-AA copolymers, and SAA copolymers. The VAE copolymers as well as PVAc employed in this study are listed in Table I. The VAE copolymers noted as experimental were prepared via solution polymerization in *t*-butanol under pressure (with ethylene) required to incorporate various levels of ethylene in the copolymer. The acrylate-AA copolymers were synthesized by solution polymerization in methanol (at 30% solids) via conventional free-radical polymerization employing Trigonox 23-C-75. The resultant polymers were isolated via precipitating in water and drying in a vacuum (60°C/1 Torr). After drying, the inherent viscosity (at 25°C using a 0.2 wt % solution in

tetrahydrofuran [THF]), the glass transition temperature (DSC), and composition (employing ¹³C-NMR) were determined. The compositions and results are listed in Table II. Several acrylate-AA copolymers prepared via reaction extrusion polymerization were also utilized in the blend studies. Homopolymers of polyacrylates were obtained from commercial sources as noted in Table II.

SAA copolymers at 8, 14, 18, 20, 22, and 31 wt % AA were prepared via reaction extrusion polymerization (8, 14, 18, and 20 wt % AA), and solution polymerization in *t*-butanol (30 wt % solids) (2.0 mmol benzoyl peroxide/mol monomer), at 80°C (22 and 31 wt %). The inherent viscosity (25°C; 0.2 wt % solution in THF), the glass transition temperature (DSC), and the composition (¹³C-NMR) for these copolymers are listed in Table III.

The polymers utilized in these studies were prepared at high conversion in order to obtain sufficient examples for several melt-blending experiments. With acrylate/AA copolymers, the reactivity ratios are quite close; thus, compositional drift during the reaction should not be a problem. This is not the case with SAA copolymers, and although lower conversions were generally employed, compositional drift undoubtedly occurred. All polymers utilized including the SAA copolymers were transparent and exhibited sharp, single glass transition temperatures.

In addition to the polymers noted above, poly(vinylidene fluoride) (PVF₂), PEO, and nitrocellulose (obtained from Scientific Polymer Products) were utilized in blends with VAE (70% VAc). These polymers have been well documented in the literature as yielding miscible blends with PVAc; however, no studies with VAE copolymers have been reported to our knowledge.

Blend samples were prepared via melt mixing in a Brabender or by solution in a common solvent followed by devolatilization. The blends were then compression-molded for dynamic mechanical property determination utilizing a Rheometrics RSA-II at a frequency of 1 Hz. Glass transition temperatures were determined using a Perkin-Elmer DSC-2C by rapidly heating above the *T_g*, cooling at 320°C/min, and reheating from -50°C at 10°C/min to determine the *T_g*. This procedure was followed to eliminate molded-in stress.

The heat of mixing measurements were determined utilizing an adiabatic calorimeter similar to that previously reported by investigators at the University of Texas.³⁰ The glass calorimeter was divided into two chambers which contain the respective organic liquids prior to mixing. Mercury was

Table I Property Characterization of Vinyl Acetate-Ethylene (VAE) Copolymers

Composition ^a	IV (dL/g) ^b	<i>T_g</i> (°C) ^c	Source ^d
PVAc	0.87	35	SP ²
VAE (94% VAc)	0.50	19	APCI
VAE (88% VAc)	0.32	7	APCI
VAE (75% VAc)	0.54	-3	APCI
VAE (75% VAc)	0.55	-4	APCI
VAE (70% VAc)	1.24	-9	SP ²
VAE (65% VAc)	0.62	-17	APCI
VAE (65% VAc)	0.51	-18	APCI
VAE (50% VAc)	1.08	-26	SP ²

^a Composition determined via NMR.

^b Determined on a 0.2 wt % solution in THF at 25°C.

^c Glass transition temperatures from DSC (second heating cycle).

^d SP² = Scientific Polymer Products; APCI = Air Products and Chemicals, Inc. (experimental).

Table II Property Characterization of Poly(meth)acrylates and (Meth)acrylate–Acrylic Acid Copolymers

Polymer	Composition ^a (wt %)	IV ^b dL/g	T _g ^c (°C)	Source ^d
PMA		n.d.	6	SP ²
PEA		0.39	-16	SP ²
PBA		0.33	n.d.	SP ²
PMMA		0.35	110	SP ²
MA/AA ^e	90/10	0.64	28	APCI
MA/AA	60/40	1.01	58	APCI
MA/AA	48/52	0.87	81	APCI
EA/AA ^e	90/10	0.66	2	APCI
EA/AA	77/23	0.81	28	APCI
EA/AA	55/45	0.89	42	APCI
BA/AA	97/03	0.27	n.d.	APCI
BA/AA ^e	87/13	0.60	-15	APCI
BA/AA	77/23	0.80	10	APCI
BA/AA	50/50	0.92	67	APCI
2-EHA/AA	85/15	0.51	n.d.	APCI
2-EHA/AA	77/23	0.58	11	APCI
2-EHA/AA	67/33	0.80	42	APCI
MMA/AA	92/08	0.42	117	APCI
MMA/AA	76/24	0.45	121	APCI

MA = methyl acrylate; EA = ethyl acrylate; BA = *n*-butyl acrylate; 2-EHA = 2-ethylhexyl acrylate; MMA = methyl methacrylate; AA = acrylic acid.

^a Compositions determined via ¹³C-NMR.

^b Determined on a 0.2 wt % solution in THF at 25°C.

^c Glass transition temperatures determined on second heating cycle.

^d SP² = Scientific Polymer Products; APCI = Air Products and Chemicals, Inc. (experimental).

^e Bulk-polymerized.

utilized to displace the lower chamber liquid and is separated from the lower chamber by a glass plunger. The chambers were surrounded by an evacuated shell in order to minimize the heat transfer during mixing. The cell was placed in a water bath at 33°C. After equilibrium was established (3–4 h), the

plunger was lifted, allowing the lower chamber liquid to be displaced by mercury and to mix with the upper chamber liquid. The change in temperature was determined by a platinum resistance thermometer located in the center of the upper chamber. The model compounds selected for this investigation are noted in Table IV. Heat capacities were determined using a DuPont Model 910 DSC with a Model 2100 controller. The heat of mixing was computed from the expression

$$\Delta H_m = -[m_{LC}c_{p,LC} + m_{UC}c_{p,UC} + K]\Delta T$$

where *m* and *c_p* represent the mass and the heat capacity, *LC* and *UC* represent lower chamber fluid and upper chamber fluid, ΔT is the experimentally observed temperature change, and *K* represents the calorimeter cell constant determined separately employing known mixtures. A Setaram C-80 calorimeter was also employed to independently determine cell constants as well as to check specific values of the experimental mixtures investigated.

Table III Property Characterization of Styrene/Acrylic Acid Copolymers

Composition ^a (by Wt) S/AA	IV (dL/g) ^b	T _g ^c (°C)
92/8	—	125
86/14	—	137
82/18	—	—
80/20	—	142
78/22	0.48	130
69/31	0.34	144

^a Determined by ¹³C-NMR.

^b Determined on a 0.2 wt % solution in THF at 25°C.

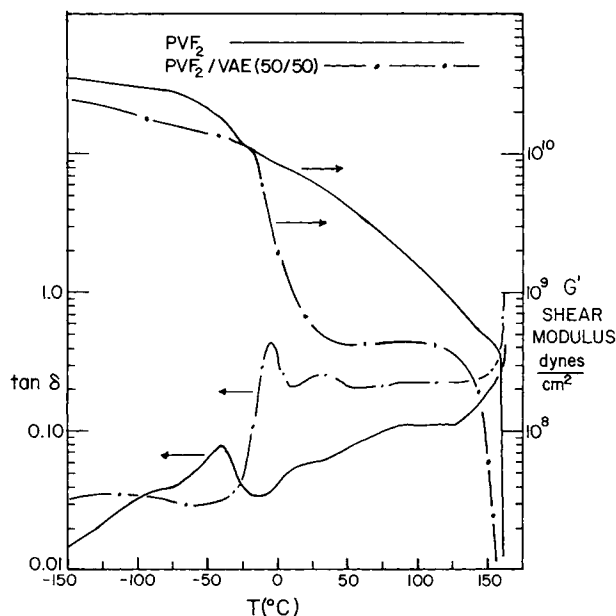
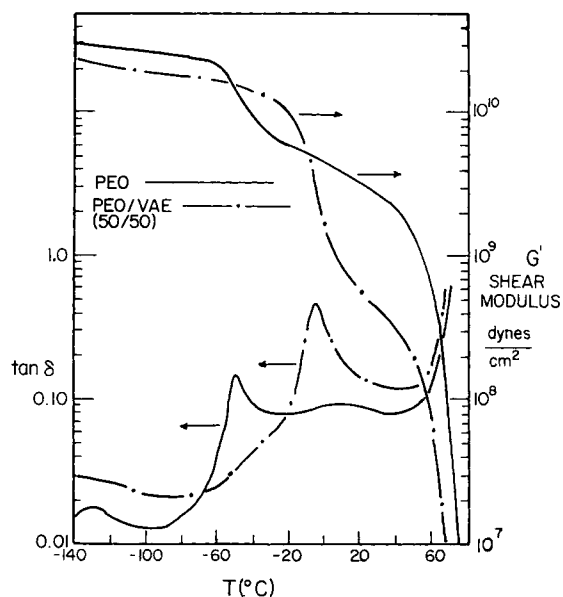
^c Determined by DSC.

Table IV Low Molecular Weight Analogs Employed for the Polymers in This Study

Polymer	Analog
Poly(vinyl acetate)	Ethyl acetate
Polyethylene	Hexane
Poly(acrylic acid)	Acetic Acid
Poly(acrylic acid)	Propionic Acid
VAE (60 wt % VAc)	Hexyl acetate
VAE (85 wt % VAc)	iso-Propyl acetate
VAE (75 wt % VAc)	sec-Butyl acetate
Poly(methyl acetate)	Methyl propionate
Poly(ethyl acrylate)	Ethyl propionate
Poly(<i>n</i> -butyl acrylate)	Butyl propionate
Poly(2-ethylhexyl acrylate)	2-Ethylhexyl propionate
Poly(methyl methacrylate)	Methyl isobutyrate

RESULTS

The comparison of VAE copolymers with known PVAc miscible blends was conducted with PVF₂, PEO, and nitrocellulose. The dynamic mechanical data are illustrated in Figure 1 for a 50/50 VAE (30 wt % ethylene)/PVF₂ blend showing a single T_g and the disappearance of the low temperature peak (T_g) at -40°C for PVF₂. The dynamic mechanical data for a 50/50 VAE (30% ethylene)/PEO blend are illustrated in Figure 2 showing a single T_g for the

**Figure 1** Dynamic mechanical data for VAE (30 wt % ethylene)/PVF₂ 50/50 (by wt) blend compared with unblended PVF₂.**Figure 2** Dynamic mechanical data for a VAE (30 wt % ethylene)/PEO 50/50 (by wt) blend compared with unblended PEO.

blend and a disappearance of the PEO T_g (-55°C). Blends of nitrocellulose with PVAc and VAE (30% ethylene) are compared in Figure 3, showing dynamic mechanical results. Both blends exhibit single T_g 's, although the nitrocellulose/VAE appears broader, thus indicating the onset of microheterogeneity. Thus, VAE (30% ethylene) displays similar

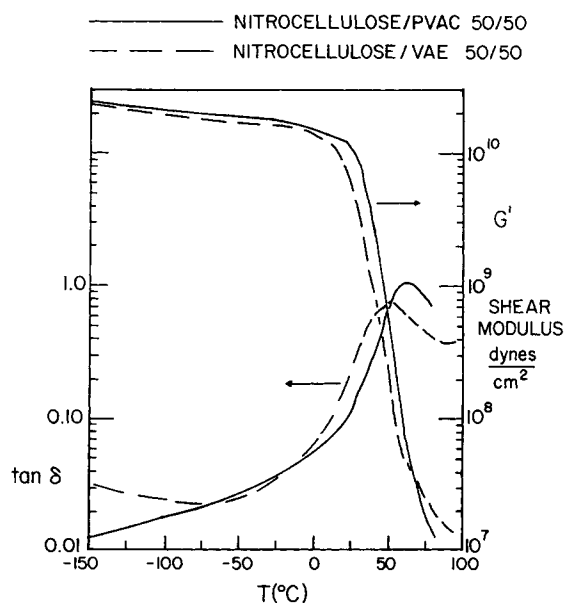
**Figure 3** Dynamic mechanical data for nitrocellulose blends with PVAc and VAE (30% ethylene) 50/50 (by wt).

Table V Calorimetry Data

Polymer	Heating Cycle (10°C/min)			Cooling Cycle (10°C/min)	
	T_g (°C)	T_m (°C)	ΔH_f cal/g	T_c (°C)	ΔH_f cal/g
PVAc	35	—	—	—	—
VAE (70 wt % VAc)	-7	—	—	—	—
50% PVAc/50% PVF ₂	21	148	5.1	115	-6.1
50% VAE (70 wt % VAc)/50% PVF ₂	-8	156	5.8	129	-7.0
PVF ₂	—	161	12.3	131	-11.3
50% PVAc/50% PEO	36	66	19.2	16	13.8
50% VAE (70 wt % VAc)/50% PEO	-10	66	18.8	39	16.9
PEO	—	69	36.6	39	33.0

miscibility with several polymers known to be miscible with PVAc. The calorimetry results on PVF₂ and PEO blends with PVAc and VAE are compared in Table V. The data indicate a higher melting point depression for PVF₂ and PEO in blends with PVAc as compared with VAE (30% ethylene). This implies a higher degree of interaction, as would be predicted by a calculation of the Flory-Huggins interaction parameter employing melting point depression data. It must be noted that equilibrium melting point data would be required to reach a rigorous comparison employing this approach.

The data in Table V indicate minor differences in the T_g for the VAE (30% ethylene) blends with PEO or PVF₂ compared to unblended VAE. This is due to the high degree of crystallinity of PEO or PVF₂, leaving an amorphous phase predominately composed of VAE. Additionally, the crystalline regions have the result of "pseudo"-crosslinking of the residual amorphous phase, thus increasing the T_g . This combination yields a T_g value quite similar to unblended VAE. As no residual T_g is observed for PEO or PVF₂, these blends have been judged as miscible.

Polystyrene is immiscible with both PVAc and VAE (30% ethylene). With PVAc, it was found that a window of miscibility exists with SAA copolymers in the range of 18 to > 31 wt % AA. AA levels higher than 31 wt % AA were not investigated. Lower AA content SAA copolymers (8 and 14 wt % AA) were phase-separated in blends with PVAc. Dynamic mechanical results on PVAc blends with SAA (22 and 31 wt % AA) are illustrated in Figure 4, showing intermediate T_g 's for the blends. The phase behavior (T_g) using DSC analysis confirmed the dynamic mechanical results noted above.

Utilizing the same SAA copolymers, VAE (30% ethylene) blends were prepared and subjected to dynamic mechanical and calorimetry analysis. With VAE, the window of miscibility was shifted to lower AA levels (8–22 wt % AA) (Fig. 5). At 31 wt % AA, phase separation was starting to appear, yielding a partially miscible system as illustrated in Figure 6. A styrene/2-ethylhexyl acrylate/acrylic acid (60/15/25) terpolymer exhibited partial miscibility with

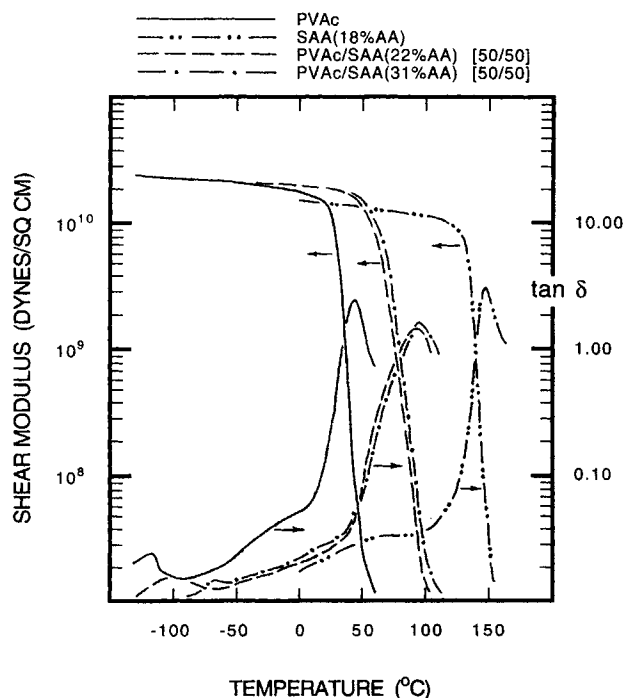


Figure 4 Dynamic mechanical data for PVAc blends with SAA copolymers (22 and 31 wt % AA) 50/50 (by wt) blends.

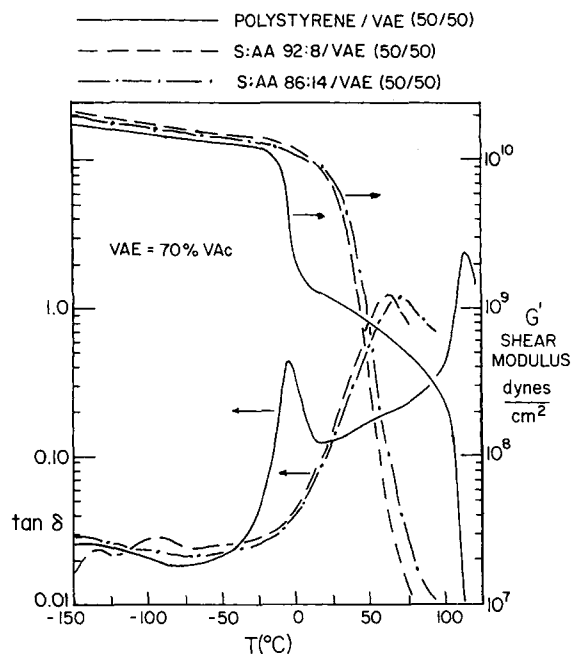


Figure 5 Dynamic mechanical data for VAE (30 wt % ethylene) blends with SAA copolymers (0, 8, 14 wt % AA) 50/50 (by wt) blends.

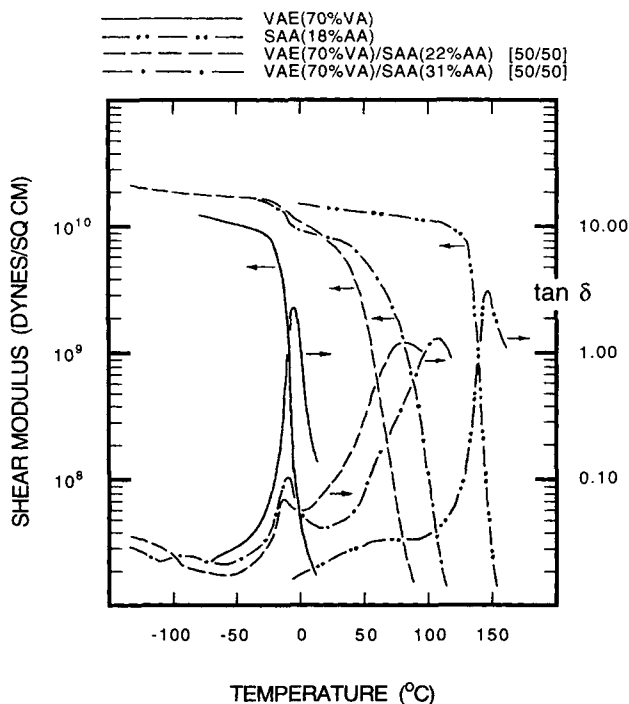


Figure 6 Dynamic mechanical data for VAE (30 wt % ethylene) blends with SAA copolymers (22 and 31 wt % AA); 50/50 (by wt) blends.

VAE (30% ethylene). A small transition exists at the T_g of VAE for the blend, indicating that the bulk of VAE is phase-mixed with the styrene terpolymer.

The primary subject of this article involves VAE copolymer blends with acrylate-AA copolymers as a function of ethylene content and AA level. Examples of miscible blends include PVAc and an EA-AA (86/14) copolymer and PVAc and a methyl acrylate-acrylic acid (MA-AA) (75/25) copolymer as illustrated in Figures 7 and 8, showing dynamic mechanical results. The VAE (see Table I) blends with the acrylate-AA copolymers (see Table II) were experimentally investigated employing calorimetry results to ascertain miscibility. In certain cases, dynamic mechanical results were obtained to confirm calorimetry results. There were several cases where the T_g 's of the VAE copolymer and the acrylate-AA copolymer were too close to unambiguously determine the phase behavior. Transparency of the samples and orientation (to observe stress whitening [if phase-separated]) were employed to estimate phase behavior. The results are tabulated in Table VI.

To analyze the miscibility range that experimentally exists in the VAE copolymers with acrylate-AA copolymers, the following analysis was employed: The heat of mixing results were obtained on low molecular weight analogs for VAE copolymers and (meth)acrylate-AA copolymers yielding binary interaction energy densities (B) tabulated in Table

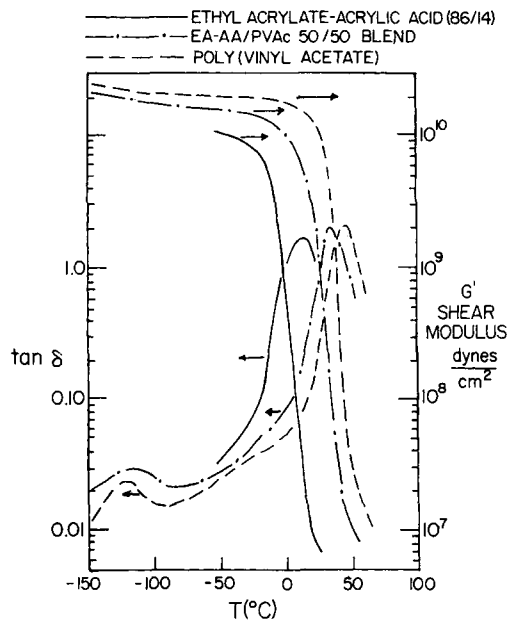


Figure 7 Dynamic mechanical data on PVAc-EA/AA (86/14 by wt) copolymer blend (50/50 by wt).

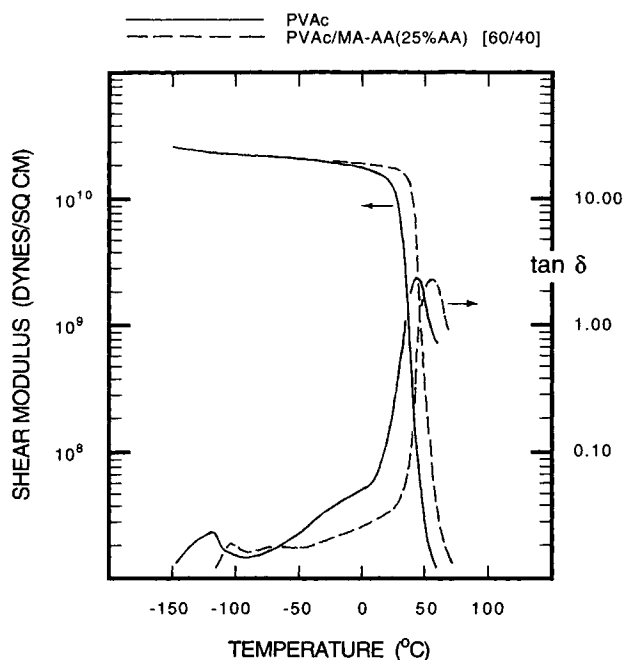


Figure 8 Dynamic mechanical data on PVAc-MA/AA (75/25 by wt) copolymer blend (60/40 by wt).

VII. Values of B were obtained from a Van Laar-type expression for the heat of mixing:

$$\Delta H_m = B_{AB} V \phi_A \phi_B \quad (2)$$

B_{AB} is the binary interaction energy density for components A and B ; V , the total volume of the mixture; and ϕ_A and ϕ_B , the volume fractions of components A and B . It is interesting to note that all values except for ethyl acetate-methyl propionate are positive. Ethyl acetate-methyl propionate is the low molecular analog for the PVAc-poly(methyl acrylate) blend, which is known to be miscible. A comparison of various binary interaction energy densities determined in this study are compared in Table VIII with literature values, generally showing excellent agreement. The AA analogs (acetic acid and propionic acid) showed only qualitative agreement overall; thus, both values will be compared in the ensuing analysis.

The data in Table VII were utilized for prediction of the window of miscibility for VAE copolymer blends with acrylate-AA copolymers as a function

Table VI Miscibility Results on VAE Copolymers with Acrylate-Acrylic Acid Copolymers

VAE Copolymers (Wt % VAc)	Wt % AA				Wt % AA				
	0	10	40	52	0	10	23	45	
Methyl acrylate-acrylic acid (MA-AA) copolymers					Ethyl acrylate-acrylic acid (EA-AA) copolymers				
100	M	M	I	I	I	M	M	I	
94	M	I	I	I	I	M	M	I	
88	M	I	I	I	I	M	M	I	
75	I	I	I	I	I	M	I	I	
70	I	I	I	I	I	I	I	I	
65	I	I	I	I	I	I	I	I	
50	I	I	I	I	I	I	I	I	
	Wt % AA				Wt % AA				
	0	13	23	50	0	15	23	33	
<i>n</i>-Butyl acrylate-acrylic acid (BA-AA) copolymers					2-Ethylhexyl acrylate-acrylic acid (2EHA-AA) copolymers				
100	I	I	I	I	I	I	I	I	
94	I	I	M	I	I	I	M	I	
88	I	I	M	I	I	I	M	I	
75	I	I	M	I	I	I	M	I	
70	I	M	I	I	I	I	I	I	
65	I	I	I	I	I	I	I	I	
50	I	I	I	I	I	I	I	I	

I = immiscible; M = miscible.

Table VII Binary Interaction Energy Densities (*B*) Determined from Heat of Mixing Measurements Between Low Molecular Weight Analogs for VAEs and Meth(acrylate)-Acrylic Acid Copolymers

	Values of <i>B</i> in cal/cc						
	EA	Hexane	MP	EP	BP	2-EHP	MIB
Hexane	12.21 ± 0.32	—	—	—	—	—	—
MP	-0.21 ± 0.03	12.15 ± 0.29	—	—	—	—	—
EP	0.26 ± 0.06	8.52 ± 0.13	0.06 ± 0.00	—	—	—	—
BP	1.41 ± 0.08	5.29 ± 0.25	0.86 ± 0.02	0.22 ± 0.05	—	—	—
2-EHP	3.12 ± 0.19	2.53 ± 0.13	2.53 ± 0.02	1.34	0.17	—	—
MIB	0.25 ± 0.07	8.12 ± 0.25	0.25 ± 0.09	0.04 ± 0.03	0.32 ± 0.07	1.38 ± 0.02	—
AA	0.13 ± 0.05	10.95 ± 0.28	1.61 ± 0.04	1.75 ± 0.13	2.32 ± 0.05	3.54 ± 0.13	1.83 ± 0.17
PA	2.27 ± 0.16	6.50 ± 0.25	3.26 ± 0.13	2.20 ± 0.08	1.48 ± 0.15	1.65	2.29 ± 0.07

EA = ethyl acetate; MP = methyl propionate; EP = ethyl propionate; BP = butyl propionate; 2-EHP = 2-ethylhexyl propionate; MIB = methyl isobutyrate; AA = acetic acid; PA = propionic acid.

of ethylene and AA content. The acrylates chosen for this comparison were MA, EA, *n*-butyl acrylate (BA), and 2-ethylhexyl acrylate (2EHA). For the condition of blends of two random copolymers $[(A_x B_{1-x})_m / (C_y D_{1-y})_n]$, six independent B_{AB} values were determined. The effective interaction energy density parameter for the blend, B , can be determined from a mean field approach:

$B =$

$$B_{AC}xy + B_{BC}(1-x)y + B_{AD}x(1-y) + B_{BD}(1-x)(1-y) - B_{AB}x(1-x) - B_{CD}y(1-y) \quad (3)$$

where x and y represent variation in copolymer

composition based on the volume fraction. The effective B values were determined for the various copolymer-copolymer blends and 2-D plots were generated displaying the variation of B with copolymer composition. For simplicity, only the contour line where $B = 0$ is displayed. Values inside the contour are negative, thus predicting the region of miscibility. This represents the minimum criteria for miscibility at high (infinite) molecular weight. The predictions described above are illustrated in Figures 9-12 for VAE with MA-AA, EA-AA, BA-AA, and 2EHA-AA copolymers, respectively. Note that these figures are for copolymer compositions based on volume fraction. Table VI lists the copolymer composition in wt %. For MA-AA copolymers, the propionic acid analog for AA yields slightly better

Table VIII Comparison of Binary Interaction Energy Densities (*B*) with Literature Values

	<i>B</i> (cal/cc)	Literature Value <i>B</i> (cal/cc) (Ref.)
Methyl propionate-toluene	0.76	0.72 (31)
Methyl propionate-ethylbenzene	1.81	1.74 (31)
Ethyl propionate-toluene	-0.64	-0.60 (31)
Ethyl propionate-ethylbenzene	0.13	0.12 (31)
Toluene-propionic acid	-0.20	-0.24 (31)
Ethylbenzene-propionic acid	0.25	0.57 (31)
Ethylbenzene-acetic acid	2.66	3.19 (31)
Ethyl acetate-heptane	11.43	11.8 (28)
Acetic acid-hexane	10.95	6.73 (32)
		10.38 (33)
Acetic acid-heptane	9.30	9.40 (32)
		11.34 (33)
		9.21 (34)

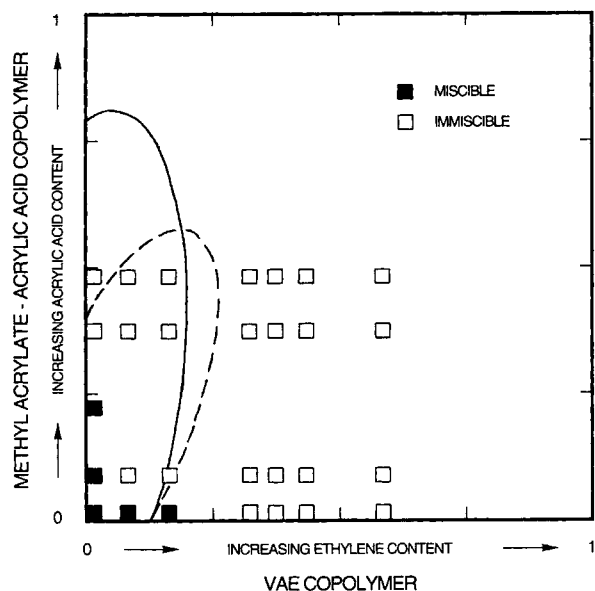


Figure 9 Miscibility prediction for blends of VAE copolymers with MA-AA copolymers based on heat of mixing data. Predicted miscible compositions enclosed by (—) were obtained when AA analog = acetic acid. Predicted miscible compositions enclosed by (---) were obtained when AA analog = propionic acid. Copolymer compositions are in volume fraction.

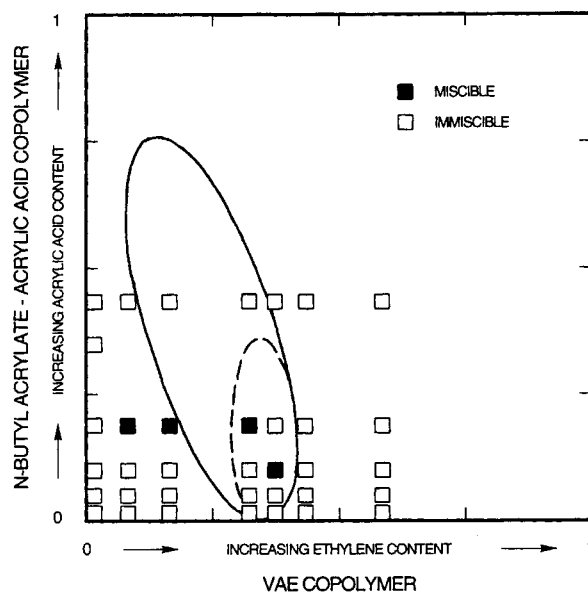


Figure 11 Miscibility prediction for blends of VAE copolymers with BA-AA copolymers based on heat of mixing data. Predicted miscible compositions enclosed by (—) were obtained when AA analog = acetic acid. Predicted miscible compositions enclosed by (---) were obtained when AA analog = propionic acid. Copolymer compositions are in volume fraction.

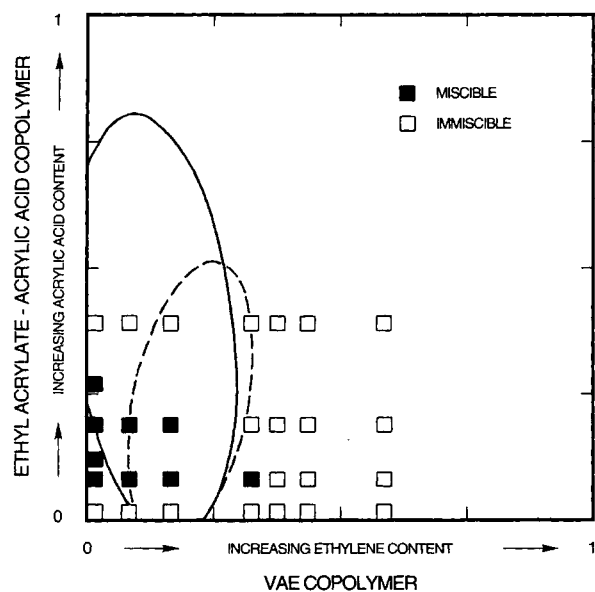


Figure 10 Miscibility prediction for blends of VAE copolymers with EA-AA copolymers based on heat of mixing data. Predicted miscible compositions enclosed by (—) were obtained when AA analog = acetic acid. Predicted miscible compositions enclosed by (---) were obtained when AA analog = propionic acid. Copolymer compositions are in volume fraction.

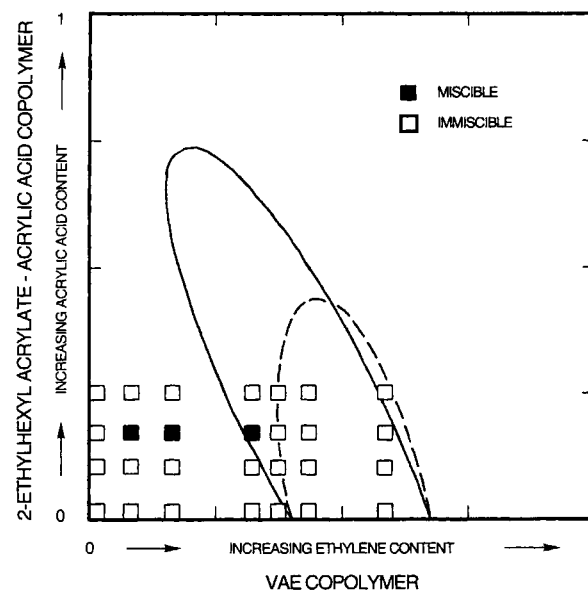


Figure 12 Miscibility prediction for blends of VAE copolymers with 2EHA-AA copolymers based on heat of mixing data. Predicted miscible compositions enclosed by (—) were obtained when AA analog = acetic acid. Predicted miscible compositions enclosed by (---) were obtained when AA analog = propionic acid. Copolymer compositions are in volume fraction.

agreement of prediction with experimental results. For EA-AA copolymers, both analogs yield only a qualitative agreement with experimental results, with acetic acid overpredicting the size of the miscibility window. For BA-AA, propionic acid predicts the size of the window, but it is displaced from the observed experimental window. For 2EHA-AA copolymers, the poorest agreement of prediction with experimental results is observed. Overall, the predicted results give only qualitative agreement with experimental results, predicting a window of miscibility in roughly the small area as experimentally observed miscibility. However, the shape and overall size of the predicted window does not show quantitative agreement. Propionic acid yields a better overall prediction of miscibility than does acetic acid as an AA analog.

It is not unexpected that the heat of mixing predictions based on the Van Laar expression presented earlier, results in problems with prediction of miscibility for AA-containing copolymers.³⁵ In both the low molecular weight model compounds and the polymeric blends, the association of acid groups through dimerization or other secondary structures results in a significant enthalpy of mixing which is insufficiently accounted for in the calculation of the binary interaction (B) values. It is not possible, through this analysis, to separate the relative contributions of these various inter- and intramolecular associations. In this work, the heat of mixing measurements were used as a guide to the compositional variables which were then sampled experimentally by the synthesis of appropriate copolymers and the preparation of representative blends. The utility of the analysis is apparent from its prediction of the existence of miscibility windows and the proximity, although not quantitative, of those predictions to experimentally observed miscible compositions.

In the comparison of the binary interaction energy densities (B) for the model compounds, the high positive value of ethyl acetate (VA analog) and hexane (ethylene analog) yields the large value of B_{AB} [eq. (3)] required to yield an overall negative B . Additionally, the values of B_{CD} are favorable for yielding an additional contribution leading to a negative value for B . This analysis indicates that the window of miscibility is due to specific rejections involving unfavorable interactions between the constituent comonomer units of the blend copolymers.

To determine if any specific carbonyl/carboxylic acid interactions existed in these blends, infrared spectra were obtained on representative acrylate-AA copolymer blends with VAE. Inspection of the resultant spectra revealed no separate peaks due to

complex formation between the two components. The acetate carbonyl region was then inspected for shifts relative to the unblended VAE copolymer. Again, no significant shifts were observed. Some small changes in the absorption maximum, less than 2 cm^{-1} , were noted, but these were within the resolution of the collected spectra and could not therefore be used to quantify any complex formation. Although it is expected that some specific interaction between the ester and carboxylic acid exists in these blends, the low concentration of the acid functionality in the materials makes spectroscopic identification of the complexes difficult.

In the case where only homopolymers of (meth)acrylates are considered [e.g., $(1 - y) = 0$], eq. (3) reduces to three terms. The predicted values for B as a function of ethylene content in VAE copolymers for blends with poly(meth)acrylates are illustrated in Figure 13. These results agree with experimental data in that PVAc is predicted to be miscible with only poly(methyl acrylate). VAE is predicted to be immiscible with the poly(meth)acrylates, except for poly(methyl methacrylate) (PMMA) around 15 wt % ethylene in VAE; however, no experimental sample exhibited miscibility. The transition from miscibility to phase separation for poly(methyl acrylate)-VAE occurs above 12% ethylene in VAE, thus showing good agreement of predicted vs. experimental results.

Other blends investigated in this study involved MMA-AA copolymers. Somewhat surprisingly, no MMA-AA copolymer blends with VAE or PVAc were observed. As poly(ethyl acrylate) and PMMA are isomeric, the comparison of their respective compound heat of mixing results (ethyl propionate and methyl isobutyrate) was made. Comparison of the binary interaction energy densities (see Table VII) for binary mixtures employing ethyl propionate or methyl isobutyrate with the remaining members of the database revealed similar results. Subsequently, the miscibility predictions of VAE/EA-AA and VAE/MMA-AA are quite similar, although the experimental observations are quite different. This indicates that structural features are quite important and not capable of being adequately treated by the analog heat of mixing approach.

Although not exhaustively studied, substitution of methacrylic acid for AA did not reveal any miscible blend combinations. Styrene/maleic anhydride (maleic acid) (maleic anhydride content 25 and 50 wt %) blends were found to be miscible with PVAc. Styrene/allyl alcohol (6 and 8% allyl alcohol) gave phase-separated blends. In addition, PVAc blends with VAE (30% ethylene) were phase-separated. A

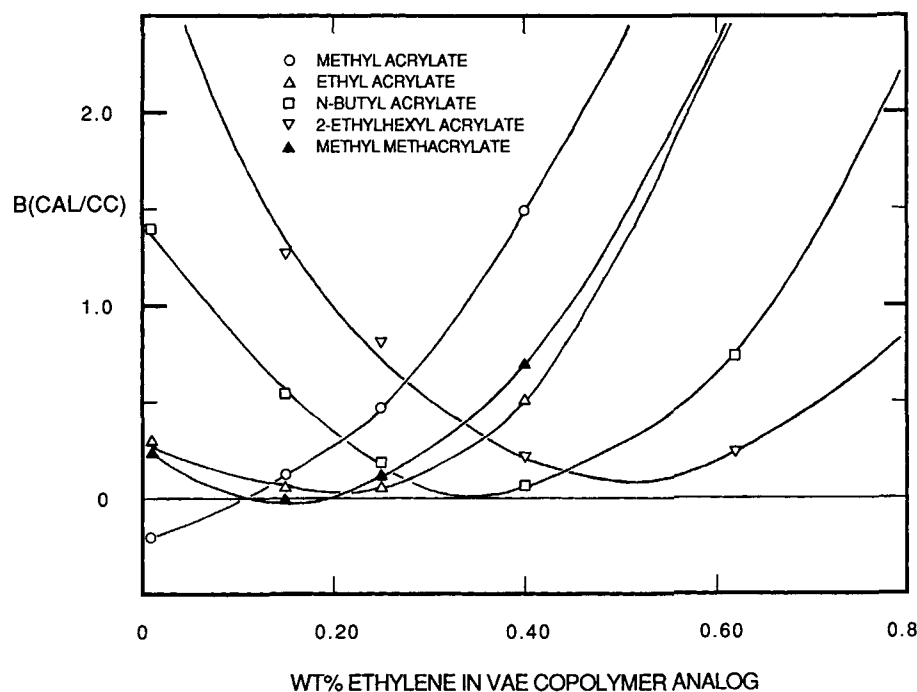


Figure 13 Miscibility predictions for blends of VAE copolymers with poly(meth) acrylates based on heat of mixing data.

styrene/ α -methyl styrene/AA copolymer (1/1/1) blend with PVAc was phase-separated.

CONCLUSIONS

The miscibility profile of VAE copolymers up to 30 wt % ethylene is quite similar to PVAc. PVF₂, PEO, and nitrocellulose previously noted to be miscible with PVAc maintain miscibility with VAE (30 wt % ethylene); however, the degree of interaction appears reduced.

PVAc is immiscible with polystyrene and various homopolymer polyacrylates with the exception of poly(methyl acrylate). Addition of AA to polystyrene and polyacrylates results in ranges of miscibility at low AA content. VAE copolymers also exhibit windows of miscibility with styrene and acrylate copolymers containing AA. Heat of mixing results utilizing analog heat of mixing procedures yield only qualitative agreement with the observed experimental phase behavior. This is believed partially due to the differences between the low molecular weight analog compound acid dimerization compared to their high molecular weight structures. Based on the heat of mixing studies, only VA-MA mer units exhibit negative interaction energy densities for the model compounds, thus implying specific interac-

tion. The miscibility of acrylate-AA copolymers with VAE copolymers is thus proposed to be due to specific rejections involving more unfavorable interactions (positive B) between the comonomer units of the respective copolymer than the interactions between these units and comonomer units of the blended polymer. Miscibility of PVAc and poly(methyl acrylate), however, can be explained via a weak specific interaction.

REFERENCES

1. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
2. S. Akiyama, Y. Komatsu, and R. Kaneko, *Polym. J.*, **7**, 172 (1975).
3. A. Dobry and F. Boyer-Kawenoki, *J. Polym. Sci.*, **2**, 90 (1947).
4. L. J. Hughes and G. E. Britt, *J. Appl. Polym. Sci.*, **5**, 337 (1961).
5. D. R. Paul, J. W. Barlow, R. E. Bernstein, and D. C. Wahrmund, *Polym. Eng. Sci.*, **18**, 1225 (1978).
6. R. E. Bernstein, D. R. Paul, and J. W. Barlow, **18**, *Polym. Eng. Sci.*, 683 (1978).
7. C. F. Hammer, *Macromolecules*, **4**, 69 (1971).
8. R. J. Kern and R. J. Slocombe, *J. Polym. Sci.*, **25**, 183 (1955).

9. A. K. Nandi, B. M. Mandal, and S. N. Bhattacharyya, *Macromolecules*, **18**, 1454 (1985).
10. V. O. Fuchs, *Angew. Makromol. Chem.*, **6**, 79 (1969).
11. B. V. Li, X. P. Bi, D. H. Zhang, and F. S. Wang, in *Advances in Interpenetrating Polymer Networks*, D. Klemperer and K. C. Frisch, Eds., Technomic, Lancaster, PA, 1989, Vol. 1.
12. K. H. Hsieh and B. J. Wong, *J. Chi. I. Ch. E.*, **19**, 17 (1988).
13. S. Cimmino, E. Martuscelli, and C. Silvestre, *Makromol. Chem. Macromol. Symp.*, **16**, 147 (1988).
14. E. Martuscelli, L. Vicini, and A. Seves, *Makromol. Chem.*, **188**, 607 (1987).
15. Y. Jinghua, G. G. Alfonso, A. Turturro, and E. Pedemonte, *Polymer*, **34**, 1465 (1993).
16. C. Bhattacharyya, S. N. Bhattacharyya, and B. M. Mandal, *J. Indian Chem. Soc.*, **63**(1), 157 (1986).
17. E. M. Pearce, T. K. Kwei, and B. Y. Min, *J. Macromol. Sci.-Chem. A*, **21**(8,9), 1191 (1984).
18. M. M. Coleman, A. M. Lichkus, and P. C. Painter, *Macromolecules*, **22**, 586 (1989).
19. E. J. Moskala, S. E. Howe, P. C. Painter, and M. M. Coleman, *Macromolecules*, **17**, 1671 (1984).
20. P. Greco and E. Martuscelli, *Polymer*, **30**, 1475 (1989).
21. M. M. Coleman, X. Yang, H. Zhang, P. C. Painter, and K. V. Scherer, Jr., *J. Polym. Sci. Part A Polym. Chem.*, **31**, 2039 (1993).
22. M. M. Coleman, J. F. Graf, and P. C. Painter, *Specific Interactions and the Miscibility of Polymer Blends*, Technomic, Lancaster, PA, 1991.
23. S. Dutta, S. S. Chakraborty, B. M. Mandal, and S. N. Bhattacharyya, *Polymer*, **34**, 3499 (1993).
24. H. Vazquez-Torres and C. A. Cruz-Ramos, *J. Appl. Polym. Sci.*, **32**, 6095 (1986).
25. G. A. Zakrzewski, *Polymer*, **14**, 348 (1973).
26. D. Feldman and M. Rusu, *Eur. Polym. J.*, **12**, 559 (1976).
27. Y. J. Shur and B. G. Ranby, *J. Appl. Polym. Sci.*, **19**, 1337 (1975).
28. C. A. Cruz-Ramos and D. R. Paul, *Macromolecules*, **22**, 1289 (1989).
29. L. M. Robeson and J. E. McGrath, *Polym. Eng. Sci.*, **17**, 300 (1977).
30. C. A. Cruz, J. W. Barlow, and D. R. Paul, *Macromolecules*, **12**, 726 (1979).
31. G. R. Brannock, J. W. Barlow, and D. R. Paul, *J. Polym. Sci. Part B Polym. Phys.*, **28**, 871 (1990).
32. I. Nagata, M. Nagashima, K. Kazuma, and M. Nakogawa, *J. Chem. Eng. Jpn.*, **8**, 261 (1975).
33. M. Woycicka, *Pure Appl. Chem.*, **2**, 147 (1961).
34. J. Liszi, *Acta Chim. Acad. Sci. Hung.*, **66**, 411 (1970).
35. G. R. Brannock, J. W. Barlow, and D. R. Paul, *J. Polym. Sci. Part B Polym. Phys.*, **28**, 871 (1990).

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