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Compatibility in Chlorinated Poly(vinyl chloride)/Poly(ethylene-co-vinyl acetate) Blends

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Recently, the miscibility and phase separation behavior in blends containing random copolymers have been investigated.¹⁻¹⁵ Several homopolymer/copolymer blends were found to be miscible for a certain range of copolymer compositions even though no specific interactions between the component monomer units occurred.⁵⁻¹⁵ This region of miscibility has been termed a "miscibility window" and has been explained by the Flory-Huggins theory¹⁻³ in terms of an unfavorable interaction between the two different monomer units comprising the copolymer. The Flory-Huggins theory for mixtures of homopolymers and copolymers has also been extended to blends of two random copolymers.^{2,4} According to ten Brinke et al.,² the interaction parameter χ_{blend} between two random copolymers $(A_x B_{1-x})_{n_1}$ and $(C_y D_{1-y})_{n_2}$ can be written as

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

where the respective χ_{ij} are the segmental interaction parameters between the different monomers corresponding to their subscripts and x and y are the copolymer compositions expressed in volume fractions. When the value

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Table I
Compositions and Sources of Copolymers Used

VAc Contents of Et-co-VAc Copolymers			
sample	wt %	mol %	source
Et-co-VAc-1	87.1	68.7	Kuraray Co., Japan
Et-co-VAc-2	83.2	61.7	Kuraray Co., Japan
Et-co-VAc-3	79.5	55.8	Kuraray Co., Japan
Et-co-VAc-4	70.0	43.0	Bayer, Germany
Et-co-VAc-5	50.0	25.0	Bayer, Germany
Et-co-VAc-6	45.0	21.0	Bayer, Germany
Et-co-VAc-7	40.0	18.0	Scientific Polymer Products, Inc.
Et-co-VAc-8	33.0	14.0	Scientific Polymer Products, Inc.

Chlorine Contents of CPVC^a

sample	wt %	sample	wt %
CPVC-1	61.9	CPVC-5	65.5
CPVC-2	62.3	CPVC-6	66.5
CPVC-3	63.7	CPVC-7	67.1
CPVC-4	64.4	CPVC-8	68.5

^a Prepared by solution chlorination of poly(vinyl chloride) with $\bar{M}_w = 2.1 \times 10^6$ (The B. F. Goodrich Co.).

of χ_{blend} at a given temperature is less than χ_{crit} , a parameter given by

$$\chi_{crit} = \frac{1}{2}(n_1^{-1/2} + n_2^{-1/2})^2 \quad (2)$$

(where n_1 and n_2 are the degrees of polymerization of the two copolymers, respectively), the two copolymers attain miscibility at that temperature.² Even if all χ_{ij} are greater than zero, because the signs of the last two terms in eq 1 are negative, χ_{blend} may be smaller than χ_{crit} for certain ranges of x and/or y if χ_{AB} and/or χ_{CD} are sufficiently large. Thus, the two copolymers may be miscible because of the repulsions between the monomers A and B and/or between the monomers C and D even if unfavorable pairwise segmental interactions prevail. In contrast, if χ_{AB} and/or χ_{CD} are negative and their absolute values are sufficiently large, the two copolymers may indeed be immiscible in a certain range of x and/or y because of these effects even though all the segmental χ_{ij} are negative. Thus, miscibility in copolymer blends depends on the copolymer compositions as well as on the relationships among the segmental χ_{ij} .

In a previous publication⁴ we presented representative examples of experimentally determined and theoretically possible "miscibility maps", i.e., miscibility plotted as a function of copolymer composition for blends of two random copolymers having a common monomer, the case $(A_x B_{1-x})_{n_1} / (C_y D_{1-y})_{n_2}$. The present contribution presents the miscibility map for ethylene-co-vinyl acetate/chlorinated poly(vinyl chloride) (Et-co-VAc/CPVC) blends and compares the experimental and calculated data. In addition to the analysis implied above in terms of an $(A_x B_{1-x})_{n_1} / (C_y D_{1-y})_{n_2}$ system, we have also taken cognizance of the complications introduced by the presence of CCl_2 units in certain CPVC polymers and have extended the formulation to include the system $(A_x A'_x B_{1-x-x'})_{n_1} / (C_y D_{1-y})_{n_2}$. Lehr²¹ also discussed recently the importance of CCl_2 units when considering the interactions of CPVC with other polymers.

Experimental Section

The Et-co-VAc and CPVC copolymers used were the same as those described previously.^{4,16} Vinyl acetate and chlorine contents are listed together with the sources of the copolymers in Table I. Additional characterization details are in ref 4 and 16.

Blends were prepared by casting from a common solvent, THF. The two component polymers were dissolved in THF (2.5% (w/v)) at a blend ratio of 50/50 wt %. All solutions were clear. The solvent was allowed to evaporate at room temperature and the

Table II
Composition of CPVC Employed^a

sample ^b	CH ₂ CHCl, mol %	CHClCHCl, mol %	CHClCCl ₂ , mol %	CH ₂ CCl ₂ , mol %
CPVC-1	77.4	18.9	0.7	3.0
CPVC-2	75.3	20.2	1.2	3.3
CPVC-3	68.3	25.5	2.1	4.1
CPVC-4	64.8	28.1	2.6	4.5
CPVC-5	59.0	32.0	3.8	5.2
CPVC-6	53.1	35.1	6.0	5.8
CPVC-7	49.4	36.8	7.8	6.0
CPVC-8	37.8	43.0	12.4	6.8

^a Calculated from ref 18. ^b See Table I for weight percent chlorine.

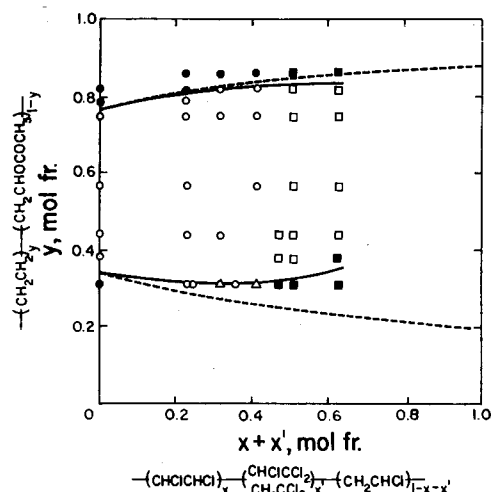


Figure 1. Miscibility map for blends of CPVC and Et-co-VAc copolymers: (O, Δ, □) miscible; (●, ■) immiscible. The circles indicate data obtained at 150 °C, the squares at 170 °C, and the triangles at both 150 and 170 °C. The data for the blends of PVC homopolymer and Et-co-VAc were obtained previously.⁴ The broken and solid lines are the calculated miscibility/immiscibility boundaries (see text).

resulting film was dried under vacuum for at least 3 days at 70 °C.

The miscibility of the blends was assessed in the normal manner by observation of the glass transition temperatures with a Perkin-Elmer DSC-4 differential scanning calorimeter. The procedures are described in ref 4. Annealing of samples was carried out in the DSC. Thermal analyses were performed at a heating rate of 20 °C/min with sample sizes of 15–20 mg.

Results and Discussion

CPVC polymers prepared by solution chlorination may contain CCl_2 units in addition to CH_2 and $CHCl$ units.^{17,18} Komoroski et al.¹⁸ evaluated the relative amounts of these units in solution-chlorinated PVC using ¹³C NMR spectroscopy. For example, according to Komoroski et al. the content of CCl_2 in CPVC is about 9 mol % at ca. 69 wt % chlorine content of the polymer but is negligible at low degrees of chlorination. Thus, in general, the CPVC polymer may be regarded as a random copolymer containing the following four vinyl monomer units if adjacent CCl_2 units are neglected: $CHClCHCl$ (A), CH_2CHCl (B), $CHClCCl_2$, and CH_2CCl_2 . The last two structures are present in relatively small amounts and as an approximation, they have been combined (A') to facilitate analysis. Table II summarizes the copolymer compositions for the CPVC polymers employed here, which were estimated from data presented in ref 18 using the triad-diad relationship.¹⁹

Figure 1 shows a miscibility map plotted as a function of the compositions of the two component copolymers

Table III
Calculated Segmental Interaction Parameters at ~150 °C

segment pair	χ_{ij}
CHClCHCl/CH ₂ CHOCOCH ₃	0.17 ₃ ^a (χ_{AD})
CH ₂ CHCl/CH ₂ CHOCOCH ₃	0.26 ₇ ^a (χ_{BD})
CH ₂ CH ₂ /CH ₂ CHOCOCH ₃	1.01 ^a (χ_{CD})
CHClCHCl/CH ₂ CHCl	0.042 ₄ ^a (χ_{AB})
CH ₂ CHCl/CH ₂ CH ₂	0.15 ₅ ^a (χ_{BC})
CHClCHCl/CH ₂ CH ₂	0.10 (χ_{AC})
(CHClCCl ₂ , CH ₂ CCl ₂)/CH ₂ CHOCOCH ₃	0.65 (χ_{AD})

^a From ref 4.

CPVC and Et-co-VAc. In this figure x' is the sum of the mole fractions of the CHClCCl₂ and CH₂CCl₂ units listed in Table II. The data points show the results obtained for blend samples annealed for 20 min at temperatures that are at least 10 °C above the glass transition temperatures of the CPVCs (150 °C for the blends with CPVC-1, -2, -3, -4, and -5, 170 °C for the blends with CPVC-6, -7, and -8, and 150 and 170 °C for the two blends of Et-co-VAc-1 with CPVC-3 and -5 (see Table I)). The experimental results for the blends of the PVC homopolymer and the Et-co-VAc copolymer are those obtained by us previously.⁴

As shown in Figure 1, the miscibility region becomes slightly wider in terms of the Et-co-VAc composition with increasing chlorine content up to about $x + x' = 0.35$, corresponding to Cl contents of less than ca. 64 wt %. In this range of chlorine content the combined amounts of CHClCCl₂ and CH₂CCl₂ units are less than 8 mol %.¹⁸ The segmental χ_{ij} representing interaction of the CHClCHCl and VAc monomer units (χ_{AD}) is marginally smaller than that for the VC and VAc interaction (χ_{BD}) as shown in Table III, which results in an extension of the miscibility region with increasing Cl content. (The values of these segmental χ_{ij} were obtained from the previous paper.⁴) Conversely, at high chlorine contents ($x + x' > 0.45$) Et-co-VAc copolymer with high VAc content becomes less miscible with CPVC as the chlorine content increases. (This immiscibility does not arise from the higher annealing temperature used because the two blends containing CPVC with lower chlorine content, denoted by triangles in Figure 1, display miscibility even at 170 °C.) In this high chlorine content range (corresponding to a Cl content of more than 65 wt %) the total amount of CH₂CCl₂ and CHClCCl₂ units may be above 10%.¹⁸ The latter two units may overall interact less favorably with VAc in comparison with CHClCHCl units because there are fewer α -hydrogens that can interact attractively with the carbonyl oxygen of VAc.²⁰ Furthermore, since the values of the segmental χ_{ij} between the different monomer units comprising CPVC are not very large,⁴ one cannot expect miscibility due merely to an intramolecular repulsive effect in CPVC. Thus, immiscibility at high chlorine contents arises from the mass action effect of the increase in the combined amounts of CHClCCl₂ and CH₂CCl₂ units.

To calculate the boundaries between miscibility and immiscibility with the relationships of the type given in eq 1, the values of the respective segmental χ_{ij} and of χ_{crit} are needed. If the monomer units CHClCCl₂ and CH₂CCl₂ can be ignored, this system can be regarded as a blend of the copolymers (A_xB_{1-x})_{n₁} and (C_yD_{1-y})_{n₂}, and eq 1 is applicable. In this case, six segmental χ_{ij} and χ_{crit} are required for the calculations. The value of χ_{crit} was determined to be 0.001 from the degrees of polymerization averaged for the polymers used in this study^{4,16} using eq 2. Five of the six χ_{ij} were obtained in the previous paper⁴ and are listed in Table III. The remaining χ_{ij} , i.e., χ_{AC} , representing CHClCHCl and CH₂CH₂ interactions, was cal-

culated to be 0.10 by fitting the upper experimental miscibility/immiscibility boundary in Figure 1 (i.e., for high ethylene contents of Et-co-VAc) at low degrees of chlorination (in which case the amounts of the CHClCCl₂ and CH₂CCl₂ units are negligible). The broken lines in Figure 1 are the boundaries calculated with these combined values of the segmental χ_{ij} and may thus be regarded as the fit of the experimental data with one adjustable parameter, i.e., χ_{AC} . The calculated upper boundary is in reasonable agreement with the experimental data even at high chlorine contents. On the other hand, the calculated lower boundary does not agree very well with that determined experimentally for the higher chlorine contents. This discrepancy may arise from neglect of the CH₂CCl₂ and CHClCCl₂ units.

The miscibility/immiscibility boundaries were also calculated by taking into account the presence of the CHClCCl₂ and CH₂CCl₂ units. To minimize the number of χ_{ij} that were needed, it was assumed that r_1 CHClCCl₂ units and r_2 CH₂CCl₂ units in the CPVC molecule are equivalent to $(r_1 + r_2)$ A' units with respect to interactions. Then CPVC is regarded as a random terpolymer containing the three monomer units CHClCHCl (A), (CHClCCl₂, CH₂CCl₂) (A'), and CH₂CHCl (B), i.e., as (A_xA'_xB_{1-x-x'})_{n₁}. (CPVC can also be regarded as a polymer consisting of the three units, CH₂, CHCl, and CCl₂, but in this representation the microstructure is not random because the originating PVC is of course an alternate structure.) For blends of the polymers (A_xA'_xB_{1-x-x'})_{n₁} and (C_yD_{1-y})_{n₂}, χ_{blend} can be expressed by an extension of eq 1 as follows:

$$\chi_{blend} = y(x\chi_{AC} + x'\chi_{AC'}) + y(1 - x - x')\chi_{BC} + (1 - y)(x\chi_{AD} + x'\chi_{AD'}) + (1 - y)(1 - x - x')\chi_{BD} - (1 - x - x')\chi_{AB} + x'\chi_{AB'} - y(1 - y)\chi_{CD} - xx'\chi_{AA'}$$
 (3)

To calculate a miscibility map using eq 3, four segmental χ_{ij} are needed in addition to the six χ_{ij} mentioned above. However, these χ_{ij} cannot all be evaluated at present. Therefore, further approximation is required to reduce the number of χ_{ij} . As described above, the upper boundary calculated with eq 1 is in agreement with the experimental data over the whole composition range of CPVC despite the fact that the CHClCCl₂ and CH₂CCl₂ contents were neglected. On the other hand, the other calculated boundary does not agree with the experimentally determined boundary in the high VAc composition range, especially at high chlorine contents, suggesting that the interaction between VAc and CCl₂ units is significant for miscibility (or immiscibility) in this system. Therefore, only the interaction between vinyl acetate and the monomer A' (CHClCCl₂, CH₂CCl₂), i.e., χ_{AD} , is considered and other interactions concerning monomer units containing CCl₂ are ignored. Furthermore, χ_{AD} is assumed to be independent of the Cl content of CPVC even though the ratio of the amount of CHClCCl₂ units changes with the Cl content.¹⁸ The solid lines in Figure 1 are the miscibility/immiscibility boundaries calculated with these approximations and assumptions from eq 3 with $\chi_{AD} = 0.65$ and the segmental χ_{ij} determined previously (i.e., a two-parameter fit). The solid lines provide a very satisfactory agreement with the experimentally determined miscibility/immiscibility boundaries compared to the simplified analysis represented by the broken lines. The agreement between theory and experiment could be improved further by future independent determinations of the additional χ_{ij} using other systems.

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