

## Miscibility in Copolymer Blends of Poly(vinyl chloride-co-vinyl acetate) and Poly(methyl-co-hexyl acrylate)

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**ABSTRACT:** The phase behavior in 50/50 wt% binary random copolymer blends of poly(vinyl chloride-co-vinyl acetate) and poly(methyl-co-hexyl acrylate) was studied. The blends had a miscibility window and exhibited LCST behavior. The miscibility was determined as a function of composition of each copolymer and displayed in composition-composition diagram [C-C diagram]. The segmental interaction parameters between monomer units comprising the blends were calculated by applying the mean field theory expression to the C-C diagram. Using the segmental interaction parameters, blend interaction parameters which represent the miscibility of the blend system quantitatively, were also estimated. From the calculated values, it was found that the segmental interactions of vinyl acetate unit with other units were strongly repulsive and had significant effect on the miscibility.

**KEY WORDS** Miscibility / Poly(vinyl chloride-co-vinyl acetate) Copolymer / Poly(methyl-co-hexyl acrylate) Copolymer / Segmental Interaction Parameter / Mean Field Theory / Composition-Composition Diagram /

Currently, there is considerable interest in the miscibility of blends containing random copolymers. The blends are miscible in certain range of copolymer composition even though their component homopolymers are immiscible. Mean field theory for the miscibility of copolymer blends, which was proposed by Kambour *et al.*<sup>1</sup> and ten Brinke *et al.*,<sup>2</sup> was presented to explain this phenomenon. According to this model, the mutual repulsive interaction between different monomer units within copolymer plays an important role in determining the miscibility of the copolymer blends. Using the mean field theory, an expression has been developed to quantify this effect in terms of segmental interaction parameters.

Shiomi *et al.*<sup>3,4</sup> showed several cases of

copolymer composition dependence of miscibility for the copolymer blends containing a common monomer unit by using this expression. Cowie *et al.*<sup>5,6</sup> and Kang *et al.*<sup>7</sup> estimated the miscibility boundary of binary copolymer blends containing four different monomer units from the independently obtained segmental interaction parameters. They also showed that the experimental results agreed well with the prediction of the mean field theory. Recently, Huh *et al.*<sup>8</sup> and others<sup>9,10</sup> applied the theoretical expression to the experimental miscibility diagram for the binary copolymer blends and estimated a set of segmental interaction parameters between monomer units comprising the copolymer blend.

In our previous paper,<sup>11</sup> we demonstrated

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that poly(vinyl chloride) (PVC) formed miscible blends with poly(methyl-*co*-hexyl acrylate) for a certain range of copolymer composition even though poly(methyl acrylate) and poly(hexyl acrylate) are immiscible with PVC, respectively. In this paper, we extended this scheme to binary copolymer blend system of poly(vinyl chloride-*co*-vinyl acetate) [PVC-VAc] and poly(methyl-*co*-hexyl acrylate) [MHA]. For the system of this type, poly(vinyl chloride-*co*-vinyl acetate) can be represented as  $(A_x B_{1-x})_{n_1}$ , where A=vinyl acetate unit [VAc], B=vinyl chloride unit [VC],  $x$  is the volume fraction of the monomer unit A, and  $n_1$  is the degree of polymerization of PVC-VAc copolymer. Also, poly(methyl-*co*-hexyl acrylate) can be represented as  $(C_y D_{1-y})_{n_2}$ , where C=hexyl acrylate unit [HA], D=methyl acrylate unit [MA],  $y$  is the volume fraction of the unit C, and  $n_2$  is the degree of polymerization of MHA copolymer. In this case, six segmental interaction parameters which represent the binary combinations of four different monomer units are required to describe the phase behavior of this blend system.

The purpose of this study is to investigate the effect of copolymer composition on the miscibility and to calculate the segmental interaction parameters by fitting theoretical expression to the experimental data. By using the calculated values, blend interaction parameters for PVC-VAc/MHA blends system were also derived.

## EXPERIMENTAL

### Materials

The methyl acrylate monomer used in this study was commercial grade from the Kasei Chemical Company and *n*-hexyl acrylate was obtained from the Scientific Polymer Product Company. They were purified by washing with aqueous sodium hydroxide solution first and then with distilled water twice. They were then dried over anhydrous calcium chloride

for 24 hours and distilled under reduced pressure.

The MHA copolymers differing in composition were synthesized by radical copolymerization in the bulk. A mixture of the monomers (100 part), 2-propanol (chain transfer agent, 5 part), and lauroyl peroxide (initiator, 0.1 part) was added to a flask and then stirred under nitrogen atmosphere. The reaction was run for approximately 15 min at 70°C. In order to prevent the autoacceleration during the polymerization reaction and limit the reaction to low conversion, methyl ethyl ketone (100 part) was added and the reaction was continued for 5 min. The solution was poured into excess methanol to precipitate the copolymer synthesized. The resulting copolymers were dried in a vacuum oven at 60°C for 3 days until no further weight loss was observed. The yield ranged from 5% to 10%.

The copolymer compositions and molecular weights were determined by <sup>1</sup>H NMR (300 MHz) and Waters Associate 150-C model GPC, respectively. The synthesized copolymer composition was almost close to the monomer feed composition. DSC measurements were performed using du Pont 910 DSC at a heating rate of 20°C min<sup>-1</sup> under nitrogen atmosphere. All pure copolymers showed a single narrow  $T_g$  that varied linearly with the copolymer composition, which was distinctive

Table I. Composition, molecular weight, and glass transition temperature of MHA copolymers

Samples	HA vol. ratio	$\bar{M}_n \times 10^{-4}$	$T_g$ (°C)
MHA15	0.15	17.3	10
MHA24	0.24	18.2	4
MHA29	0.29	19.1	0
MHA35	0.35	18.3	-4
MHA41	0.41	17.5	-9
MHA46	0.46	18.1	-12
MHA50	0.50	18.9	-15
MHA55	0.55	18.8	-22
MHA66	0.66	18.7	-30
MHA75	0.75	18.0	-39
MHA88	0.88	13.0	-50

**Table II.** Copolymer composition and molecular weight of poly(vinyl chloride-co-vinyl acetate)

Samples	VAc vol%	$\bar{M}_n \times 10^{-4}$	Source
PVC		5.0	Han Yang Chem.
PVC-VAc5	5.7	4.7	Han Yang Chem.
PVC-VAc8	7.9	4.5	Han Yang Chem.
PVC-VAc12	11.5	4.3	Sci. Polym. Pro.
PVC-VAc15	14.7	1.3	Sci. Polym. Pro.
PVC-VAc20 <sup>a</sup>	19.5	2.3	Sci. Polym. Pro.
PVC-VAc24 <sup>a</sup>	23.7	0.7	By fractionation

<sup>a</sup> Excluding maleic acid.

feature of random copolymer. Compositions, molecular weights and  $T_g$ 's of the MHA copolymers are listed in Table I. A numeral after MHA represents the approximate volume percent of the hexyl acrylate in the copolymer.

PVC and PVC-VAc copolymers were obtained from the Han Yang Chemical Company and the Scientific Polymer Products. The copolymer of high VAc content PVC-VAc24 was prepared by fractioning PVC-VAc20 using non-solvent addition method.<sup>12</sup> Composition and molecular weight of PVC and PVC-VAc copolymers used in this study are listed in Table II.

### Blend

The two polymers (50/50 wt%) were dissolved in MEK while stirring at 60°C for 3–4 hours. All the solutions were transparent. The solvent was allowed to evaporate slowly at room temperature for at least 1 day. The resulting films were further dried in a vacuum oven for 2 days at 60°C to completely remove residual solvent. All the films prepared in this way were transparent or opaque. The miscibility of the blends was determined by observing the presence of single or double glass transition temperature in the DSC thermogram. The samples were annealed at 100°C and 120°C for 15 min in the DSC cell and then were rapidly quenched. The thermal analysis was carried out at a heating rate of 20°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Phase Behavior of PVC-VAc/MHA Blends

Miscibility in 50/50 wt% blends of PVC with several MHA copolymers differing in composition was examined by DSC and the results were displayed in Figure 1. The MHA copolymer with the HA content equal to or less than 29% was found to be immiscible with PVC, which was identified by the existence of two  $T_g$ 's. The two  $T_g$  values observed did not correspond to those of the pure components, which indicated a partial miscibility. This partial miscibility increased as the HA content of MHA copolymer approached the critical copolymer composition for miscibility.

Figure 2 displayed the DSC thermograms of 50/50 wt% PVC-VAc/MHA copolymer blends varying the VAc content of PVC-VAc. The PVC-VAc15/MHA35 blend was miscible as demonstrated by the appearance of a single  $T_g$ . But, in the case of PVC-VAc copolymers with the VAc content equal to or more than 20%, the blends formed two phases. As the VAc content of PVC-VAc copolymer increased, two distinct  $T_g$ 's were further separated.

Based on a series of DSC thermograms and film clarity, the composition-composition diagram for 50/50 wt% PVC-VAc/MHA blends at 100°C was constructed and shown in Figure 3. This figure has been so called miscibility map and designated as "C-C diagram" or

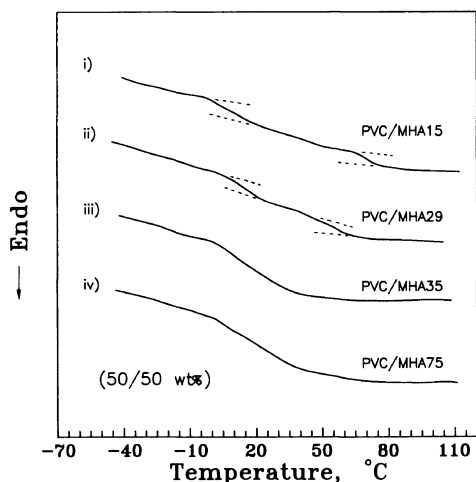


Figure 1. DSC thermograms of 50/50 wt% blends of PVC with MHA copolymer of different copolymer composition.

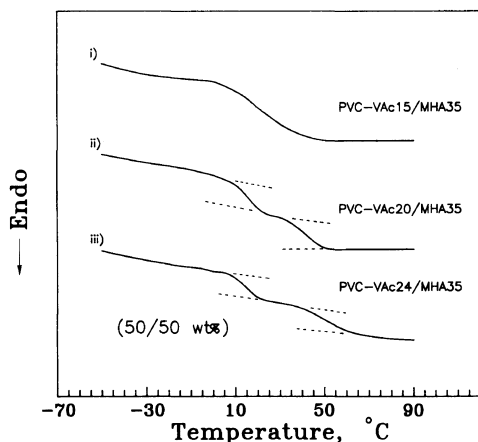


Figure 2. DSC thermograms of 50/50 wt% PVC-VAc/MHA35 blends for three different PVC-VAc copolymer compositions.

“C-C plots” from which miscibility-immiscibility boundary is determined. The dashed line drawn in Figure 3 represented the estimated miscibility-immiscibility boundary. The isothermal composition-composition diagram for the PVC-VAc/MHA system at 120°C was also constructed and shown in Figure 4. When compared to the C-C diagram at 100°C, the miscible region became narrower at 120°C.

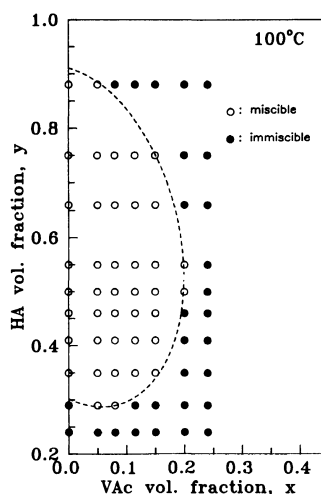


Figure 3. Isothermal composition-composition diagram of PVC-VAc/MHA 50/50 wt% blends at 100°C. (Dashed line represents predicted miscibility-immiscibility boundary obtained from eq 3 using parameters in Table III.)

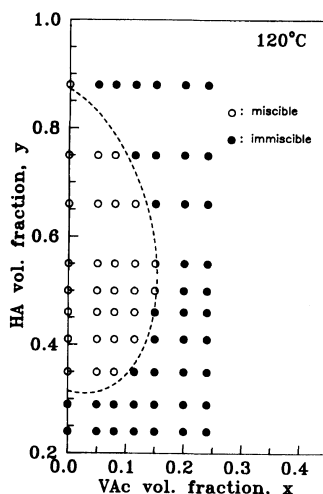


Figure 4. Isothermal composition-composition diagram of PVC-VAc/MHA 50/50 wt% blends at 120°C. (Dashed line represents predicted miscibility-immiscibility boundary obtained from eq 3 using parameters in Table III.)

This suggested that PVC-VAc/MHA blend system had LCST behavior.

#### Calculation of Segmental Interaction Parameters

The PVC-VAc/MHA blend system involves

four different monomer units and can be represented as  $(A_x B_{1-x})_{n_1} / (C_y D_{1-y})_{n_2}$ . For the blends of this type, the blend interaction parameter,  $\chi_{\text{blend}}$ , can be expressed as a linear combination of the segmental interaction parameters according to the mean field theory:

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

A critical point occurs at a temperature for which  $\chi_{\text{blend}}$  equals  $\chi_{\text{blend}}^{\text{crit}}$ , where

$$\chi_{\text{blend}}^{\text{crit}} = \frac{1}{2} (n_1^{-0.5} + n_2^{-0.5})^2 \quad (2)$$

By rearranging eq 1 and equating  $\chi_{\text{blend}}$  to  $\chi_{\text{blend}}^{\text{crit}}$ , a quadratic boundary equation can be represented in general form

$$F(x, y) = \chi_{\text{blend}} - \chi_{\text{blend}}^{\text{crit}} = ax^2 + by^2 + cxy + dx + ey + f \quad (3)$$

where  $a = \chi_{AB}$ ;  $b = \chi_{CD}$ ;  $c = \chi_{AC} + \chi_{BD} - \chi_{BC} - \chi_{AD}$ ;  $d = \chi_{AD} - \chi_{BD} - \chi_{AB}$ ;  $e = \chi_{BC} - \chi_{BD} - \chi_{CD}$ ;  $f = \chi_{BD} - \chi_{\text{blend}}^{\text{crit}}$ .

The boundary condition is given by  $F(x, y) = 0$  and any experimentally determined boundary between the miscible and immiscible region can be used to determine a set of  $\chi_{ij}$ 's. The molecular weight difference between component copolymers may affect the miscibility-immiscibility boundary. But we assumed that this effect was considerably smaller than that caused by composition variation. The enclosed area of miscibility in Figure 3 was found to be best fitted by elliptical contour although there is some difficulty in defining exact location of the boundary of the miscibility region. After extending the elliptical curvature of the boundary to the other plane ( $-1 < x < 0$ ), an experimental equation which represents the elliptical contour in Figure 3 can be obtained. By measuring the lengths of the major and minor axes and determining the focal point and tilt angle, the specific equation representing the miscibility-

immiscibility boundary was calculated and given by the following equation

$$F(x, y) = 0.226x^2 + 0.080y^2 + 0.064xy - 0.044x - 0.097y + 0.022 = 0 \quad (4)$$

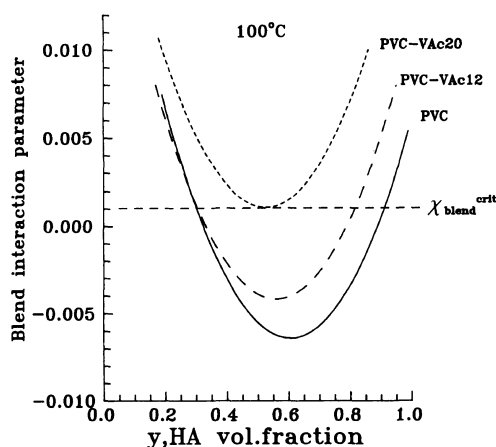
The quadratic equation has a general property that all the coefficient may be scaled by any nonzero real number. In order to obtain the absolute values of the coefficients, one of them must be known previously from another independent experiment. We used the value of  $\chi_{CD} = 0.080$  which was determined from our study of MHA copolymers blend system.<sup>11</sup> The  $\chi_{CD}$  value was used directly as the coefficient  $b$  and the remaining coefficients shown in eq 3 were determined.

For the PVC-VAc/MHA system, the value of  $\chi_{\text{blend}}^{\text{crit}}$  was calculated to be approximately 0.001 from the given degree of polymerization. Besides  $\chi_{CD}$ , we had available data of  $\chi_{BC} = 0.006$ ,  $\chi_{BD} = 0.023$  which were determined from our previous study of PVC/MHA blend system.<sup>11</sup> Thus, only three other segmental interaction parameters were unknown. The remaining  $\chi_{ij}$ 's were calculated by fitting the experimental boundary eq 4 to the mean field eq 3. The calculated segmental interaction parameters were listed in Table III. The VAc monomer unit had an unfavorable segmental interaction with other units in the order of  $HA > VC > MA$  and played significant role in

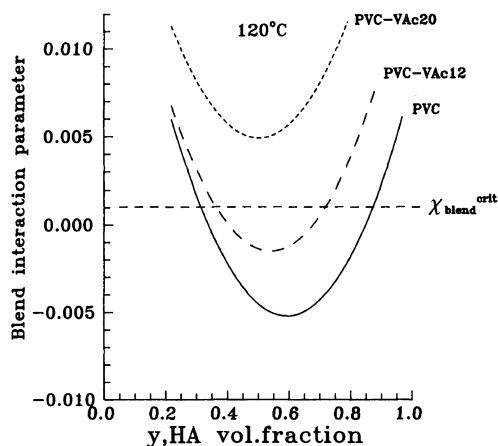
**Table III.** Calculated segmental interaction parameters for PVC-VAc/MHA blends at 100°C and 120°C ( $\chi_{\text{blend}}^{\text{crit}} = 0.001$ )

Segment pairs	$\chi_{ij}$	At 100°C	At 120°C
VAc/HA	$\chi_{AC}$	0.252	0.278
VC/HA	$\chi_{BC}^a$	0.006	0.008
VAc/MA	$\chi_{AD}$	0.205	0.220
VC/MA	$\chi_{BD}^a$	0.023	0.023
VAc/VC	$\chi_{AB}$	0.226	0.233
MA/HA	$\chi_{CD}^a$	0.080	0.080

<sup>a</sup> Values obtained from previous study.<sup>11</sup>



**Figure 5.** Calculated blend interaction parameter of PVC-VAc/MHA 50/50 wt% blends as a function of HA vol. fraction with varying VAc content at 100°C.



**Figure 6.** Calculated blend interaction parameter of PVC-VAc/MHA 50/50 wt% blends as a function of HA vol. fraction with varying VAc content at 120°C.

the miscibility. The  $\chi_{AB}$  value between VAc unit and VC unit was in reasonably good agreement with the result reported by Shiomi *et al.*<sup>3</sup> considering the temperature difference.

The segmental interaction parameters at 120°C were also calculated by using the mean field approach and phase boundary in Figure 4, and listed in Table III. The  $\chi_{CD}$ ,  $\chi_{BC}$ , and  $\chi_{BD}$  values of the previous study at 120°C were also used in obtaining the three other parameters ( $\chi_{CD}=0.080$ ,  $\chi_{BC}=0.008$ ,  $\chi_{BD}=0.023$ ). In comparing the  $\chi_{ij}$ 's values between them, the segmental interaction parameters between VAc unit and other units, *i.e.*,  $\chi_{AB}$ ,  $\chi_{AC}$ , and  $\chi_{AD}$  increased with increasing temperature, but the others were almost constant.

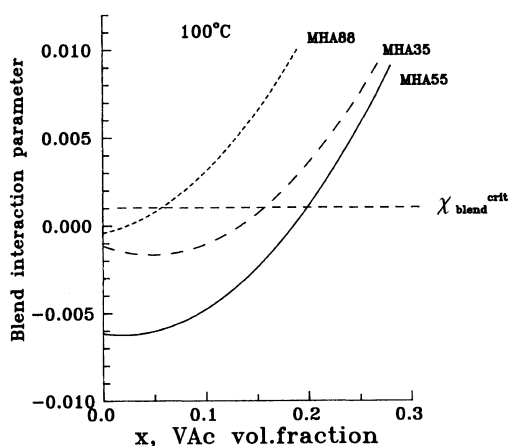
#### Blend Interaction Parameter

Blend interaction parameters,  $\chi_{blend}$  for the 50/50 wt% PVC/MHA and PVC-VAc/MHA copolymer blend system were calculated as a function of MHA copolymer composition and displayed in Figure 5. A concave curve was obtained and the blend had miscibility in the region of  $\chi_{blend} < \chi_{blend}^{crit}$ . The PVC-VAc/MHA blend had a narrower miscibility window than PVC/MHA blend and PVC-VAc copolymer with higher VAc content had less miscibility

with MHA copolymer. The PVC-VAc copolymer shifted the minimum of  $\chi_{blend}$  curve slightly toward high MA content. This was caused by the higher  $\chi_{AC}$  of VAc-HA than  $\chi_{AD}$  of VAc-MA.

As the temperature was increased to 120°C, the blend interaction parameter increased (Figure 6). It was also found that the increment of the blend interaction parameter of PVC-VAc/MHA blend was higher than that of PVC/MHA blend with increasing temperature. This suggested that the segmental interactions between VAc unit and the other units were more sensitive to the temperature rise and, therefore, had more unfavorable effect on the miscibility than the other segmental interactions.

The blend interaction parameters of PVC-VAc/MHA blends at 100°C are plotted as a function of PVC-VAc copolymer composition for three different MHA copolymers (Figure 7). The PVC-VAc/MHA55 blend showed better miscibility and was miscible in broader copolymer composition range than others. It was observed that both the MHA88 and MHA55 copolymer had the lowest  $\chi_{blend}$  value when blended with homo PVC and  $\chi_{blend}$  increased monotonously with increasing VAc



**Figure 7.** Calculated blend interaction parameter of PVC-VAc/MHA 50/50 wt% blends as a function of VAc vol. fraction for three different MHA copolymers at 100°C.

content. But the  $\chi_{\text{blend}}$  curve of MHA35 showed a minimum at about 5% VAc content. This phenomenon can be explained as follows. The VAc unit had an unfavorable segmental interaction with other units in the order of HA > VC > MA. Thus, for the blend of MHA copolymer containing relatively low HA content, the  $\chi_{\text{blend}}$  can be more influenced by the repulsion between VAc unit and VC unit.

### CONCLUSIONS

The PVC-VAc/MHA blend had a miscibility window and exhibited LCST behavior. From the composition-composition plots, segmental interaction parameters between monomer units were calculated by using the mean field theory expression. The miscibility window in PVC/MHA blend system could be

explained as repulsion effect within the MHA copolymer chain. But, for the PVC-VAc/MHA blend system, unfavorable intermolecular interactions of VAc unit with acrylate units had more significant effect on the miscibility than the repulsion of VAc unit with VC unit. Therefore, the miscibility of PVC-VAc/MHA blend was reduced as the VAc content of PVC-VAc increased. Also, the segmental interactions of VAc unit with other units were more sensitive to the temperature rise and had more unfavorable effect on the miscibility.

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