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Miscibility Behavior in Blends of Poly(acrylonitrile-*co*-butadiene) and Chlorinated Poly(vinyl chloride)

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ABSTRACT: The miscibility and phase behavior in 50/50 wt % blends of chlorinated poly(vinyl chloride) (CPVC) and poly(acrylonitrile-*co*-butadiene) (AN–BT) copolymer have been investigated. By utilizing differential scanning calorimetry measurements, the miscibility–immiscibility boundary at 150 °C was determined. It was found that the extent of miscibility of the CPVC/(AN–BT) system becomes larger with increasing chlorine content of CPVC, compared to that of the PVC/(AN–BT) system. The maximum miscibility region was found around 63 wt % Cl in the CPVC blend system. By assuming a random copolymer structure for both components and applying the first-order mean field theory to the experimental results, the respective segmental interaction parameters, χ_{ij}'s, were determined. The theoretical phase boundary is consistent with experimental data. By studying the temperature effect on the phase behavior of this blend, lower critical solution temperature behavior was identified as evidenced by the contraction of miscibility region at 170 °C.

Introduction

The miscibility behavior in polymer–polymer blends has been studied for more than 30 years in part for the purpose of developing new polymer systems with desirable material properties. These efforts to identify new miscible polymer systems are still underway since relatively few polymer blends exhibit thermodynamic miscibility. Miscible systems of blends containing high molecular weight polymers have been identified usually when a favorable specific interaction such as hydrogen bonding, dipole interaction, or ionic interaction exists between two components. As far as the present system is concerned, Prud'homme et al.[1–4] and Paul and co-workers[5,6] have examined the miscibility behavior of blends of chlorinated PVC with aromatic polyesters, polycaprolactone, and poly(alkyl methacrylates). They found that a high chlorine content (48–56 wt % Cl) in the chlorinated polymer and an optimum CH_2/COO ratio in the polyesters and polymethacrylates were required to obtain maximum dipole–dipole interactions which resulted in a negative value for the thermodynamic interaction parameter and hence in miscibility.

According to recently developed theories of polymer mixing such as the equation of state or lattice–fluid theory, the Gibbs free energy of mixing contains three contributions: a combinatorial entropy of mixing, an exchange interaction, and a free-volume effect. For a mixture of high molecular weight materials, the combinatorial entropy term is negligible and a negative exchange interaction is required for a miscible system. However, some polymer blends in which at least one of the components consists of a random copolymer have been found to be miscible for a certain copolymer composition range, even though none of the binary combinations of the corresponding homopolymers is miscible. No specific intermolecular interactions have been identified for these systems. The "miscibility window" arises due to a so-called repulsive interaction between the two different monomer units comprising the copolymer.[7–9] Examples of miscible systems of the type $(A_{1-x}B_x)_n/C_m$ are poly(vinyl chloride)/poly(ethylene-*co*-vinyl acetate),[10] poly(methyl methacrylate)/poly(styrene-*co*-acrylonitrile),[11] and other blend systems containing poly(phenylene oxide) (PPO).[12–14] Copolymer–copolymer systems of the type exemplified by $(A_{1-x}B_x)_n/(C_{1-y}D_y)_m$, blends of poly(butadiene-*co*-styrene)/poly(vinyl chloride-*co*-vinyl acetate) and other copolymer–copolymer blend systems containing sulfonated poly(phenylene oxide) (SPPO), show miscibility for a certain range of copolymer compositions.[15–18] In this case, six segmental interaction parameters which represent the binary combination of the four different monomer units are required to describe the phase behavior of random copolymer–copolymer mixtures. The free energy of mixing is given by

$$\Delta G/RT = (\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2 + \phi_1\phi_2((1-x)(1-y)\chi_{AC} + y(1-y)\chi_{AD} + x(1-y)\chi_{BC} + xy\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD}) \quad (1)$$

in the mean field approximation, where x and y are the copolymer mole compositions and ϕ_1 and ϕ_2 are the volume fractions of the two components. N_1 and N_2 represent the degrees of polymerization of each copolymer, and χ_{ij} are the respective segmental interaction parameters. By utilizing the approach of ten Brinke et al.,[7] one can thus obtain the isothermal phase boundary between two copolymer mixtures if all interaction parameters are determined.

For blends of chlorinated PVC with poly(ethylene-*co*-vinyl acetate) studied by Shiomi et al.,[16] the phase diagram predicted by the mean field approach displays good agreement with the experimental results. Kang, Karasz, and MacKnight used the mean field theory for the phase behavior study of blends of sulfonated poly(phenylene oxide) with other copolymer systems.[17,18] They calculated the phase boundaries of copolymer blends from the independently obtained segmental interaction parameters, χ_{ij}'s. It was found that the experimental results agree well with the prediction of mean field theory.

In our laboratory, a major effort has been made to understand the complex phase behavior of blends containing chlorinated copolymers. A recent study of blends of chlorinated polyethylene (CPE) with different chlorine contents has revealed that a maximum in the miscibility window occurs at a chlorine content of around 50 wt %.[19,20] These systems display upper critical solution temperature (UCST) type behavior for a chlorine content below 50 wt

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Table I
Compositions of Chlorinated PVCs[a]

CPVC Cl, wt %	CPVC T_g, °C	CH_2CHCl mol %[b]	CHClCHCl mol %	$CHClCCl_2$ mol %	CH_2CCl_2 mol %
56.7	85.5	100.0 (0.0)	0.0	0.0	0.0
59.0	91.0	90.0 (10.0)	8.2	0.3	1.5
61.9	103.8	77.4 (22.6)	18.9	0.7	3.0
62.3	107.5	75.3 (24.7)	20.2	1.2	3.3
63.7	113.2	68.3 (31.7)	25.5	2.1	4.1
64.4	121.3	64.8 (35.2)	28.1	2.6	4.5
65.5	138.8	59.0 (41.0)	32.0	3.8	5.2
66.5	143.9	53.1 (46.9)	35.1	6.0	5.8
67.1	146.4	49.4 (50.6)	36.8	7.8	6.0
68.1	157.0	41.1 (58.9)	41.4	11.0	6.5
68.5	162.3	37.8 (62.2)	43.0	12.4	6.8

[a] Reference 16. [b] Values in parentheses represent the combined mole percentages of the three units CHClCHCl, $CHClCCl_2$, and CH_2CCl_2. This combined mole percentage is the variable represented on the x axis in Figures 2 and 6.

% and lower critical solution temperature (LCST) type behavior for a chlorine content above 50 wt %.

The miscibility of poly(vinyl chloride) (PVC) with poly(acrylonitrile-*co*-butadiene) (AN–BT) has been studied extensively:[21–28] Matsuo and co-workers[21] investigated the viscoelastic properties and the morphology of the PVC/(AN–BT) system. Zakrzewski[22] reported that the miscibility window in blends of PVC and the (AN–BT) copolymer occurs at a copolymer composition range between 23 and 45 wt % acrylonitrile composition. Within this range, a one-phase homogeneous structure has been indicated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and electron microscopy. Similar results for the miscible PVC/(AN–BT) system were reported using rheological measurements, wide-angle X-ray analysis, light scattering analysis, and transmission electron microscopy (TEM).[25–27]

In this study, chlorinated PVC (CPVC) is viewed as a random copolymer consisting of CH_2CHCl and CHClCHCl units while PVC is considered as an alternating copolymer. By changing the microstructure and chemical composition of two copolymers, the phase behavior was investigated and interpreted using mean field theory.

Experimental Section

Poly(vinyl chloride) of Geon 103-EP grade (M_w = 209 000 and M_n = 136 000) was obtained from B. F. Goodrich Co. Chlorinated poly(vinyl chloride) was prepared by solution chlorination; the chlorine content was controlled by changing the reaction residence time. The chemical composition of CPVC was determined by elemental analysis (University of Massachusetts Microanalysis Laboratory). Table I lists chlorine weight percent and all CH_2CHCl, CHClCHCl, $CHClCCl_2$, CH_2CCl_2 mol %. All of the poly(acrylonitrile-*co*-butadiene) (AN–BT) (M_w = 180 000) copolymers were obtained from Scientific Polymer Products Inc., except 10 and 16 AN mol % (AN–BT) copolymers, which are from B. F. Goodrich Co. Nine different (AN–BT) copolymer compositions ranging from 10 to 51 AN mol % were used. All molecular weights were determined by GPC and corrected for hydrodynamic volume. CPVC molecular weight measurements indicate essential absence of degradation in the chlorination process.

The blends were prepared by dissolving (AN–BT) and PVC or CPVC in the common solvent, THF; the mixture was stirred for several days and precipitated into a tenfold excess of methanol. The blend ratio of the two polymers was 50/50 by weight. The precipitated samples were washed with fresh methanol several times to remove the remaining THF and then dried at 65 °C for 3 days.

The miscibility behavior of the blends was studied by observing the glass transitions using a Perkin-Elmer DSC-4 differential scanning calorimeter. The T_g's were determined from the locations of the maxima in plots of dC_p/dT versus temperature, where C_p is the heat capacity. The samples were annealed at a specified temperature for 15 min in the DSC and then quenched to a temperature below that of the lower component T_g. The heating rate was 20 °C/min.

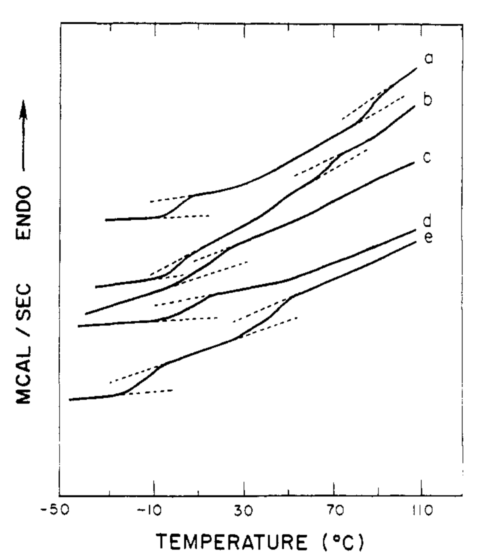

Figure 1. Differential scanning calorimetry thermogram of PVC/(AN–BT) blends: (a) PVC/(51% AN–BT); (b) PVC/(44% AN–BT); (c) PVC/(33% AN–BT); (d) PVC/(27% AN–BT); (e) PVC/(20% AN–BT).

Results and Discussion

Poly(vinyl chloride) has a T_g of 85.5 °C and a chlorine content of 56.7 wt %. Chlorination increases the number of CHCl units and increases the T_g as shown in Table I. For example, CPVC containing 68.1 wt % Cl (CPVC-9) has a T_g of 157 °C, while the T_g of CPVC containing 59 wt % Cl (CPVC-1) is 91 °C. As shown in Table I, CPVC contains CH_2CHCl, CHClCHCl, and also $CHClCCl_2$ and CH_2CCl_2 units depending upon the chlorination level. From ^{13}C NMR results, it has been reported that the presence of CCl_2 units is small compared with other units at lower levels of chlorination.[30] As an approximation, CPVC can be represented as $(A_{1-x}B_x)_n$, where A is the PVC component (CH_2CHCl unit) and B are the components comprising CHClCHCl, $CHClCCl_2$, and CH_2CCl_2 units. Here, x is the mole fraction of the repeat unit B and n is the degree of polymerization. The (AN–BT) copolymer consists of acrylonitrile (AN) and butadiene (BT) units randomly arranged and can be represented as $(C_{1-y}D_y)_m$, where C ≡ BT, D ≡ AN, y is the mole fraction of the repeat unit D, and m is the degree of polymerization. By varying x and y from 0 to 1 independently, the composition of the CPVC/(AN–BT) blend system can be changed.

Figure 1 shows DSC thermograms of PVC/(AN–BT) blends annealed at 150 °C for 15 min; the AN content of the AN–BT copolymer was varied from 20 to 51 mol %. Blends containing an AN content of 27 and 33 mol % show typical miscible behavior as demonstrated by the appearance of a single T_g, while the other systems containing 20, 44, and 51 AN mol % exhibit two T_g's corresponding to those of pure PVC and (AN–BT) copolymers, respectively.

To identify the phase boundary for 50/50 wt % CPVC/(AN–BT) blends, samples containing between 56.7 and 68.5 wt % chlorine and between 10 and 51 mol % acrylonitrile were annealed at 150 °C for 15 min. Figure 2 shows the isothermal miscibility–immiscibility boundary of the CPVC/(AN–BT) system. In this diagram, the x axis represents the mole fraction of CHClCHCl (including

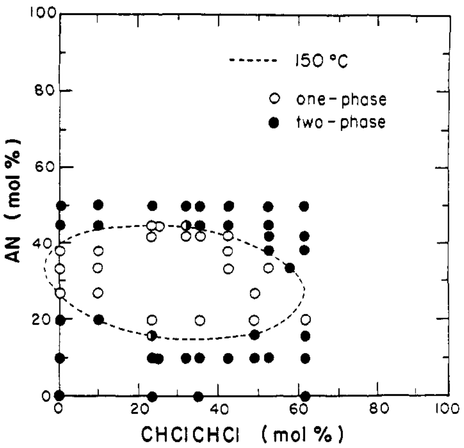

Figure 2. Isothermal miscibility-immiscibility diagram of chlorinated PVC/(AN-BT) blends at 150 °C. The half-filled circles represent equivocal assignments.

Table II
Calculated Interaction Parameters at 150 and 170 °C[a]

segment pairs	χ_{ij} 150 °C	170 °C
$CH_2CHCl/CHClCHCl$	$\chi_{AB} = 0.042$	$\chi_{AB} = 0.026$
$CH_2CHCl/CH_2CHCHCH_2$	$\chi_{AC} = 0.021$	$\chi_{AC} = 0.021$
CH_2CHCl/CH_2CHCN	$\chi_{AD} = 0.080$	$\chi_{AD} = 0.089$
$CHClCHCl/CHCH_2CH_2CH$	$\chi_{BC} = 0.024$	$\chi_{BC} = 0.028$
$CHClCHCl/CH_2CHCN$	$\chi_{BD} = 0.131$	$\chi_{BD} = 0.114$
$CH_2CHCHCH_2/CH_2CHCN$	$\chi_{CD} = 0.183$	$\chi_{CD} = 0.195$
	$\chi_{blend} = 0.001$	

[a] Estimated accuracy of χ_{ij} parameters is ±0.005.

$CHClCCl_2$ and CH_2CCl_2) units, and the y axis represents the mole fraction of acrylonitrile (AN) units. The ordinate represents the phase behavior of blends of PVC with the (AN-BT) copolymer, and a miscible region between 27 and 38 mol % AN can be observed. This is consistent with the result of Zakrzewski.[22] The abscissa displays the fact that blends of polybutadiene with chlorinated PVC of any chlorine content are immiscible. The origin represents a blend of PVC and polybutadiene which is also immiscible. As seen in the diagram, the miscibility window of CPVC/(AN-BT) blends expands until the chlorine content in the CPVC reaches about 63 wt %. At this composition, maximum miscibility occurs for AN content between 17 and 44 mol %, and the miscibility region at this composition is more than twice as large as that of the PVC/(AN-BT) system.

For the CPVC/(AN-BT) system, the increased miscibility can be explained using several factors. The expansion of the miscibility window is predicted by the mean field theory in blends containing random copolymers. Due to the repulsive interaction between the molecular segments in each random copolymer, the miscibility window increases compared with that observed in the PVC/(AN-BT) system. On a molecular level, it may be noted that there exists an induced dipole-dipole interaction between C-Cl in CPVC and C≡N in (AN-BT). With increasing chlorine content in CPVC, the number of dipole interactions between the molecular segments is increased, and this results in the expansion of the miscibility window. When the chlorine content of CPVC reaches around 63 wt % CPVC in the blend, the molar ratio of α-hydrogens of CHCl to the AN of poly(AN-BT) approaches the optimum number for favorable intermolecular interaction, resulting in the maximum miscibility. Above that chlorine content, the presence of CCl_2 units increases and the microstructure of CPVC, which matches that of the (AN-BT) random copolymer at low chlorine content, begins to deviate as the number of CCl_2 units increases. Eventually, less favorable interactions between the highly chlorinated molecules prevent the formation of segmental interactions leading to miscibility, and this leads to the contraction of the miscibility region at high chlorine contents of CPVC.

By utilizing the mean field approach of ten Brinke et al.,[7] the experimental phase behavior of this copolymer-copolymer blend can be analyzed. From eq 1, the overall interaction parameter for the blends, χ_{blend}, can be expressed as a linear combination of the segmental interaction parameters for the $(A_{1-x}B_x)_n/(C_{1-y}D_y)_m$ system:

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

In this expression, the six interaction parameters, χ_{ij}'s, may be of either sign but are typically positive. When χ_{AB} and χ_{CD} are sufficiently large, χ_{blend} can be negative, and miscibility can occur for a certain copolymer composition range. This can be viewed as a repulsive effect between two different covalently bonded segments on a given copolymer chain. In the usual Flory-Huggins representation,[31,32] a critical point occurs at a temperature for which χ_{crit} is equal to CCl_2, where

$$\chi_{blend} = {}^1/_2(m^{-1/2} + n^{-1/2})^2 \quad (3)$$

In the present CPVC/(AN-BT) system, χ_{crit} is 0.001 calculated from the known degrees of polymerization. χ_{AB}, representing the interaction between the CH_2CHCl and CHClCHCl units, was obtained from the experimental data of Shiomi.[16] The remaining χ_{ij}'s were calculated by fitting the experimental miscibility-immiscibility boundary to the mean field equation. The broken line in Figure 2, which represents this boundary, is elliptical in shape as required by the mean field theory. The specific equation for this ellipse is

$$F(x,y) = 0.042x^2 + 0.1827y^2 - 0.0399x - 0.1243y + 0.0491xy + 0.0204 \quad (4)$$

The boundary condition is given by $F(x,y) = \chi_{blend} - \chi_{crit} = 0$. All the constants of the quadratic generalized equations are directly related to the χ_{ij}'s. From the experimentally determined phase boundary (eq 4), the interaction parameters are calculated and are listed in Table II. By utilizing these interaction parameter values, the miscibility region in CPVC/(AN-BT) blends can be reconstructed on the basis of mean field theory (eqs 2 and 3).

χ_{blend} for the CPVC/(AN-BT) systems was calculated for several chlorinated PVC blends and is shown as a function of AN content in Figure 3. CCl_2 units, which are present in highly chlorinated PVC, may render the interaction between acrylonitrile and CHClCHCl less favorable because the number of available α-hydrogens in CPVC is reduced. Therefore, the maximum in the miscibility window occurs around 23 mol % CHClCHCl (63 wt % Cl in CPVC); at higher chlorine contents, the width of the miscibility window decreases, and as shown in Figure 3, the curve indicates a smaller region of miscibility.

The phase behavior of blends is dependent upon the temperature as well as on the composition of the two blend components. Figure 4 shows the phase diagram of PVC/(AN-BT) blends containing 44 mol % (AN-BT). A single glass transition is observed for the whole composition

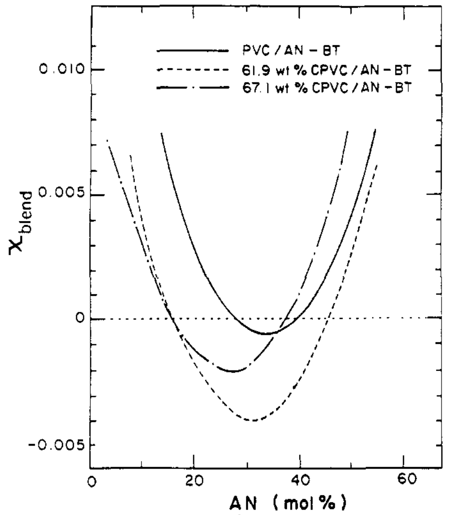

Figure 3. Calculated χ_{blend} of the chlorinated PVC/(AN–BT) system showing the miscibility window as a function of the (AN–BT) system.

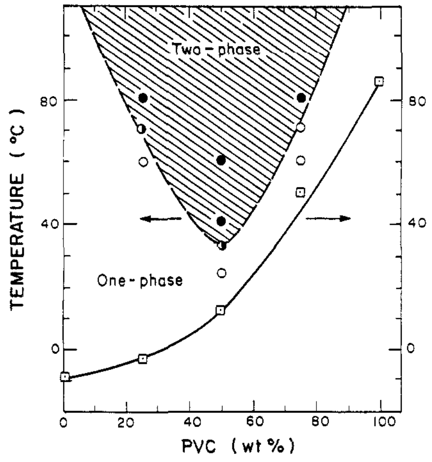

Figure 4. Phase diagram of the PVC/(AN–BT) system. The half-filled circles represent equivocal assignments. The T_g's of the respective blends are also shown.

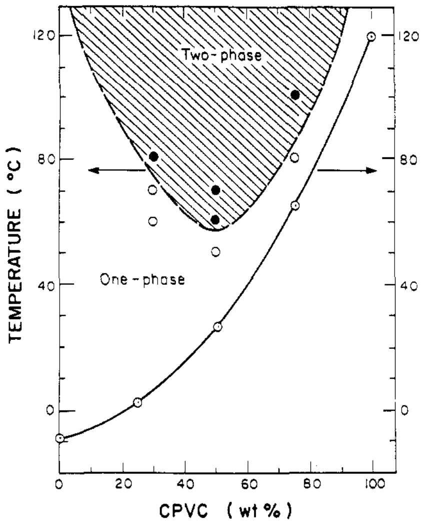

Figure 5. Phase diagram of the 64.2 wt % CPVC/(AN–BT) system. The T_g's of the respective blends are also shown.

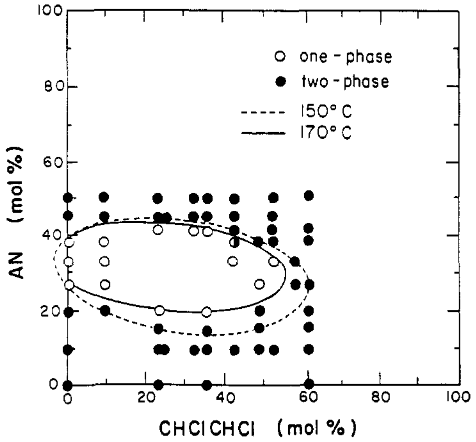

Figure 6. Isothermal miscibility–immiscibility diagram of chlorinated PVC/(AN–BT) blends at 170 °C. The half-filled circles represent equivocal assignments. The miscibility window (dashed line) shown in Figure 2 has been superimposed on this figure to facilitate comparison of the window sizes at 150 and 170 °C.

range. With increasing temperature, the system becomes phase separated and lower critical solution temperature behavior is observed. This result is consistent with the study of Yoon et al.[33] It can be seen that an LCST occurs around 30 °C. Thus, if high temperature was used to remove the solvent during sample preparation, the sample would be phase separated as a result.

To understand the composition dependence of the phase behavior of blends containing copolymers, a phase diagram for 64.2 wt % CPVC/44 mol % (AN–BT) blend was constructed (Figure 5). The same behavior shown in Figure 4 is observed while the LCST occurs around 55 °C, an increase of 20 °C. This demonstrates directly that the LCST can be controlled by changing the chemical composition of blends.

In a system displaying LCST behavior, it is expected that the size of the miscibility region decreases when the temperature is raised. Thus, the miscibility–immiscibility phase diagram of the CPVC/(AN–BT) system at 170 °C is shown as a solid line in Figure 6. When compared to the phase boundary at 150 °C (dashed line), the miscibility region decreases. Some miscible mixtures around the critical boundary at 150 °C become immiscible when the temperature is increased to 170 °C. It can be seen that the decreased miscibility region is somewhat asymmetric and that the region representing components with high chlorine content is affected more by the increased temperature.

By using the geometrical analysis and the mean field approach as described above, the interaction parameters χ_{ij}'s at 170 °C can be calculated by assuming that χ_{AC} at 150 °C is identical to that at 170 °C. χ_{AC}, the interaction parameter between the PVC and polybutadiene components, is least affected as evidenced by the similar miscibility window at 150 and 170 °C. The calculated χ_{ij}'s at 170 °C are shown in Table II. When compared with χ_{ij}'s at 150 °C, the interaction parameter values are almost same, and it can be said that the above assumption is a reasonable one for this calculation.

Conclusion

The CPVC/(AN–BT) blend exhibits a broader miscibility window than the PVC/(AN–BT) blend system; the maximum miscibility window was found at 63 wt % Cl in the CPVC/(AN–BT) blends. By studying the effect of temperature on phase behavior, both systems, PVC/(AN–BT) and CPVC/(AN–BT), were found to show LCST behavior. It was found that the LCST of the CPVC/(AN–BT) system was raised compared with that of the PVC/(AN–BT) system. The mean field approach provides a satisfactory explanation of the phase composition diagram of copolymer–copolymer blends.

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