Miscibility of Poly(vinyl chloride) and Poly(vinyl acetate)

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In a recent communication Coleman and co-workers[1] questioned the applicability of the so-called repulsion model to mixtures of poly(vinyl chloride) (PVC) and random copolymers of ethylene and vinyl acetate (EVA). Evidence was presented that, contrary to common belief, PVC is miscible with poly(vinyl acetate) (PVAc). Here, we present results showing that, at least for the samples we used, PVC and PVAc are immiscible. Furthermore, arguments are given why in many cases the repulsion model should also work for systems involving specific interactions.

Almost a decade ago, a simple mean-field theory (binary interaction model) describing phase behavior in random copolymer and homopolymer blends in terms of the various groups present was introduced.[2–4] For a mixture of a random copolymer consisting of units A and B and a homopolymer consisting of units C, a simple expression for the Gibbs free energy of mixing ΔG was formulated:

$$\Delta G/nkT = \varphi/N_1 \ln \varphi + (1-\varphi)/N_2 \ln (1-\varphi) + \chi_{\mathrm{eff}}\varphi(1-\varphi) \quad (1)$$

where φ is the volume fraction of the random copolymer component 1 in the mixture, N_1 and N_2 are the chain lengths of the random copolymer and the homopolymer, respectively, n is the total number of units in the mixture, and χ_{eff} is given by

$$\chi_{\mathrm{eff}} = x\chi_{\mathrm{AC}} + (1-x)\chi_{\mathrm{BC}} - x(1-x)\chi_{\mathrm{AB}} \quad (2)$$

In this equation, x represents the volume fraction of A units in the random copolymer. The last term represents the dilution effect on the number of A–B interactions and is in certain cases responsible for miscibility. This kind of situation, corresponding to $\chi_{\mathrm{AB}} > 0$, is usually referred to as the repulsion effect. In writing down these equations, it is important to realize that all the units are chosen in such a way that they have equal molar volume, which for specific applications implies that the basic unit (or reference volume) should be pointed out explicitly.

Paul and Barton[4] used an alternative expression in terms of interaction densities. Although, this has certain advantages, we prefer eq 2, together with an explicit statement about the basic unit size, since the χ parameters occurring in eq 2 are really exchange *free-energy* parameters rather than exchange interaction parameters. This is particularly clear when blends are considered in which directionally specific interactions like hydrogen bonding are present. Many years ago[5] it was demonstrated that very often these types of interactions lead to a positive χ parameter. Because of the directional specific nature of the interaction, the exchange interaction between the unlike monomers (groups) will be positive for a majority of relative orientations and negative for only a few. In that case, the χ parameter consists of an entropic part χ_s and an enthalpic part χ_h. They are of opposite sign ($\chi_s > 0$, $\chi_h < 0$) and of comparable magnitude. At sufficiently high temperatures (not necessarily very high), the entropic contribution dominates and χ becomes positive. Here the fact that the χ parameter is a *free-energy* parameter rather than an interaction parameter is essential. The situation becomes even more complex, but conceptually similar, if self-association between the polymers is also possible.

Table I
Sample Characterization

sample	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	T_g, °C
PVC[a]	60.0	33.0	80.2
PVAc[b]	190.0	75.0	37.1

[a] Lucovyl/RB8010 (Péchiney et St. Gobain). [b] Mowilith-50 (Hoechst).

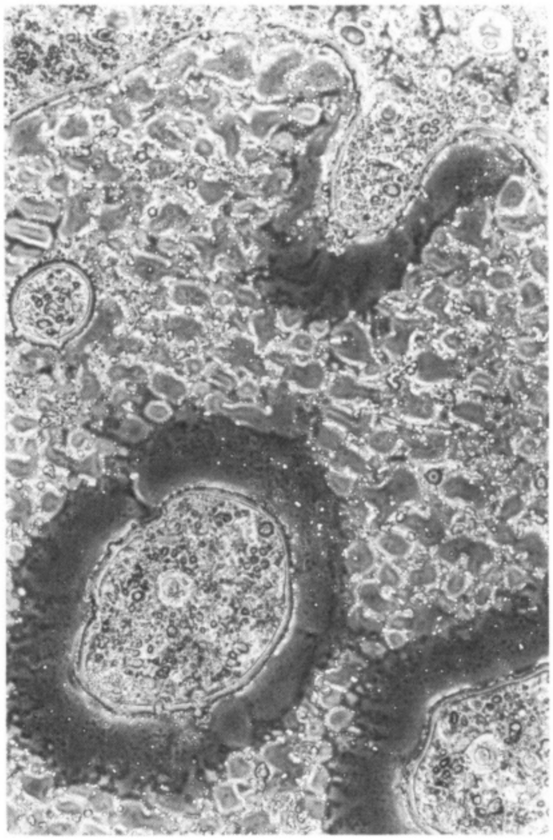

Figure 1. Phase-separated PVC/PVAc/MEK blend observed by phase-contrast microscopy during evaporation of the solvent MEK.

Another point is that the binary interaction model is based on the assumption of random mixing, which will become less accurate if very strong specific interactions like hydrogen bonding are present. The application of the model to these kinds of systems will therefore obviously introduce some error; however, the concept remains very useful, as demonstrated convincingly by the extensive research on polyamide blends by Ellis.[6]

A possible example of specific interactions and a positive χ parameter is given by blends of poly(vinyl chloride) and poly(vinyl acetate). Most research efforts show that PVC is miscible with random copolymers of ethylene and vinyl acetate for a window of vinyl acetate fractions only.[7,8] In particular, PVC appeared to be immiscible with poly(vinyl acetate). The application of the binary interaction model (eq 1) to these systems led to a positive value for the χ parameter between all the groups involved, including vinyl chloride and vinyl acetate. The driving force for miscibility turned out to be the repulsion effect, i.e., the large positive value for the χ parameter between ethylene and vinyl acetate.

As already mentioned, these findings were questioned by Coleman and co-workers[1] on the basis of results obtained by film casting of PVC and PVAc from methyl

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ethyl ketone (MEK), which apparently led to a homogeneous system, and hence a negative value for the χ parameter between vinyl chloride and vinyl acetate. As a consequence, they also questioned the applicability of the repulsion idea to blends of PVC and EVA. Confronted with this controversy we decided to repeat the measurements of Coleman and co-workers[1] and to perform some additional experiments as well.

Blends of PVC and PVAc (Table I presents the relevant data of these polymers) were obtained in two different ways. The first procedure was the same as used by Coleman and co-workers and consists of solvent casting from methyl ethyl ketone. It involves slowly evaporating MEK over a period of 3 days in a closed Petri dish at room temperature. The samples are then heated to 70 °C for 1 day under vacuum to remove the last traces of the solvent. In most previous studies THF, a solvent that associates preferentially with PVC, was used. The phase-separated nature of the blends that result from this solvent was attributed by Coleman and co-workers to this preferential solvation (a $\Delta\chi$ effect). In contrast to their results, we always found a phase-separated system with two different T_g's. In addition, ternary blends of PVC, PVAc, and MEK were studied by phase-contrast microscopy during evaporation of the solvent. Figure 1 shows a characteristic result demonstrating the phase-separated morphology after evaporation of a large part of the solvent.

In another attempt, blends of PVC and PVAc were prepared by freeze-drying a dioxane solution of these polymers. The first DSC scan showed a single endothermic peak, probably either due to evaporation of the residual solvent or alternatively due to enthalpy relaxations. In any case, the second DSC scan invariably showed two glass transitions, again confirming the immiscibility of PVC and PVAc.

In our mind, there is no doubt that the given polymers are immiscible. However, since they first published their results, Coleman and co-workers have repeated their measurements with different samples (higher molecular weights) and confirmed the original conclusions. Hence, although we believe PVAc and PVC to be immiscible, more work seems to be necessary to fully resolve the phase behavior of these two polymers.

References and Notes

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