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William MacKnight, *University of Massachusetts Amherst*

Ronald Koningsveld

Karel Sole

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Communications to the Editor

Thermodynamic Aging of Immiscible Polymer Blends

Ronald Koningsveld,^{*,†} Karel Šolc,[‡] and William J. MacKnight[†]

Polymer Science & Engineering, University of Massachusetts, Amherst, Massachusetts 01003, and Michigan Molecular Institute, Midland, Michigan 48640-2696

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Many discussions of miscibility in polymer blends are based on the Gibbs free energy for a strictly-binary system, usually in the approximation of Flory,¹ Huggins,^{2,3} and Staverman and Van Santen,^{4,5} which we call the FHS model. We find, by sample calculations described below, that the presence of polydispersity in one or both constituents of a blend results in significant mutual solubility under conditions where a comparable strictly-binary blend would not show any detectable miscibility.

This finding has an important practical consequence for the blending of supposedly immiscible polymers. Normally the blending process initially produces a more or less finely dispersed two-phase system in which the two phases initially consist of the two unmixed polydisperse constituents. In the course of time, interdiffusion will occur as the system strives for the thermodynamic equilibrium state in which mutual solubility reigns to some degree. The diffusion process may be slow, but it cannot be stopped unless special measures are taken. Thus, blends must be expected to be subject to such thermodynamic aging, a phenomenon differing in kind from the more commonly known chemical and physical aging processes. Vitrification of one or both phases will halt thermodynamic aging, but reprocessing of the blend will trigger further interdiffusion. Cross-linking probably provides the most effective means of preventing such aging, because a network deswells upon addition of free chains and thus will tend to expel the other constituent.

The situation described above for quasi-binary systems is shown schematically in Figure 1 and has been fully discussed in previous works.⁶⁻¹⁰ The cloud-point curve (CPC) is the envelope of the miscibility gap and does not straightforwardly represent coexisting phases as it does in the strictly-binary case. Each cloud-point bulk phase coexists with an incipient phase, the polymer compositions in which differ from the initial molar mass distributions (MMD) in the bulk polymers. The shadow curve, which represents those incipient phases conjugate to the CPC,^{7,8} is in fact a projection onto the quasi-binary plane $T(\phi_2)$ of a curve lying outside that plane. If a system like ϕ_{2b} is brought into the miscibility gap at T_b and allowed to equilibrate, the two phases a and b both have MMD's differing from those of the initial polymers but their overall compositions may also be projected onto plane $T(\phi_2)$ and

Figure 1. Typical quasi-binary phase diagram for a blend containing two polydisperse polymers P_1 and P_2 , showing a miscibility gap (schematic). Heavy curves: drawn, cloud-point curve; dash-dot, shadow curve. Light curves: drawn, spinodal; dashed, projected coexistence curves. Horizontal dashed lines terminated by filled circles: projected tie lines. Coexisting phases at T_b and overall composition ϕ_{2b} ; a and b. Critical point: open circle at C. A and B do not represent coexisting phases.

connected by projected tie lines. Thus we obtain coexistence curves indicating the overall compositions of the two phases for a given overall composition ϕ_{2b} of the blend. The liquid-liquid critical point does not occur at the extreme of the CPC, unless the ratios $\xi_w (=m_z/m_w)$, the quotient of z - and weight-average chain lengths of the two polymers, are the same; then the slope of the CPC at the critical point is zero.¹¹⁻¹⁴

Quasi-binary phase diagrams for polymer blends, based on the Flory-Huggins-Staverman (FHS) model, may be computed for chosen MMD's.^{13,14} In this paper we represent the distributions in 1 and 2 each by a binary mixture of homologues differing in chain length, which is known already to suffice to bring out the essentials of phase relations in multicomponent blends.^{7,15} We fix the weight-average values m_{w1} and m_{w2} to 1000 and the weight-to number-average ratios ξ_n to 2 and vary the values of ξ_w .

Figure 2 shows a quasi-binary phase diagram for a FHS blend, symmetrical in m_w , ξ_n , and ξ_w . The most striking feature is that the cloud-point curve indicates negligible mutual solubility at $\chi \geq 0.005$. It is also seen, however, that the CPC is useless as a measure of mutual solubility unless the system is strictly binary. In the multicomponent blend the shadow curve indicates a marked mutual solubility which obtains up to high values of χ .

* Address for correspondence: Waldfeuchtstraat 13, 6132 HH Sittard, The Netherlands.

[†] University of Massachusetts.

[‡] Michigan Molecular Institute.

Figure 2. Quasi-binary phase diagram calculated for symmetrical polymer blends: $m_{w1} = m_{w2} = 1000$. Curve 1: strictly-binary mixture. Curve 2: $\xi_{n1} = \xi_{n2} = 2$; $\xi_{w1} = \xi_{w2} = 1.5$. Chain lengths in each constituent: 293 and 1707 (equal weight). Further definitions are in the caption to Figure 1. Coexistence curves shown for overall blend compositions $\phi_2 = 0.15$ and 0.4 .

The location of the shadow curve already suggests appreciable mutual solubility, but coexistence curves are needed to judge whether fully phase-separated blends should be expected to exhibit a similar phenomenon. Figure 2 shows that such is the case; note that, for example, a blend containing 40% of polymer 2 will separate in two phases, one rich in 2 and the other rich in 1 but with each containing a sizable amount of the other constituent. There is no true immiscibility though the occurrence of such would be concluded on the basis of a measurement of the CPC. The same conclusion holds true for other bulk compositions; an example is given for $\phi_2 = 0.15$. If we make the blend asymmetric with respect to m_w , retaining the symmetry in ξ_w and ξ_n , we obtain the diagram of Figure 3. It is seen that quite analogous behavior must be expected, and, compared with blends, symmetrical in m_w , even larger ranges of miscibility may be expected to occur in mixtures rich in the constituent with the larger m_w . In accordance with earlier results,¹⁶ the present calculations indicate that the phase separation is accompanied by effective fractionation. It is the lower molar mass fraction of constituent 1 that goes into the phase rich in 2 and vice versa, whereas the higher fractions stay with the majority of their own kind.

Analogous conclusions apply to asymmetric systems, other MMD's, and non-FHS behavior ($\chi = \chi(\phi)$).¹⁴ We might add that the outlined approach includes the possibility of the determination of the temperature and concentration dependence of the interaction function from experimental CPC's provided the two MMD's are known.

Figure 3. Quasi-binary phase diagram calculated for an asymmetric blend: $m_{w1} = 1000$, $m_{w2} = 5000$, $\xi_{n1} = \xi_{n2} = 2$, $\xi_{w1} = \xi_{w2} = 2$. MMD in 1st constituent: $w_1 = 0.7236$, $m_1 = 382$, $w_2 = 0.2764$, $m_2 = 2618$. MMD in 2nd constituent: $w_1 = 0.7236$, $m_1 = 1910$, $w_2 = 0.2764$, $m_2 = 13\,090$. Coexistence curves shown for $\phi_2 = 0.1$ and 0.5 .

Apart from the phenomena described above, which we refer to as thermodynamic aging of the first kind, a second type may also be important. Less extremely immiscible blends may age by another thermodynamic mechanism even if they are strictly binary. Such blends may arise when the two-phase region originates from the coalescence of a lower-critical two-phase area with an upper-critical miscibility gap. The two two-phase areas may merge by coalescence of their extrema.^{17,18} However, in most practical cases the interaction parameter depends on concentration, and the merging process may then occur sideways and pass through a complex pattern of metastable equilibria.¹⁹ Such metastable states differ very little in free energy from the stable situation, and it is certainly conceivable that they arise in blend preparation, to be turned into more stable states during further processing. This second type of thermodynamic aging can occur in strictly-binary as well as quasi-binary blends.²⁰

There is a major difference between the two types of thermodynamic aging. In the first kind, time works toward better dissolution, whereas the second type is characterized by the opposite behavior. The possible metastable and unstable states the system may get caught up in are inside the stable envelope and transformation into a more stable state will decrease mutual solubility.

We are not aware of any direct evidence for the features described in this paper. An experimental approach is conceivable in which blends are subjected to periods of annealing between successive measurement of the two glass transition temperatures (T_g), for instance, by DSC. Thermodynamic aging of the first kind, if detectable in this fashion, should then be accompanied by a shift of one or both T_g 's toward each other.

It would seem to be worthwhile to consider thermodynamic aging as a possible cause when stability problems

are met in blend processing or reprocessing. Nonequilibrium states do not need to be expected on thermodynamic grounds when strictly-binary blends are prepared. When blends showing some mutual solubility are processed and irreproducible physical behavior is found, one might consider the possible existence of metastable states. The latter may arise in strictly-binary and quasi-binary blends alike when the pair-interaction function depends on concentration.

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References and Notes

- (1) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660; **1942**, *10*, 51; **1944**, *12*, 425.
- (2) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.
- (3) Huggins, M. L. *Ann. N.Y. Acad. Sci.* **1942**, *43*, 1.
- (4) Staverman, A. J.; Van Santen, J. M. *Recl. Trav. Chim. Pays-Bas* **1941**, *60*, 76.
- (5) Staverman, A. J. *Recl. Trav. Chim. Pays-Bas* **1941**, *60*, 640.
- (6) Tompa, H. *Polymer Solutions*; Butterworths: London, 1956.
- (7) Koningsveld, R.; Staverman, A. J. *Kolloid Z.* **1966**, *210*, 151; **1967**, *220*, 31.
- (8) Koningsveld, R. *Adv. Colloid Interface Sci.* **1968**, *2*, 151.
- (9) Šolc, K. *Macromolecules* **1975**, *8*, 819.
- (10) Šolc, K. *Macromolecules* **1977**, *10*, 1101.
- (11) Koningsveld, R. *Discuss. Faraday Soc.* **1970**, No. 49, 144.
- (12) Koningsveld, R.; Chermin, H. A. G.; Gordon, M. *Proc. R. Soc. London, A* **1970**, *319*, 331.
- (13) Koningsveld, R.; Kleintjens, L. A.; Schoffeleers, H. M. *Pure Appl. Chem.* **1974**, *39*, 1.
- (14) Šolc, K.; Koningsveld, R., in preparation.
- (15) Gordon, M.; Irvine, P.; Kennedy, J. W. *J. Polym. Sci., Polym. Symp.* **1977**, *61*, 199.
- (16) Beaucage, G.; Stein, R. S.; Koningsveld, R. *Macromolecules*, **1993**, *26*, 1603.
- (17) Ten Brinke, G.; Zacharius, S. L.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 381.
- (18) Šolc, K.; Stockmayer, W. H.; Lipson, J. E. G.; Koningsveld, R. *Multiphase Macromolecular Systems*; Colbertson, B. M., Ed.; Plenum: New York, 1989; p 5.
- (19) Šolc, K.; Koningsveld, R. *J. Phys. Chem.* **1992**, *96*, 4056.
- (20) Vanhee, S.; Koningsveld, R.; Berghmans, H.; Šolc, K., to be published.