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Prediction of Miscibility Windows for Poly(4-vinylphenol) Blends with Methacrylate Copolymers

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In this paper we report the results of a set of experiments designed to test another facet of the predictive potential of the association model we have developed and used to calculate miscibility windows and maps for hydrogen-bonded polymer blends.[1] In previous studies we employed copolymers that were derived from two monomers, only one of which contained a hydrogen-bonding functional group or single "specific interaction site", e.g., 4-vinylphenol, vinyl acetate, ethyl methacrylate, etc., and the other which may be viewed as an "inert diluent", e.g., styrene, ethylene, butadiene, etc. (i.e., a monomer that does not contain a site capable of forming a strong specific interaction). Such copolymers include styrene-*co*-vinylphenol, styrene-*co*-methyl acrylate, ethylene-*co*-methyl methacrylate (EMMA), etc.

Naturally, there are numerous copolymers, many of industrial significance, that do not fall under this classification. Random copolymers synthesized from two, three, or more different (meth)acrylate monomers, for example, are commonplace in the surface coatings industry, where factors such as the glass transition temperature, water sensitivity, etc., may be optimized by judicious selection of the number and concentration of the (meth)acrylate comonomers. A question that we have been asked repeatedly is, can we use our methodology to predict miscibility windows and maps for polymer blends involving such copolymers? This turns out to be a relatively straightforward task if one accepts the basic underlying premise of our model, that the "physical" may be separated from the "chemical" forces. This permits us to view the problem in the following manner.[1] Consider, for example, poly(*n*-hexyl methacrylate) (PHMA). As we have described previously (see Reference 1, Chapter 7), for the purposes of our model, PHMA is entirely equivalent to a random EMMA copolymer containing 71.4 mol % (41.2 wt %) ethylene. Their solubility parameters are identical, and this approach is sound as long as the specific interaction site (in this case the carbonyl group) remains chemically the same and steric factors are not significantly altered. In a similar manner, we can conveniently express any copolymer composed of many different methacrylates (with or without additional ethylene) in terms of an equivalent EMMA copolymer.

Blends of poly(4-vinylphenol) (PVPh) and atactic poly(methyl methacrylate) (PMMA) form amorphous single-phase materials[1] over the entire composition range and at all accessible temperatures from below ambient to the onset of significant degradation ($\approx$220 °C). In marked constrast, analogous PVPh blends with PHMA are immiscible at all temperatures and form two-phase materials over a wide range of blend compositions.[1] A detailed description of phase diagrams, miscibility windows, and maps for these and other hydrogen-bonded polymer blends, and the computer programs required to calculate them, is included in our recent book to which the interested reader is referred.[1] A theoretical miscibility window for PVPh–EMMA blends at 25 °C is included in this work (Figure 7.55) and was determined together with the values of the molar volumes, non-hydrogen-bonded solubility parameters, equilibrium constants, and enthalpies of hydrogen-bond formation employed.

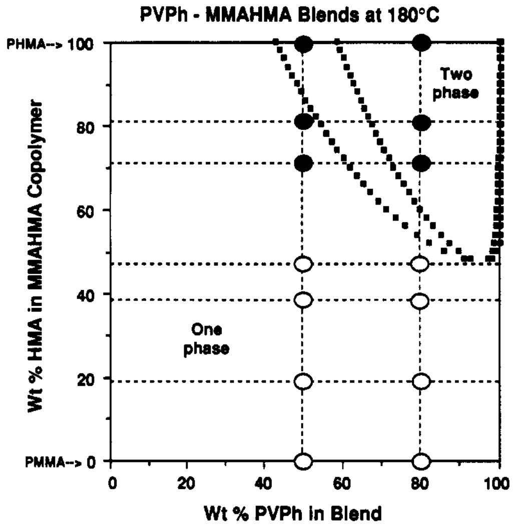

Figure 1. Theoretical miscibility window for PVPh–MMAHMA blends at 180 °C.

Using the principles outlined above, it is a straightforward task to modify our computer program to permit the direct calculation of miscibility windows for blends involving methyl methacrylate-*co*-*n*-hexyl methacrylate (MMAHMA) copolymers and the like. For more complicated terpolymers, etc., it will probably still be more convenient to transform them to their equivalent EMMA (or another appropriate analog). Figure 1 shows the miscibility window calculated for PVPh–MMAHMA blends at 180 °C (above the T_gs of both pure materials), and we see that MMAHMA copolymers containing <48% HMA are predicted to be miscible.

To experimentally test this predicted miscibility window, we performed both infrared and thermal analyses on solution-cast blends prepared from the PVPh and MMAHMA polymers listed in Table I. These MMAHMA copolymers were synthesized using free-radical solution polymerization and characterized using conventional size-exclusion chromatography, ^{1}H NMR spectroscopy, and thermal analysis. Figure 2 shows infrared spectra in the carbonyl stretching region from 1650 to 1800 cm^{-1} of pure MMAHMA[81] (denoted A) and 80:20 wt % PVPh blends with MMAHMA copolymers of varying copolymer composition, all recorded at 180 °C. The band at approximately 1733 cm^{-1} is assigned to "free" (non-hydrogen-bonded) carbonyl groups. Fortunately, the frequency maxima of the carbonyl stretching bands of the MMA and HMA segments are within 1 cm^{-1} of one another, resulting in a single band. The significant contribution from a band at about 1710 cm^{-1} in the three top spectra (D–F) is attributed to the carbonyl stretching band of the carbonyl groups that are hydrogen bonded to PVPh hydroxyl groups (i.e., –O—H···O═C–) and indicates qualitatively that significant molecular mixing has occurred in these blends, but this does not prove that these mixtures are single phase. Equivalently, the trivial contribution

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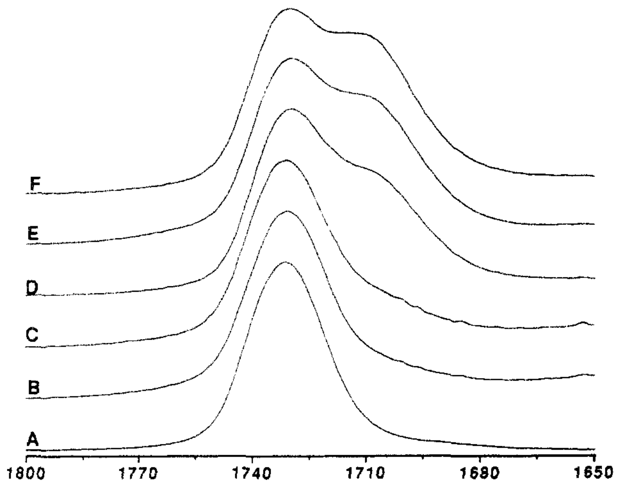

Figure 2. FTIR spectra recorded at 180 °C in the carbonyl stretching region for (A) pure MMAHMA[81] and 80:20 wt % PVPh blends with (B) MMAHMA[81], (C) [MMAHMA[71], (D) MMAHMA[48], (E) MMAHMA[38], and (F) MMAHMA-[20].

Table I. Polymers Employed

polymer	composition (wt %) MMA	composition (wt %) HMA	≡EMMA wt % Ethylene	M_n (GPC)	PDI (GPC)	T_g (°C) (DSC)
MMAHMA[20]	80.2	19.8	8.1	12 000	2.3	84
MMAHMA[38]	62.0	38.0	15.7	15 000	2.5	67
MMAHMA[48]	52.3	47.7	19.6	14 000	2.7	57
MMAHMA[71]	29.2	70.8	29.2	11 000	3.8	31
MMAHMA[81]	19.0	81.0	33.4	11 000	3.2	22
PHMA	0	100	41.2	22 000	3.0	−5
PVPh				17 000	2.0	170

Table II. Curve-Fitting Results for 80:20 wt % PVPh–MMAHMA Blends

80:20 PVPh–MMAHMA blends (wt % HMA)	free C═O band ν (cm^{-1})	free C═O band $w_{1/2}$ (cm^{-1})	free C═O band area	HB C═O band ν (cm^{-1})	HB C═O band $w_{1/2}$ (cm^{-1})	HB C═O band area	$f_F^{C=O}$ [b]
19.8	1733	20	2.05	1710	33	3.71	0.55
38.0	1733	20	1.13	1710	34	2.13	0.56
47.7	1733	20	0.88	1710	34	1.73	0.57
70.8	1733	21	3.13	1710[a]	34[a]	1.76	0.27
81.0	1733	21	2.90	1710[a]	34[a]	1.13	0.20

[a] Fixed parameters. [b] Absorptivity ratio = 1.5.[1]

Table III. Glass Transition Temperatures of PVPh–MMAHMA Blends

50:50 PVPh–MMAHMA blends (wt % HMA)	T_g (DSC)	50:50 PVPh–MMAHMA blends (wt % HMA)	T_g (DSC)
19.8	138	70.8	40, 170
38.0	121	81.0	25, 170
47.7	114		

from the band at 1710 cm^{-1} in the spectra (B and C) of the PVPh blends with MMAHMA[81] and MMAHMA[71] reveals only a scant fraction of hydrogen-bonded carbonyl groups and strongly *suggests*, but again does not prove, phase separation. To determine from infrared data whether or not a particular blend sample exists in a single phase, we compare the experimentally observed fraction of free carbonyl groups, $f_F^{C=O}$, to that calculated theoretically for a *miscible* blend using the stoichiometric equations and the equilibrium constants and enthalpies of hydrogen-bond formation previously reported.[1] The infrared spectroscopic method used to obtain $f_F^{C=O}$ has been presented many times,[1] and we will simply summarize the results in Table II. Theoretical values of $f_F^{C=O}$ for all the single-phase 80:20 PVPh–MMAHMA blends at 180 °C lie between 0.55 and 0.57. Accordingly, we can confidently conclude that PMMA and the three MMAHMA copolymers containing 20, 38, and 48 wt % HMA are single-phase materials, as the experimental values of $f_F^{C=O}$ are in excellent agreement with prediction. Conversely, PHMA and those MMAHMA copolymers containing 71 and 81 wt % HMA are not single phase. These results agree very well with the theoretically predicted miscibility window (Figure 1).

Table III lists the experimentally determined (by differential scanning calorimetry) glass transition temperatures (T_g) of 50:50 wt % PVPh blends with various MMAHMA copolymers. Single intermediate T_gs are observed for the three MMAHMA copolymers containing 20, 38, and 48 wt % HMA, indicating single-phase materials. Conversely, two distinct T_gs are observed in the case of the MMAHMA copolymers containing 71 and 81 wt % HMA, indicating two phases. Copolymers of these compositions lie just outside the theoretical binodal. However, polydispersity tends to broaden the binodal composition range, and since we are dealing with rather wide polydispersities (Table I), the agreement between theory and experiment appears satisfactory.

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References and Notes

(1) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing, Inc.: Lancaster, PA, 1991.