

## Examination of Some Miscible Polymer Blends for LCST Behavior

Over the last several years, a few dozen examples of miscible polymer-polymer blends have been discovered.<sup>1</sup> Typical studies employ the glass transition behavior of such mixtures as the primary evidence for miscibility. However, several points of view suggest that miscible polymer blends are likely to have a lower critical solution temperature, LCST; and, clearly, experimental determination of the attending phase boundary or cloud point curve would yield useful thermodynamic information about these systems. In a recent paper<sup>2</sup> we reported on five different blend systems that exhibited LCST behavior, and this more than doubled the number of blends in which such behavior had been reported by that date. LCSTs have been observed in at least two other cases<sup>3,4</sup> since that time. It was our conclusion that LCST behavior was not more commonly known in miscible polymer blends because most investigations had not specifically sought to observe this phenomenon or because the LCST occurred at too high a temperature to be observed. Based on this premise, we decided to examine a number of blend systems known to be miscible for LCST behavior, and the purpose of this note is to report the findings of this limited investigation. The polymer samples used in this study are described in Table I. Each blend was prepared by casting from an appropriate solvent. For initial screening, blends containing 25%, 50%, and 75% of each component by weight were prepared and heated to the maximum practical temperature in search of any evidence of phase separation using a simple visual technique described earlier.<sup>2</sup>

Nitrocellulose has been reported to be miscible with poly(vinyl acetate) (PVAc)<sup>5</sup> and with poly- $\epsilon$ -caprolactone (PCL).<sup>6</sup> Blends of nitrocellulose with both of these polymers were cast from MEK solutions. These blends were heated to 220–250°C without any evidence of a cloud point for either nitrocellulose grade described in Table I. Higher temperatures could not be employed because of the severe thermally induced discoloration of the nitrocellulose.

Poly- $\epsilon$ -caprolactone has been reported to be miscible with polyepichlorohydrin<sup>6</sup> and with poly(vinyl chloride) (PVC).<sup>7</sup> Blends of the former pair were cast from chloroform solutions and were heated to 350–360°C without any evidence of phase separation. Rapid heating techniques described earlier<sup>2</sup> made it possible to circumvent any thermal instability of these polymers for the brief period required for phase separation observations. However, the thermal stability problems with PVC are more severe and well known. For all blends involving this polymer, we added about 10% based on PVC content of the stabilizer Vanstay 6053. This, combined with brief thermal exposures, allowed us to search for phase separation up to about 310°C in blends containing PVC. PVC-PCL blends failed to show any evidence of a cloud point up to this temperature limit.

PVC is also known to be miscible with a variety of ethylene-vinyl acetate copolymers (EVA) and terpolymers where the third monomer is SO<sub>2</sub>, CO, and others.<sup>1,8–11</sup> Some of the latter are sold as polymeric plasticizers for PVC.<sup>1</sup> Bair et al.<sup>10,11</sup> have given extensive reports on blends of PVC and the commercial terpolymer Elvaloy 741 described in Table I. Blends of this polymer with PVC were

TABLE I  
Polymer Samples

Polymer	Source	Description
Poly(vinyl chloride)	Union Carbide	low MW suspension resin designated as QYSJ-5
Nitrocellulose	Hercules	two grades were used: 1/2 sec and 5/6 sec
Poly-( $\epsilon$ -caprolactone)	Union Carbide	PCL-700, $\bar{M}_w = 40,000$
Polyepichlorohydrin	B. F. Goodrich	Hydrin 100
Poly(vinyl acetate)	Union Carbide	medium MW product designated as AYAF
Elvaloy 741	du Pont <sup>a</sup>	polymeric PVC plasticizer, ethylene-based terpolymer, other monomers reported to be vinyl acetate and carbon monoxide <sup>11</sup> ; $\bar{M}_w \sim 250,000$
EVA (E13044-135-1)	du Pont <sup>a</sup>	ethylene/vinyl acetate copolymer containing 63% VA; $\bar{M}_w \sim 125,000$ , $\bar{M}_n \sim 15,000$

<sup>a</sup> Courtesy of C. F. Hammer.

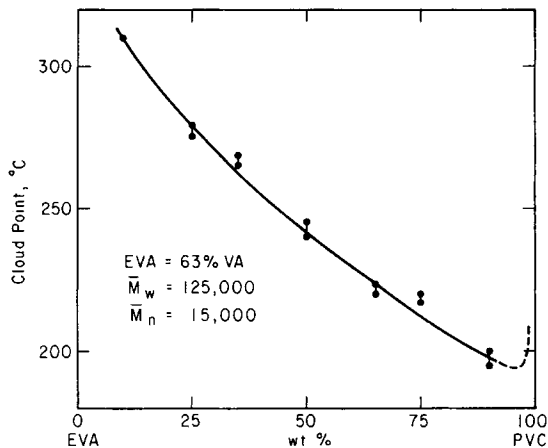


Fig. 1. Cloud point curve for PVC-EVA blends. Mixture contains about 10% stabilizer based on PVC.

cast from MEK and heated to 310°C without any evidence of a cloud point. Since polymeric plasticizers are often used in conjunction with lower molecular weight plasticizers and because such ternary mixtures can have lower cloud points than simple binary blends, we prepared blends of PVC and Elvaloy 741 which in addition contained 25% dioctyl phthalate (DOP). However, no evidence of a cloud point was found. Likewise, addition of 25% DOP to PVC-PCL blends failed to induce a cloud point.

Blends of PVC and the EVA copolymer described in Table I cast from MEK did, however, show a distinct phase separation on heating. Additional blend compositions were prepared and tested, and the results are shown in Figure 1. The duplicate points at each composition provide some insight into the reproducibility of these simple observations. An interesting feature of this cloud point curve is its failure to turn upward as the PVC axis is approached within the composition range examined. The dotted portion of the curve drawn illustrates what might be expected on theoretical grounds. It should be recalled that these blends contain an appreciable amount of stabilizer, but it is impossible to learn how the presence of this component affects the cloud point curve since heating to these temperatures would not be possible without it. We did, however, examine a mixture of PVC and stabilizer without any EVA and found no cloud point up to 310°C to assure ourselves that the observed phase separation was primarily between the PVC and EVA components.

Recently, we have demonstrated<sup>4</sup> that the value of the LCST increases as the strength of interaction between the two polymers increases, i.e., as the heat of mixing becomes more exothermic. Thus, the value of the cloud point, or preferably the LCST, may be used as a quantitative guide to the degree of miscibility or interaction in a blend. This might have practical utility for comparing, say, one polymeric plasticizer with another. We speculate that many of the other blends for which phase separation was not observed may in fact have LCSTs beyond the temperatures at which we were able to heat them because of practical issues of chemical, thermal stability of their components. This would indicate that quite strong interactions are operative in these systems. For example, on this basis we might conclude that Elvaloy 741 has a stronger interaction or a more exothermic heat of mixing with PVC than does the EVA copolymer.

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