artificial weathering.[18] The homopolymer layer in the PTFE grafts showed a high stability similar to that in the PE grafts.

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Notes

A New Technique for Determining Polymer–Polymer Miscibility

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Two-component polymer blends have long been attracting considerable interest both because of their commercial utility and their scientific importance. From either viewpoint, the phase behavior of these systems is of direct significance, considering that partial or complete solubility usually gives rise to improved properties,[1-6] and systems exhibiting high solubility are likely to provide valuable clues about the interactions between unlike macromolecules. Therefore, it is interesting to know to what extent two polymers are mutually soluble; that is, at what composition does phase separation occur. Upon correlating this with the structure, two-component systems with specific properties can be designed with greater facility, and more data will be available for testing and improving the theory[7,8] of phase behavior for polymer–polymer systems.

There are several techniques for determining the presence of two phases (e.g., glass transition temperature, microscopy, scattering methods, ternary solution methods)[7-9] but few methods for determining the extent of the miscibility of one polymer in another, particularly when the degree of miscibility is very low and the molecular weights are high. The technique we present here involves a novel method of measuring directly the solubility of one polymer in another and is applicable for systems exhibiting low solubility and high viscosity. Basically, one polymer is added to another until two phases are detected by light scattering; in a sense it is a melt titration.

The first polymer, in the melt form, is fluxed on a two-roll mill, and the second polymer is gradually added from a buret in a volatile solvent. As the milling proceeds the solvent evaporates and the polymers mix thoroughly. At certain intervals during the titration, small samples (about 1% of the total mixture) are taken from the mill and placed on a ferrotype plate. The mill rolls, running at 30 rpm, thoroughly disperse the added component in seconds, but several minutes of mixing are allowed before the sample is removed by scraping with a microspatula across the rolls. This procedure completely removes the chance of inhomogeneous sampling, as was demonstrated by replication trials.

After the air bubbles were removed, the samples are pressed under a glass plate to a constant thickness of 125 μm. These thin circular films are then observed for scattered light at room temperature to detect the presence of two phases. A "reflection" meter is used (Photovolt 670 color and gloss meter), where the search unit is placed on the glass above the film. The light coming perpendicularly

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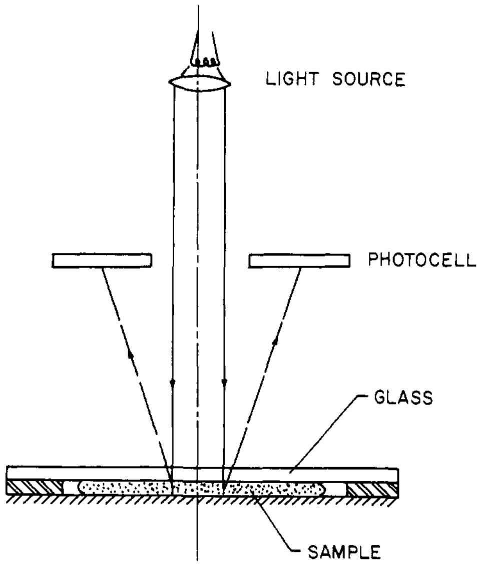

Figure 1. A sketch of the optical setup.

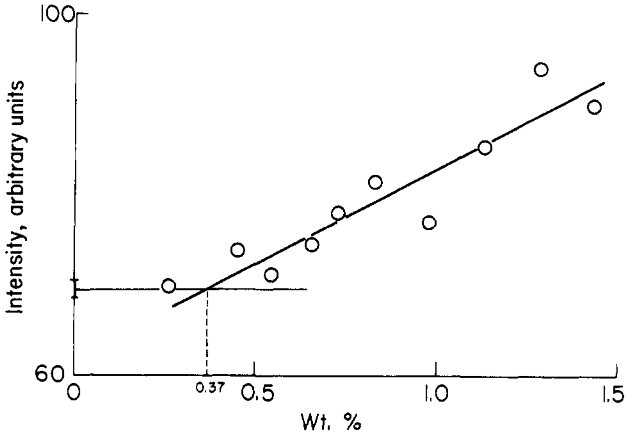

Figure 2. The linear regression result for PIB + PMMA.

Table I
Cloud Point Compositions of Two Systems (25 °C)

system	$\overline{M}_w$ of component 1	$\overline{M}_w$ of component 2	% wt of component 2
PIB + PMMA	10 000	100 000	0.37 ± 0.17
PIB + PVAC	10 000	195 000	0.03 ± 0.07

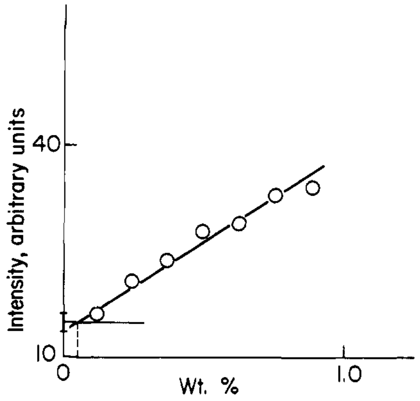

Figure 3. The linear regression result for PIB + PVAC.

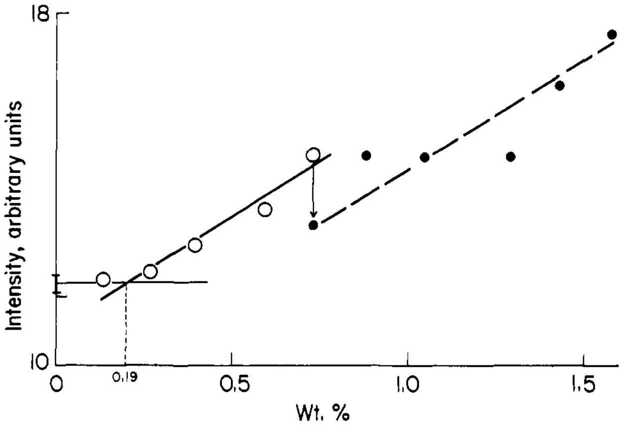

Figure 4. The PIB + PMMA system. At about 0.7 wt %, the experiment was stopped at the arrow, the polymer mixture was annealed on the rolls for 2 days, and the titration was continued (filled circles).

from the unit is reflected by the ferrotype plate and scattered forward at a low angle to a donut-shaped photocell in the search unit; this scattered intensity is read on a scale (Figure 1). The scattering is due to the presence of the second phase acting as scattering centers. The amount of the second phase is also directly proportional to the scattering if this phase is kept dispersed by the mill. This means that the scattering intensity increases linearly with composition after the cloud point is reached. By a simple linear regression, the cloud point composition can be easily and accurately determined (Figure 2). Results for the system poly(isobutylene) + poly(methyl methacrylate) and poly(isobutylene) + poly(vinyl acetate) are shown in Figures 2 and 3 and tabulated in Table I. Clearly very low solubilities can be measured by this technique with good precision.

It is also interesting to observe the effect of annealing the polymer mixture on the mill (Figure 4). This results in a decrease in intensity due to phase ripening and, apparently, a slight change of the cloud point.

The experiment that produced the data in Figure 4 was stopped for 2 days after 0.7 wt % of the second component was added. The titration was then continued (filled dots). The scattered intensity reported on the ordinate is directly proportional to the number of scattering centers or, in this case, the number of PMMA domains present. As phase agglomeration (ripening) occurs, the number of scattering centers will decrease, leading to the observed result. Further studies will demonstrate if this is a real problem or if the effect observed in Figure 4 is merely a result of the high uncertainty for a few of the data points. Also, we will determine the effect, if any, of residual solvent on the results and any changes in molecular weight due to mechanical degradation during milling.

To extend the technique to higher temperatures, we intend to use the shiny surface of the mill as a mirror, taking intensity readings during the titration process.

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