

The Analysis of Blends of Polyisobutylene and Polypropylene

A problem frequently encountered in polymer chemistry is the separation of mixtures of dissimilar macromolecules. Such mixtures are produced, for example, as a result of a stereospecific polymerization experiment where isotactic and atactic molecules and also molecules of intermediate specificity may be formed. Frequently in plastics technology, simple blends of polymers are made to obtain desirable physical properties by vigorous mixing techniques, such as extrusion or by utilizing a Banbury mixer.

When such systems are encountered, it is generally necessary to devise suitable analytical procedures to determine their composition. One attractive procedure is to dissolve the mixture in a suitable solvent and titrate with a nonsolvent to quantitatively precipitate one component. However, even though the components are presumably disentangled by this process, it has been found that the separation can be far from complete and that one component may bring down some of the other.¹ In any case, such a procedure is not convenient when there are a large number of samples. As an alternate method it has been found convenient to extract the mixture in the solid state with a selective solvent.² It is the purpose of this note to discuss some of the details of this latter type of experiment and to show that the results must be interpreted with care.

We will first discuss briefly some features of the extraction test and then describe the results of using this test to analyze mixtures of polypropylene with polyisobutylene.

The Extraction Test

The general procedure used was to mold a 0.010-in. film under standard conditions and then to extract 1 hr. in boiling solvent (generally either benzene or *n*-heptane), remove the film and dry 30 min. at 90°C. in a vacuum oven to determine the weight loss. The following are the most significant factors affecting the results.

1. Thermal History. The standard procedure was to mold at 200°C., with a 6-min. preheat and a pressure of 1000 psi applied for 1 min. Mylar (E. I. du Pont de Nemours & Co., Inc.) polyester backing films were used, and the sandwich of these films and the molten plastic was rapidly removed while hot from the press and quenched in ice water. A typical value for the heptane solubility of such a film made from polypropylene was 27% loss. If, instead of quenching, the film was cooled more slowly by passing cold water through the platens, the solubility was only 6.8%. On the other hand, if the films were subsequently annealed, for example, by boiling in water for 1 hr., the solubility fell in both cases to 2.8%.

2. Extraction Time. In all cases, the amount extracted reached a plateau after about 1 hr. For one resin, a heptane solubility of 15% was found after 1 hr., and extraction for 16 hr. removed 15.5%, this difference being less than the experimental error.

3. Remolding. Even a quenched, extracted sample may suffer further loss if remolded and re-extracted. For example, a polypropylene sample had a benzene solubility of 4% for a quenched film. Several successive remolding and re-extraction operations increased this to a final value of about 9%.³

4. Molecular Weight. In the case of polypropylene, it does not necessarily follow that a change in synthesis conditions to give a higher molecular weight will not affect the stereospecificity of the product. However, experiments with polypropylene cross-linked to give lower melt index showed that the levels of extractable material by this test were substantially unaffected by changes in melt index of up to a factor of ten.

5. Reproducibility. A single resin was subjected to eight determinations. The *n*-heptane solubility was $12 \pm 2.3\%$ for 95% confidence limits.

Mixtures of Polyisobutylene with Polypropylene

Two series of mixtures of polyisobutylenes (PIB) with commercial polypropylenes were prepared by first making concentrates containing 25% by weight PIB by adiabatic extrusion at 180°C., and subsequently re-extruding portions of these with more polypropylene at 200°C. In the first series a commercial polypropylene of melt index 1.0 (by ASTM

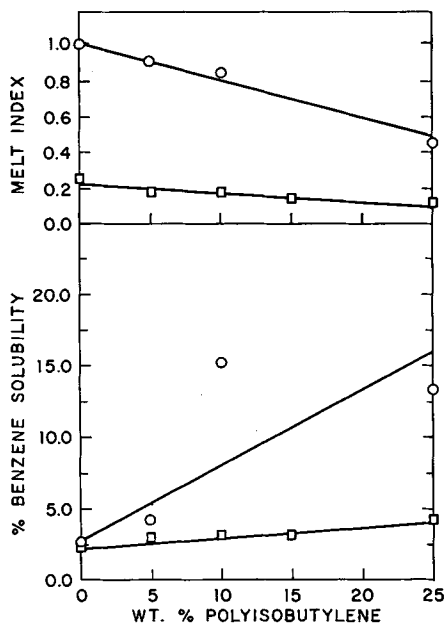


Fig. 1. Properties of mixtures of polypropylene: (O) L-300 series; (□) L-140 series.

test D-1238-57T) was mixed with Vistanex L-300 polyisobutylene (Enjay Corp.). This PIB was of very high molecular weight (ca. 10^7) and rough, granular, and not at all tacky. The second series was made from a polypropylene of the same type but of melt index 0.25; the PIB was Vistanex L-140 of molecular weight 2×10^6 and was a transparent viscoelastic solid which would flow under its own weight and was extremely tacky. Both polypropylenes had about the same benzene solubility: about 2% as measured by the above test, and both PIB samples were completely soluble in benzene. Films of 0.010-in. thickness were pressed from each mixture according to the standard procedure and were, to the eye, apparently homogeneous. Portions of these films were extracted in a large excess of boiling benzene for 1 hr. and the weight loss determined. Figure 1 shows the viscosities of the mixtures and the weight changes on extraction.

Discussion

Even though the Vistanex L-140 series contain up to 25% benzene-soluble PIB, virtually none of this is extractable by boiling benzene. The reason is that apparently the PIB chains are sufficiently entangled with the crystalline matrix of the polypropylene so that, even when the matrix is swollen, the PIB cannot be dissolved away. By contrast, in the mixtures containing the higher molecular weight PIB, almost all of the PIB can be extracted. Here the PIB is evidently dispersed as small pockets in the polypropylene. Theories of mixing would predict this sort of effect, i.e., that it is difficult to disperse a small amount of a high-viscosity material in a medium of low viscosity by the application of shear stress alone.⁴

One might suppose from these results that the lower molecular weight PIB was so thoroughly entangled on a molecular scale with the polypropylene that it had lost its identity as a separate phase. That this is not so was revealed by two experiments. If the blend containing the highest proportion of L-140 PIB was heated briefly on a hot stage microscope at 200°C. (i.e., above the melting point of polypropylene) and then cooled, there was no sign of a separate polyisobutylene phase. However, if the film was reheated to 200°C. and then cooled slowly, the PIB could be seen to have formed small pockets of a separate phase around which the polypropylene formed typical spherulites.

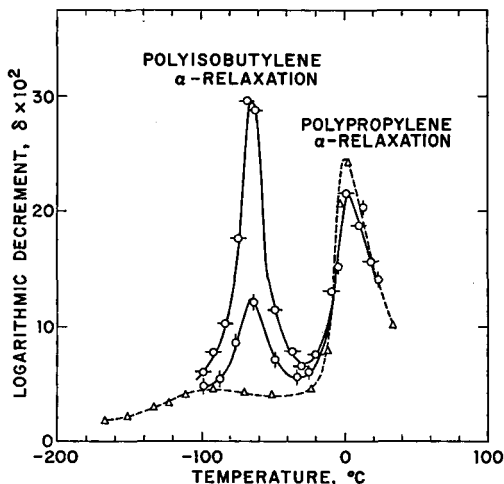


Fig. 2. Internal friction of polypropylene and mixtures with polyisobutylene: (Δ) commercial polypropylene; (\odot) mixture containing 10% L-140 polyisobutylene; (\ominus) mixture containing 25% L-140 polyisobutylene.

That the blend containing the L-140 PIB was not molecularly mixed was proved by internal friction measurements.⁵ The variation of logarithmic decrement with temperature for blends containing 0, 10, and 25% PIB is shown in Figure 2. The measurements were made with a torsion pendulum at a frequency of about 1 cycle/sec. The occurrence of the PIB α -relaxation (glass-rubber) at -65°C . is shown clearly for the blends containing 10 and 25% PIB. If the PIB was molecularly dispersed, then the PIB α -peak would not occur. This method of analysis is capable of considerable refinement if the method of deformation of the PIB could be established. It seems unlikely that these conditions would be fulfilled if the PIB were molecularly dispersed to such an extent that it had lost its identity.

In conclusion we wish to emphasize that an extraction test of the type described can give reproducible results if care is exercised, but that it does not follow at all that the amount of material extracted is all of that which is present, and which by itself would dissolve in the solvent.

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Received May 27, 1966
Revised June 22, 1966