

NOTE

Simultaneous Interpenetrating Networks

Polyblends may be synthesized in several ways, each producing a material with characteristic morphologies and mechanical behavior. Examples include the mechanical blends,^{1,2} graft-type blends,³ and block copolymers.^{1,4,5} If the mode of synthesis is restricted to crosslinked materials, several distinguishable classes of interpenetrating networks may still arise. Examples of these materials include the interpenetrating elastomeric networks (IENs) of Frisch,^{6,7} prepared by coprecipitating two polymeric latices followed by a crosslinking reaction, and the interpenetrating polymer networks (IPNs) of Sperling and co-workers,⁸⁻¹¹ prepared by swelling a crosslinked polymer I with monomer II, plus crosslinking and activating agents, and polymerizing in situ. These last materials will be termed sequential IPNs, to distinguish them from the type discussed in the following.

Let us now consider the simultaneous synthesis of two polymer networks. The major requirement involves two independent, noninterfering reactions that can be simultaneously run under the same conditions in the same container.^{12,13} These materials will be termed simultaneous interpenetrating networks (SINs).

SYNTHESIS

A simple method of preparing SINs entails the use of condensation and addition reactions. The specific material chosen to illustrate the SIN principle employs an epoxy resin formulation¹⁴ (condensation) with an ethyl acrylate formulation (addition).⁸⁻¹¹ When a tertiary amine is used to cure the epoxy, minimal interference occurs between the two reactions.¹⁵

The following components were mixed together to produce 50/50 SINs:

Poly(ethyl acrylate) portion: 100 ml ethyl acrylate, 2 ml diethylene glycol dimethacrylate (crosslinker); and 0.3 g benzoin (photosensitive activator).

Epoxy resin portion: 100 g Epon 828 (Shell Chemical Co.), principally diglycidyl ether of bisphenol-A; and 10 g triethylamine (curing agent).

The total mixture was placed in closed glass cells⁸ and subjected to three reaction conditions:

Method 1. The polymerization cell, charged with monomer mixture, was maintained at 50°C for 24 hr in the dark. At the end of this period, the cell was exposed to an ultraviolet light source for 24 hr, the temperature being maintained at -25°C.

Method 2. Polymerization was conducted in the reverse order of method 1. The cell was irradiated first, followed by heat. Methods 1 and 2 produce a semisequential, semisimultaneous type of network.

Method 3. The cell was simultaneously subjected to 50°C heat and ultraviolet light. This method produces a true SIN. Two different distances from the light source were selected to vary the photopolymerization rate.

Following polymerization, all samples were dried for 72 hr at 80°C, the last 48 hr under vacuum. Only a few per cent (at most) of volatiles were removed.

RESULTS

Method 1 produced optically clear materials, while method 2 yielded turbid materials. The turbidity of method 3 samples was intermediate and depended upon the distance from the ultraviolet light source used to initiate polymerization.

The turbidity itself was quantitatively estimated via simple transmission light-scattering photometry, employing a Brice-Phoenix light-scattering photometer Series 2000, fitted with a custom-built cell holder designed for film samples.¹⁶ Tensile strength measurements were obtained on an Instron Apparatus. Several samples of each composition were stretched to failure at an extension rate of ca. 1 in./min. The results are compared with the turbidity values in Figure 1.

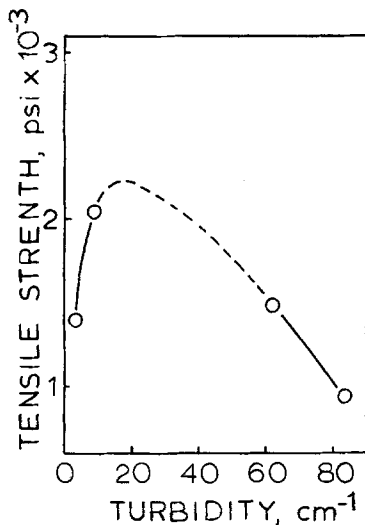


Fig. 1. Turbidity vs. tensile strength for epoxy resin/poly(ethyl acrylate) SINs. The lowest turbidity material was obtained via method 1, and the highest turbidity material was obtained via method 2.

The systematic variation in turbidity probably results from the different crosslink densities of the two networks, the epoxy portion containing a crosslink density approximately ten times higher than the poly(ethyl acrylate) portion. When the epoxy network forms first or faster, the phase divisions will tend to be finer and the material optically clearer.

It is apparent that the true SIN materials prepared by method 3 are stronger than either of the two semisequential methods. An intermediate turbidity, indicative of a controlled dispersion of the phase domains at a very fine level, produced the highest tensile strengths.

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