

Contrast Enhancement in Multicomponent Polymer Systems

INTRODUCTION

A current area of interest in polymer science is the study of multicomponent polymer systems. These include blends, graft, and block copolymers which exhibit varying amounts of compatibility depending on temperature, composition, and casting solvent. In our studies on multicomponent resist systems consisting of the binary mixtures of poly(2-methyl pentene-1 sulfone), PMPS, with a variety of different novolac resins, we found that the degree of compatibility depended markedly on novolac structure and on the casting solvent.

The morphology of such systems can be examined by a variety of microscopy techniques, but a major limitation to such microstructural studies is obtaining sufficient contrast between the various phases. Usually one attempts to provide such contrast by the use of a selective stain such as osmium tetroxide. Most polymer systems of interest, however, have intrinsic low contrast, and specific chemical stains are hard to find.

An additional complicating feature in our system was the necessity to examine samples using reflective optics since the films were supported on silicon wafers. The principle of selective staining usually applies to transmission in either a transmission electron microscope or transmission optical microscopy. We report here on the solvent-induced and radiation-induced contrast behavior of a poly(2-methyl pentene-1 sulfone)-novolac system. This contrast mechanism should be operative in any multicomponent system when one of the phases responds in a significantly different manner to either solvent or electron irradiation than the other.

EXPERIMENTAL

Films containing 10% PMPS and 90% novolac (supplied by Hunt Chemical Co.) were deposited on silicon wafers by spin coating from solution using a Headway photoresist spinner.

The samples were examined in interference contrast using a Reichert Zetopan microscope fitted with Nomarski interference contrast optics. Films were also examined by scanning electron microscopy on an Etec Autoscan instrument.

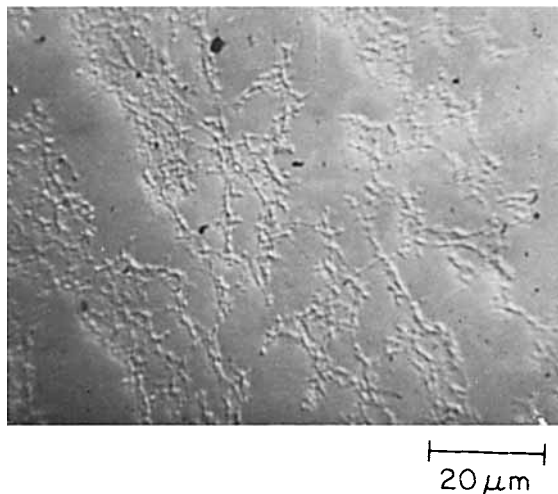
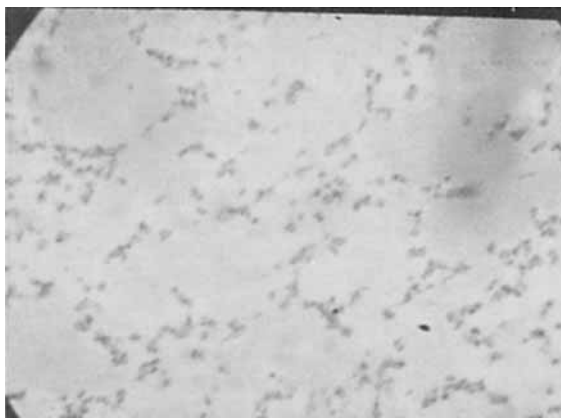
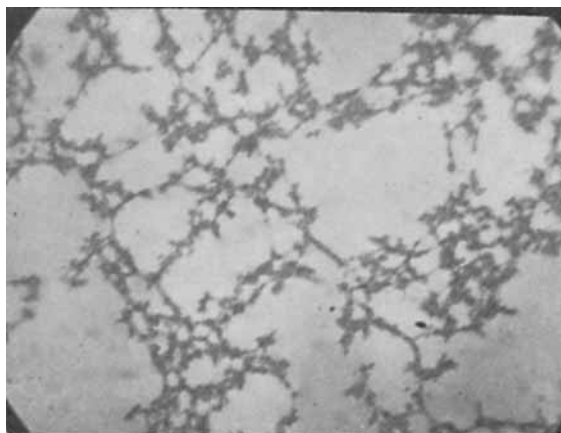


Fig. 1. Interference contrast photomicrograph of novolac (90)/PMPS (10) mixture spun from MCA.



(a)



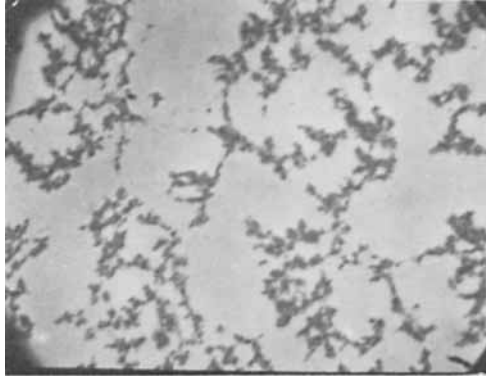
(b)

Fig. 2. Interference contrast photomicrograph of novolac (90)/PMPS (10) mixture showing development in contrast as a function of dipping time in xylene: (a) 1 min, (b) 5 min.

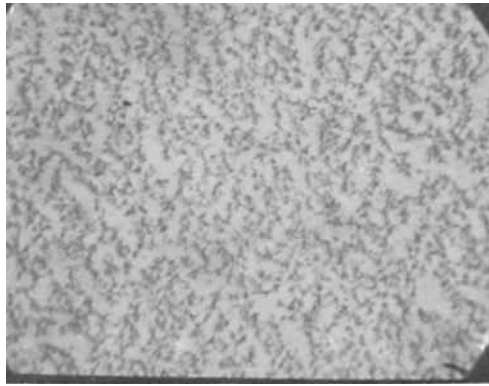
RESULTS AND DISCUSSION

The interference contrast mode of the Reichert microscope involves viewing the sample in the reflected light mode, and as such the technique is sensitive to differences in surface relief. Differences in refractive index do provide a small degree of contrast, as evidenced in Figure 1. The PMPS/novolac mixture was spun from methyl cellosolve acetate (MCA). Considerable phase separation has occurred indicative of marked incompatibility.

It was found that the contrast could be markedly enhanced by prior dipping of the films in xylene for a few minutes. Xylene is a good solvent for PMPS but is a nonsolvent for the novolac. We



(a)



(b)



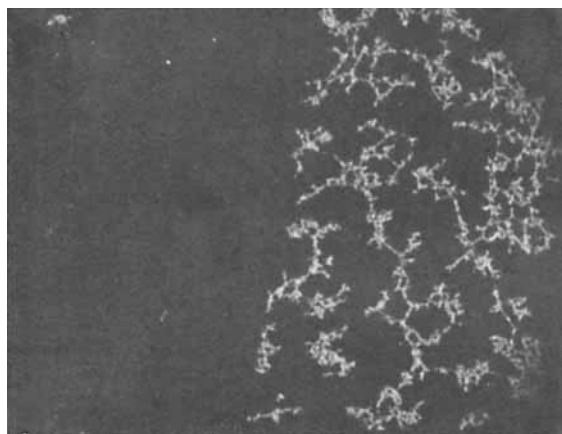
(c)

20 μm

Fig. 3. Interference contrast photomicrograph of novolac (90)/PMPS (10) mixtures spun from solutions containing different proportions of chlorobenzene (CB) and methyl cellosolve acetate (MCA): (a) 80% MCA, 20% CB; (b) 50% MCA, 50% CB; (c) 20% MCA, 80% CB.



(a)



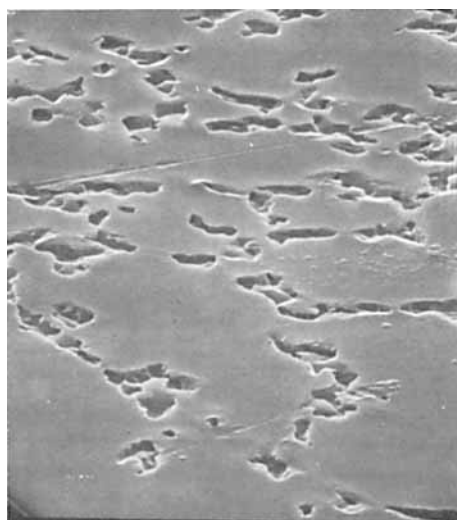
(b)

Fig. 4. Photomicrograph of novolac (90)/PMPS (10) mixtures showing development in contrast resulting from irradiation: (a) interference contrast; (b) dark field.

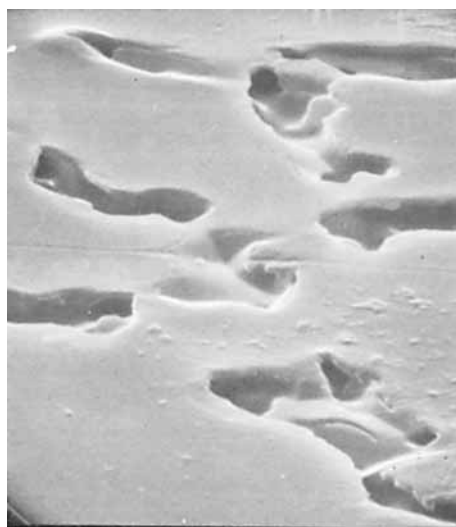
therefore suggest that xylene dissolves the surface phase domains containing PMPS leaving a "cratered" surface which shows excellent contrast in the interference microscope. Figure 2 shows the development in contrast enhancement which occurs.

The size of the phase separated domains for this particular novolac is determined by the solvent. Figure 3 shows the solvent-enhanced contrast images for samples spun from MCA/chlorobenzene mixtures. The domain size is seen to decrease with increasing proportion of chlorobenzene in the spinning solvent. Films spun from chlorobenzene/butyl acetate show no evidence of incompatibility even after treatment in xylene.

A similar contrast enhancement was observed after irradiation with electrons. A small section



(a) 5 μm



(b) 1 μm

Fig. 5. Scanning electron micrograph of surface of novolac (90)/PMPS (10) mixtures following contrast enhancement.

of a film spun from MCA was irradiated to a total dose of 10^{-5} Coulomb/cm² and then examined in the interference contrast microscope. The enhanced contrast is shown in Figure 4(a), which clearly shows the line of demarcation between the irradiated and nonirradiated portions. Figure 4(b) shows the same effect in dark-field microscopy where the irradiated area now shows marked scattering of light.

Again, the contrast enhancement must result from physical removal of the PMPS. This polysulfone undergoes extensive depolymerization on irradiation, resulting in material loss.¹ One would

therefore predict that the surface should appear extremely "cratered." Indeed, scanning electron micrographs of the irradiated areas of the phase-separated matrix show extensive "cratering" or "pocketing" (Fig. 5), thereby confirming the interpretation derived from interference contrast microscopy. It should be noted that a similar observation of contrast enhancement by selective electron beam etching of styrene/acrylonitrile (SAN)-poly(methyl methacrylate) (PMMA) blend has been reported.² Whereas SAN polymers crosslink under irradiation, PMMA undergoes chain scission and apparent thinning, thereby giving rise to surface topography and associated contrast enhancement.

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References

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