

# Radiation Degradation of Polystyrene/Poly(methyl Methacrylate) Blends

## INTRODUCTION

The effects of high-energy radiation on a wide variety of homopolymers have been examined in detail, but there have been relatively few investigations of copolymers and blends of homopolymers, although these systems are of increasing industrial importance. We have previously<sup>1</sup> examined the effects of  $\gamma$ -radiation on copolymers of styrene and methyl methacrylate. Polystyrene is highly resistant to irradiation under vacuum:  $G(X) \approx 0.04$ ,  $G(S) \approx 0.01$ ,<sup>2</sup> and the flexural strength is virtually unaffected up to 500 Mrad.<sup>1,3</sup> The behavior of poly(methyl methacrylate) is in marked contrast to that of polystyrene, as  $G(X) = 0$ ,  $G(S) \approx 1.7$ ,<sup>4</sup> and the flexural strength decreases rapidly to 50% of the initial value after about 10–20 Mrad, depending on the molecular weight of the initial polymer.<sup>1</sup> The predominance of chain scission is characteristic of polymers of 1,1-disubstituted ethenes,<sup>5</sup> and the decrease in strength is in conformity with the sigmoidal relationship between strength and molecular weight for PMMA.<sup>6</sup>

Random copolymers with molecular weights in the range  $\bar{M}_v = 200,000$ –500,000 showed rates of change in flexural strength on irradiation which were intermediate between the rates observed for the two homopolymers and consistent with the observed changes in molecular weight.<sup>1</sup>

It is of interest to examine the effect of radiation on the flexural strengths of blends of polystyrene and poly(methyl methacrylate). Both homopolymers are transparent, glassy thermoplastics at ambient temperatures with glass transition temperatures around 100°C, and the blends should have similar mechanical properties.

Shultz and Mankin<sup>7</sup> have determined the extent of chain scission of PMMA in blends of PMMA with PS by GPC. For a coprecipitated blend containing 17% PS the scission of PMMA was similar to that observed in pure PMMA; however, some radiation protection was observed in blends which had been freeze-dried from naphthalene. The molecular weight of the PMMA was very low, so that compatibility was approached. None of these blends had been subjected to melt processing.

## EXPERIMENTAL

Polystyrene, PS (Shell HR high purity,  $\bar{M}_n = 120,000$ ,  $\bar{M}_w = 280,000$ ) and poly(methyl methacrylate), PMMA ( $\bar{M}_v = 270,000$ ) prepared by bulk polymerization initiated by azobisisobutyronitrile at 60°C, were dissolved in chloroform and coprecipitated into methanol. The dried polymers were pressed between stainless steel glazing plates at 190°C and 50 kg/cm<sup>2</sup> to form 3-mm sheet. Bar specimens (50 mm  $\times$  6.5 mm  $\times$  3 mm) were cut and the edges polished, evacuated at <0.1 Pa for 50 hr, and sealed in glass tubes. Irradiations were carried out in the <sup>60</sup>Co pond facility of the Australian Atomic Energy Commission, and flexural strength measurements made with an Instron Model 1026 tensometer using a 38-mm span and a cross-head speed of 1 mm/min.<sup>8</sup> Failure under flexural testing occurred by brittle fracture in all unirradiated and irradiated specimens.

Polystyrene and poly(methyl methacrylate) form incompatible mixtures; this is apparent in concentrated solutions and results in opacity in the pressed sheets. Phase separation in the sheets is assisted by the temperature and stress of the melt pressing. The morphology depends markedly on the composition of the blends, a uniform, milky-white sheet being obtained from 10% PS, but gross incompatibility with large regions of distinct phases were observed at higher percentages of PS.

## RESULTS AND DISCUSSION

Whereas copolymers of styrene and methyl methacrylate showed slightly higher flexural strengths<sup>1</sup> than the homopolymers, blends showed markedly lower strengths (Fig. 1), the decrease being greatest at about 50% styrene. There was a decrease in modulus, but an increase in the elongation to break (fracture strain) attributable to the two-phase morphology.

The effect of various radiation doses on the flexural strength is shown in Figure 2. The decreases

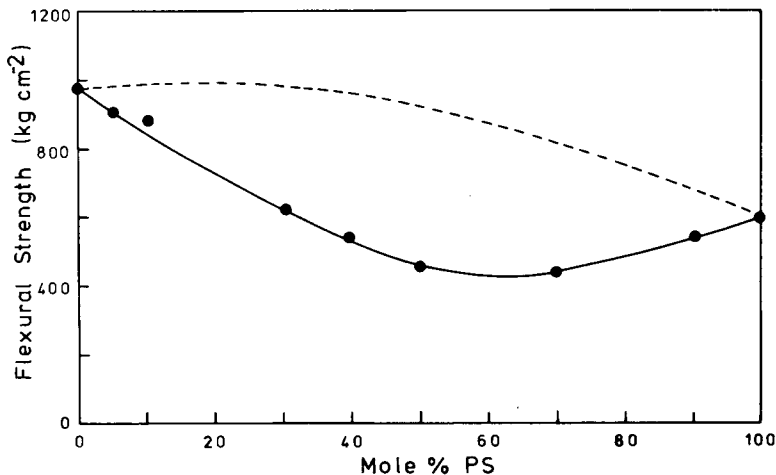


Fig. 1. Flexural strengths of unirradiated blends of PS and PMMA: (●) effect of composition, 3-mm sheet; (---) copolymers.

in strength reflect decreases in fracture strain, only a small change (increase) in modulus being observed. The compressive strength showed similar relationships with composition and dose. The dose dependence of the flexural strength was approximately exponential, and degradation rates ( $k$ ) could be obtained from eq. (1) by plotting  $\ln \sigma_D$  versus  $\ln D$ :

$$\ln(\sigma_0 - \sigma_D) = k \ln D \quad (1)$$

where  $\sigma_0$  and  $\sigma_D$  are the flexural strengths without irradiation and after a dose of  $D$  Mrad, respectively. The observed relationship between the rates of radiation-induced degradation of PS/PMMA blends, measured by  $k$  in eq. (1) for the decrease in flexural strength, or from the initial rates of degradation and the compositions of the blends is shown in Figure 3.

We note first that the flexural strength is *not* determined over the complete composition range by the PMMA component. If this were the case, curve A would be followed. In particular, blends containing 90, 70, and 50% PS would show a great increase in radiation sensitivity compared to 100% PS, contrary to our results. Secondly, there is *no* protective effect by the polystyrene on the PMMA, otherwise a relationship similar to curve B would be observed. The effect should be largest for the 10% PS blend, where *no* decrease in degradation rate was found. Such protective effects by aromatic

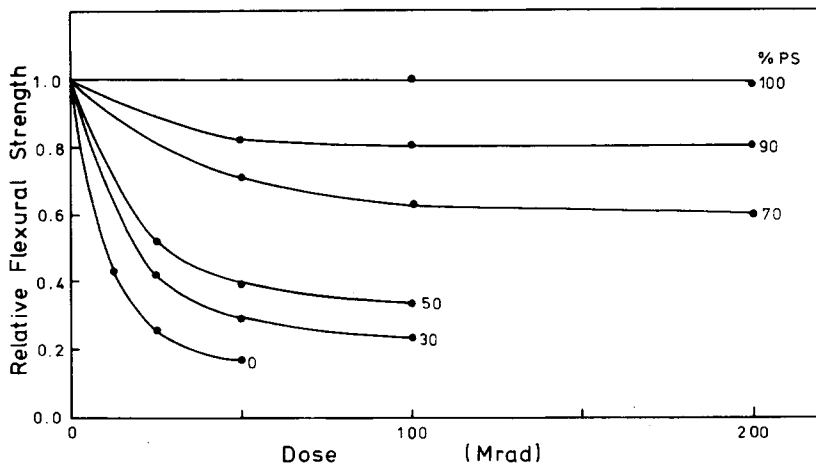


Fig. 2. Effect of  $\gamma$ -radiation on the flexural strengths of PS-PMMA blends (% PS in blend shown next to corresponding curve).

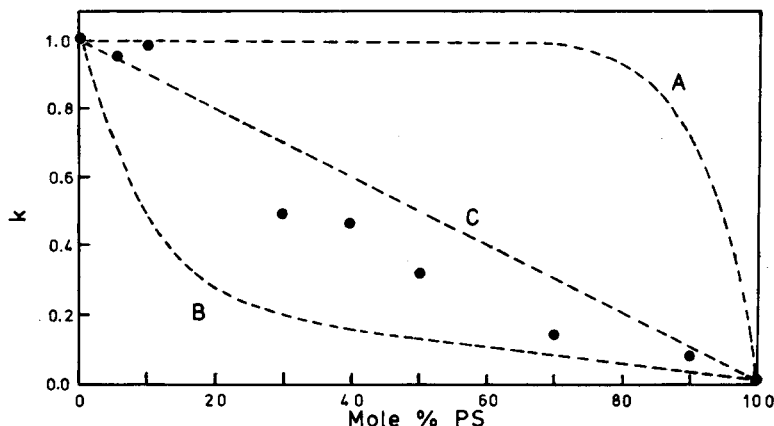


Fig. 3. Dependence of rate of decrease in flexural strength of PS-PMMA blends ( $k$  from eq. (1) in text) on the composition of the blend: (●) experimental values. Predicted relationships shown by dashed lines for A, flexural strength determined by PMMA component; B, protective effect on PMMA by PS; C, linear relationship with composition.

components have been well established in the liquid phase for small molecule systems, such as benzene-cyclohexane mixtures,<sup>9</sup> although the situation is unclear in the solid state.

Wilske and Heusinger<sup>10</sup> have deduced from ESR measurements that there is no intermolecular energy transfer in PMMA-PS mixtures, and our strength measurements lead to a similar conclusion. However, more intimate contact between PS and PMMA molecules would be achieved in freeze-dried powders, and these systems might be expected to show a protective effect. The results of Shultz and Mankin<sup>7</sup> indicate that protection does occur in freeze-dried, but not coprecipitated, PMMA-PS blends. Witt<sup>11</sup> has measured average  $G(X)$  values for blends of PS with polybutadiene and found a linear decrease in  $G(X)$  with increasing PS, indicating that the PS acts only as a diluent, but no material properties were reported.

Our experimental results in Figure 3 deviate appreciably from a linear relationship between degradation rate and blend composition (curve C). A possible interpretation of the observed behavior is that the blends can be considered as dispersions of the minor component in a matrix of the major component and that the flexural strength is determined predominantly by the matrix. Consequently, addition of PMMA will not decrease greatly the radiation resistance of PS, and likewise addition of at least 10% of PS will not increase the radiation resistance of PMMA. However, the reproducibility of strength measurements on these incompatible blends is insufficient to distinguish between this interpretation and a linear relationship.

Protection against high-energy radiation by the aromatic rings in styrene has been shown to occur in copolymers of styrene and methyl methacrylate by ESR.<sup>12</sup> The present strength measurements show that protection is negligible in melt-processed blends of PS and PMMA, but the results of Schultz and Mankin<sup>7</sup> indicate protection in freeze-dried powders. Experiments are currently in progress to obtain evidence from radical concentrations by ESR on the existence and extent of radiation protection, whether by energy transfer or other processes, in PMMA-PS blends using materials with different degrees of separation of the blend components. It would be particularly interesting to investigate whether a significant protective effect occurs in block and graft copolymers of PS and PMMA when phase separation is avoided on the macroscopic scale although the incompatibility of the segments would not be changed.<sup>13</sup> Energy transfer or radical scavenging would then have to be intermolecular or over long distances intramolecularly.

The authors would like to thank the Australian Research Grants Committee and the Australian Institute of Nuclear Science and Engineering for support, the Australian Atomic Energy Committee for irradiation facilities, and Professor F. W. Billmeyer for helpful advice.

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Received October 19, 1977  
Revised August 3, 1979