

Cement Mortar Impregnated with Poly(Methyl Methacrylate-co-Styrene)

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Synopsis

Polymer-impregnated mortars were prepared by copolymerization of a monomer mixture of methyl methacrylate and styrene in the ratios of 13:87 and 40:60 using Co-60 gamma radiation. The copolymerization characteristics *viz.* the rate of polymerization, the extent of monomer loss, polymer loading, etc., were studied. The nature and molecular weight of the extractable polymer from the composite were determined. The flexural strength of the copolymer-impregnated composites was found to be better than that of the composites impregnated with component homopolymers.

INTRODUCTION

Polymer-impregnated concrete (PIC) has been developed during the last three decades in order to enhance mechanical properties and chemical and freeze-thaw durability of ordinary concrete. Among the most extensively studied monomers in PIC are methyl methacrylate (MMA) and styrene (S) primarily because these are easily impregnable into concrete due to their low viscosity at ambient temperature, ready availability, relatively lower cost, and ability to produce PIC with excellent properties. In earlier publications^{1,2} we reported the polymerization characteristics of S and MMA inside cement mortar and in bulk, mechanical/durability properties, and fracture morphology of the PIC composites impregnated with those monomers. Comparison of polymerization characteristics of S and MMA^{1,2} inside the cement matrix shows that MMA has a faster rate of polymerization, and enhanced improvements in strength, and in durability in diluted H₂SO₄, but entails higher monomer loss and lower conversion compared to S. Combining the advantages of S with those of MMA by impregnating cement mortar with their copolymer is expected to improve the mechanical and durability properties of PIC together with lowering cost. However, relatively very little work has been reported on S-MMA copolymer-based composites.³

In this communication we report our results on the polymerization characteristics of S-MMA mixed monomer system inside mortar matrix and in bulk, and the flexural strength of PIC-Poly(MMA-co-S) composites *vis-a-vis* those of PIC-PS and PIC-PMMA.

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EXPERIMENTAL

Materials, specifications, methods of mortar specimen preparation, monomer impregnation, in situ and bulk polymerization of the monomer, extraction of the impregnated polymer from PIC, determination of molecular weight of the polymer samples, and mechanical testing of PIC samples have already been described in our earlier communications.^{1,2} Relevant experimental details pertaining to the present work are as follows.

Initial Monomer Composition

Mixtures of MMA and S have been used for impregnation into mortar matrix in two initial compositions, viz 13% MMA + 87% S and 40% MMA + 60% S (by wt). Accordingly, the resulting PIC composites have been termed as PIC-MS (13 : 87) and PIC-MS (40 : 60).

Polymerization

In situ and bulk polymerizations of the monomer mixtures were effected at ambient temperature ($30 \pm 1^\circ\text{C}$) by gamma radiation from a Co-60 source (Gamma Chamber 900, BARC, India). The intensity of the radiation was found to be 0.09 Mrad/h at the time of experiments.

Extraction of the Copolymers

Ground PIC specimen was subjected to Soxhlet extraction for 72 h using toluene as solvent. The copolymer was precipitated out in methanol and purified as described elsewhere.¹

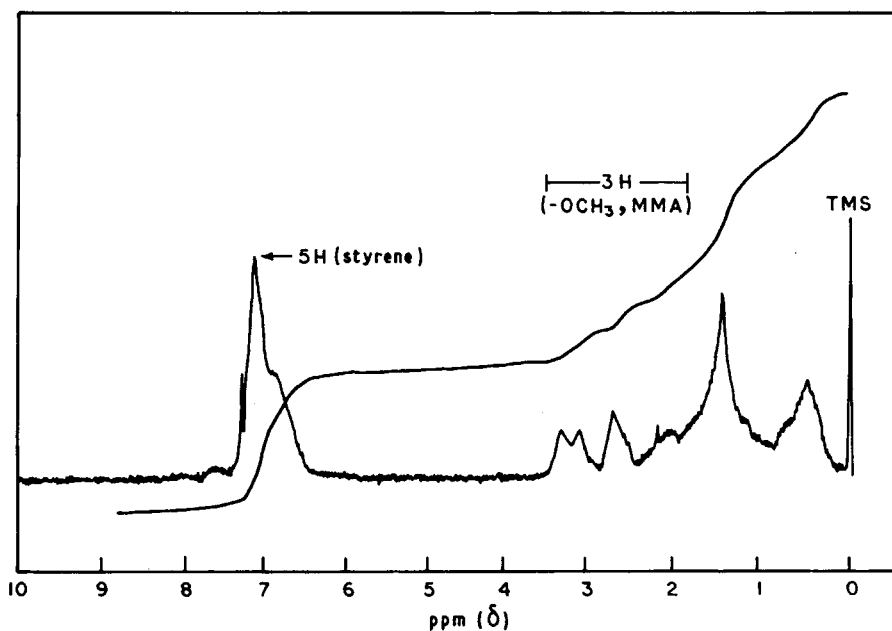


Fig. 1. NMR spectrum of poly(MMA-Co-S), 90 MHz, CDCl_3 , 30°C .

Composition of the Copolymers

The samples obtained by bulk and in situ copolymerization were termed as copolymer bulk and copolymer in situ, respectively. Compositions of the samples were determined from their $^1\text{H-NMR}$ spectra.^{4,5} Area under peaks due to protons of styrene moiety and those due to methoxy protons of MMA moiety of the copolymer were measured (Fig 1). The mole fractions of the constituent monomers were calculated as follows.

$$\text{Mole fraction of S} = \frac{3a}{3a + 5b}$$

where

a = total peak area between 6.5 and 7.0 ppm for aromatic protons

b = total peak area between 2.5 and 4.0 ppm for methoxy protons

The spectra were taken in CDCl_3 at 30°C in a Varian EM-390, 90 MHz NMR spectrometer.

Molecular Weight

The viscosity-average molecular weight (\bar{M}_v) of the copolymer in situ and copolymer bulk samples was calculated by measuring intrinsic viscosity $[\eta]$ of the copolymer solutions in toluene at $30 \pm 0.1^\circ\text{C}$ using an Ubbelohde suspended level viscometer by the equation.⁶

$$[\eta] = (7.0 + 4.X_{\text{sty}}) \times 10^{-5} (\bar{M}_v)^{0.72}$$

where X_{sty} is the mole fraction of styrene in the copolymer. In all the cases both Kraemer and Huggins equations were found to be valid with $k' + k''$ values very close to 0.5.

Flexural Strength

The flexural strength of PIC-MSC composites was measured by three-point bending test in a Universal Testing Machine (model Fu 10,000e, Veb Thuringer Industrie Werk, GDR) using prisms of dimension $10 \times 2 \times 2$ cm.

RESULTS AND DISCUSSION

Polymerization Characteristics

In the case of in situ copolymerization of MMA-S (13:87) monomer mixture, conversion increased exponentially with days of irradiation (Fig. 2). A conversion of about 84% was obtained in 4 days (~ 9 Mrads) of irradiation, and only 10% increase in conversion was recorded during subsequent 27 days (~ 58 Mrads) of irradiation. The conversion in bulk polymerization also increased exponentially; however, the conversion was only 55% after 4 days of irradiation. Cumulative monomer loss during in situ polymerization also increased to about 3% in about 3 days, and remained practically constant even up to 31 days of irradiation (Fig. 3, Curve 1)

With MMA-S (40:60) mixed monomer system the conversion increased sharply and attained the value of about 90% in 6 days (~ 13 Mrads) or

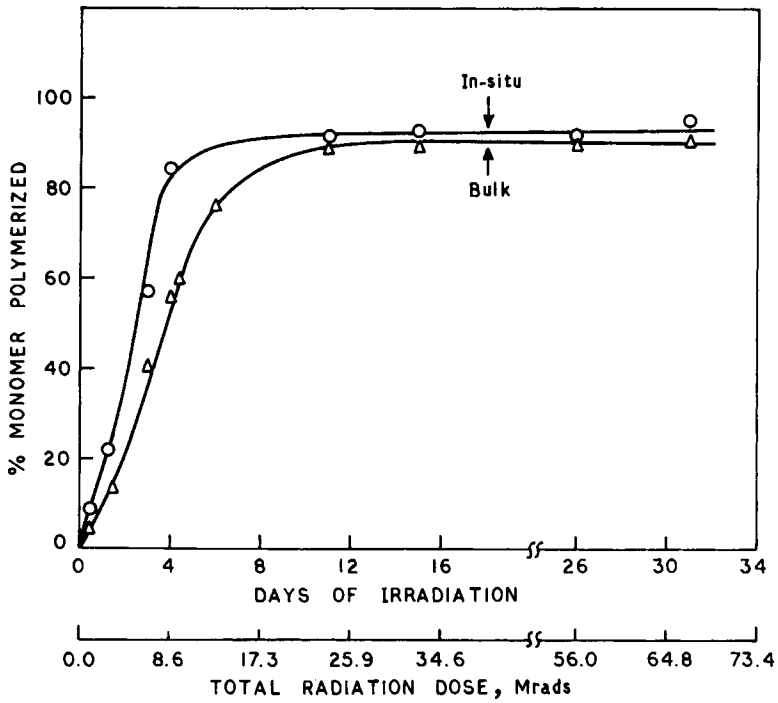


Fig. 2. Variation of % monomer conversion with days of irradiation; system: 13% MMA + 87% S.

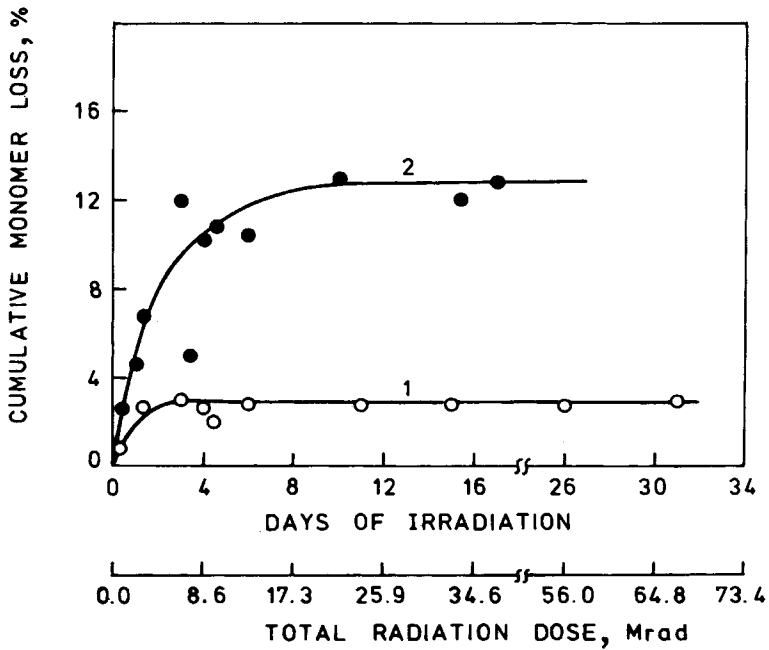


Fig. 3. Effect of irradiation dose on the monomer loss during in situ polymerization; curve 1, MMA-13% + S-87%, curve 2, MMA + 40% + S-60%.

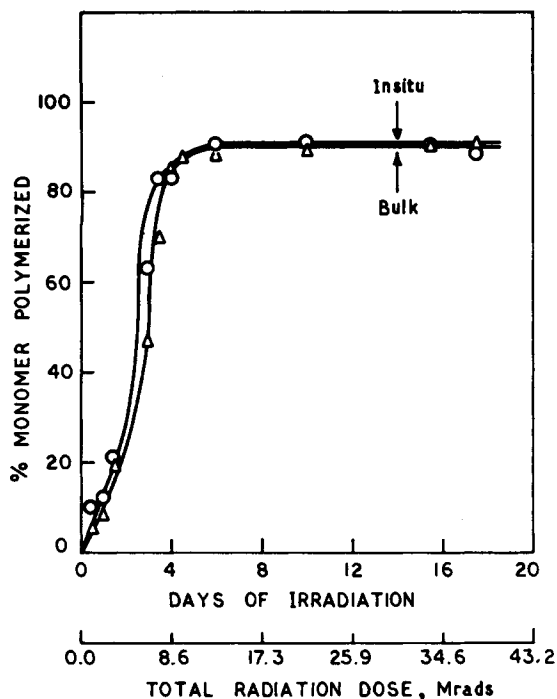


Fig. 4. Variation of % monomer conversion with days of irradiation; system: 40% MMA + 60% S.

irradiation (Fig. 4). In bulk polymerization, the conversion was somewhat lower at the initial stage but the same maximum conversion ($\sim 90\%$) was recorded in 6 days of irradiation in both cases. The percent cumulative monomer loss in the case of in situ polymerization increased exponentially and reached a maximum of around 12.5% after 10 days (~ 22 Mrads) of irradiation (Fig 3, Curve 2)

It is to be noted that the rate of polymerization of the comonomer mixture (MMA + S) is higher in the case of in situ polymerization than in bulk polymerization. This is consistent with the general observation^{1,2} with individual monomers of S and MMA.

Comparison of the Polymerization Characteristics of Homopolymer and Copolymer Systems of S and MMA

The polymerization characteristics of the (MMA-S) copolymers inside cement matrix have been compared (Table I) with those reported for the homopolymers, PS¹ and PMMA.²

With gradual replacement of S by MMA in the impregnant monomer feed, the maximum monomer loss steadily increased. Maximum monomer conversion, as well as the time for optimum cure, however, remained virtually unaffected up to a composition of 40% MMA. Maximum polymer loading improved substantially from 10.5% with 100% S to 11.5–12% with 60–87% S content.

TABLE I
Comparison of Polymerization Characteristics (In Situ) of Different Monomer Systems

Polymerization Characteristics	Monomer system			
	S ^a	MMA-S (13:87)	MMA-S (40:60)	MMA ^b
Maximum monomer loss (%)	2	3	12	21
Maximum monomer conversion (%)	87	94	90	60
Total radiation dose for optimum conversion (Mrads)	15	13	13	5
Maximum polymer leading (%)	10.5	12	11.5	7.5

^aResults are reported in Ref. 1.

^bResults are reported in Ref. 2.

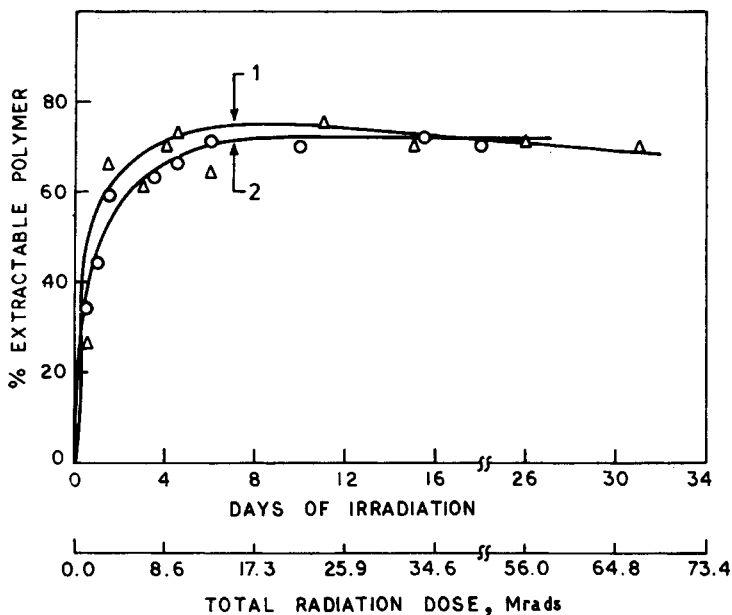


Fig. 5. Variation of % extractable polymer (PEP) with days of irradiation; Curve 1, PIC-MSC (13:87); Curve 2, PIC-MSC (40:60).

Copolymer Extraction

It has been suggested⁷ that the polymer inside PIC remains in two forms—"inserted" and "loose." It is possible to extract the loose fraction by subjecting the PIC to Soxhlet extraction. The inserted polymer is likely to provide a rough estimate of the cement-polymer interaction through which perhaps enhancement of mechanical properties in PICs occurs.

Data on percent extractable polymer (PEP) for PIC-MSC (13:87) and PIC-MSC (40:60) systems are presented in Figure 5. In the case of PIC-MSC (13:87), the PEP increased up to 11 days (~24 Mrads) of irradiation, reached

the maximum value ($PEP_{\max} = \sim 75\%$), and then declined (Fig. 5, Curve 1). On the other hand, in the case of PIC-MS (40:60) systems the PEP increased exponentially up to 6 days (~ 13 Mrad) of irradiation, attained the maximum value ($PEP_{\max} = 71\%$), and then remained fairly constant (Fig. 5, Curve 2)

It may be mentioned here that under the influence of gamma radiation, both crosslinking and chain scission of the impregnated copolymer may take place. Furthermore, MS (13:87) will be prone to predominantly crosslinking due to relatively higher percentage of styrene in it, whereas in the case of MS (40:60) the extent of crosslinking and chain scission is expected to be of comparable magnitude. These observations are in general agreement with the report⁶ that (MMA-S) copolymers with 66% S or less undergo degradation and those with 83% S or more undergo crosslinking when subjected to gamma radiations of dosage 20 Mrads or more.

Crosslinking of the impregnated MS (13:87) will result in a decrease in the solubility of the copolymer in toluene. It is also possible that a fraction of the uncrosslinked mass of the copolymer remained trapped in the crosslinked gel.¹ All of these factors will lead to a lower value of PEP. This possibly explains a slow declining trend of PEP in PIC-MS (13:87) after 11 days (24 Mrads) of irradiation (Fig. 5, Curve 1).

On the other hand, due to radiolytic degradation, the solubility of the impregnated MS (40:60) will be somewhat increased. This will ensure a faster extraction. However, the net amount of the extractable copolymer will remain fixed. This is possibly reflected in an apparent constancy in the PEP values of PIC-MS (40:60) beyond 6 days (13 Mrad) of irradiation (Fig. 5, Curve 2).

It may be mentioned here that the trend of PEP in the case of PIC-MS (13:87) is very much similar to one observed with PIC-PS.¹ The only difference is that the crosslinking in the latter starts much earlier (beyond 15 Mrads compared to 24 Mrads in the former), and is relatively more extensive. Further, the drop in PEP in the case of PIC-PS system¹ is significant (from 88% to 38%) when radiation dose increased from 13 to 25 Mrads. In PIC-MS (13:87), however, the drop in PEP is relatively much less (from 75% to 70%) even though the total radiation dose increased from 24 to 67 Mrads (Fig. 5, Curve 1). This is probably due to less extensive crosslinking in MS (13:87) caused by the presence of MMA.

The trend in PEP of PIC-MS (40:60) system (Fig. 5, Curve 2) is identical to one obtained in the case of PIC-PMMA system,² which can be justified on the same grounds as discussed earlier.

Molecular Weight

The data on molecular weight (\bar{M}_v) of copolymer in situ (extracted) and copolymer bulk are presented in Figure 6 for MS (13:87) system and in Figure 7 for MS (40:60) system. The K value in the viscosity-molecular weight relationship has been calculated, on the basis of the relative abundance of the comonomers as determined from the ¹H-NMR spectra of the polymers.

In the case of MS (13:87) system the \bar{M}_v of copolymer in situ as well as that of copolymer bulk increased slowly with increasing radiation dose even up to 31 days (67 Mrads) of radiation (Fig. 6). However, after 11 days the

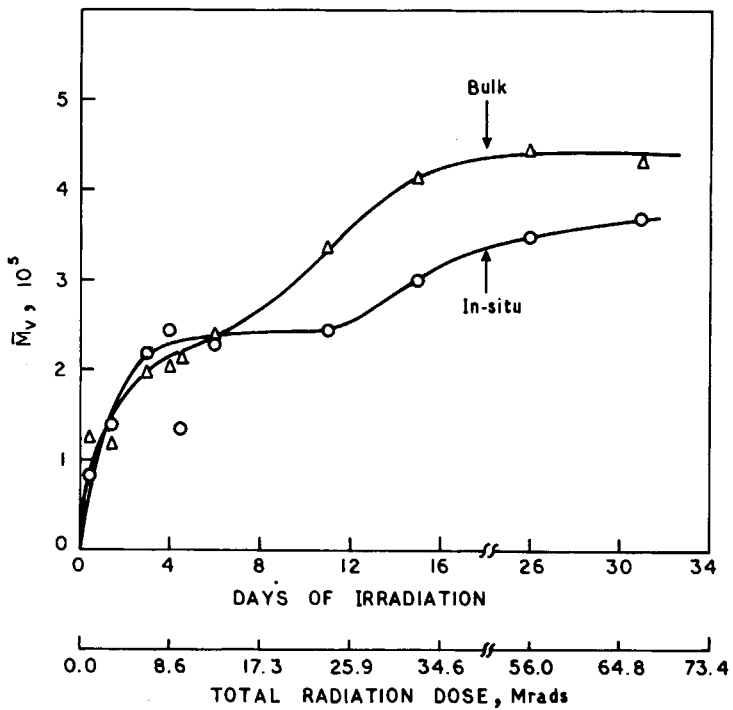


Fig. 6. Variation of \bar{M}_n of copolymer in situ and copolymer bulk with days of irradiation; system: 13% MMA + 87% S.

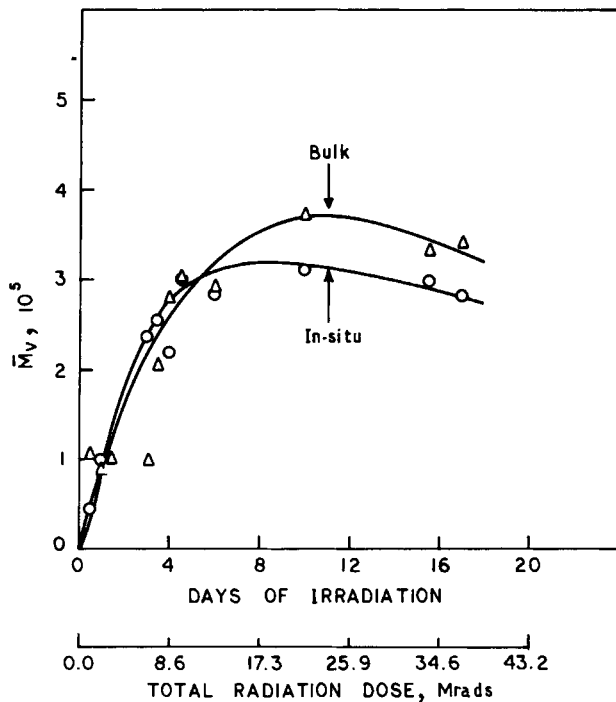


Fig. 7. Variation of \bar{M}_n of copolymer in situ and copolymer bulk with days of irradiation; system: 40% MMA + 60% S.

increase was somewhat higher, which might be due to a mild crosslinking which makes the copolymer still soluble.

In the case of MSC (40 : 60) system the \bar{M}_v of the copolymer in situ as well as that of the copolymer bulk also increased with increase in the total radiation dose. However, in contrast to MSC (13 : 87) system, \bar{M}_v registered a decline after 11 days of irradiation (Fig. 7). This is attributable to the degradation of the copolymer under the influence of gamma radiation, as explained earlier.

It is to be noted that for both the systems, the \bar{M}_v of the copolymer in situ is lower compared to that of copolymer bulk. Busfield and O'Donnell⁶ who studied the effects of gamma radiation on \bar{M}_v and mechanical properties of (MMA-S) copolymers also reported very similar results.

The trends in the variation of \bar{M}_v of the MSC (40 : 60) (bulk as well as in situ) with radiation dose are similar to those observed in the case of MMA system.² In both cases, \bar{M}_v of the polymers decreased beyond an optimum radiation dose due to chain degradation. The optimum radiation dosages are about 0.5 and 1.3 Mrad for in situ and bulk polymerized samples, respectively, in the case of MMA system.² The corresponding values are about 17 and 24 Mrad in the case of MSC (40 : 60) system (Fig. 7).

The trends of \bar{M}_v (bulk as well as in situ) in the case of MSC (13 : 87) system, however, do not resemble those obtained in the case of 100% system.¹ In the former case a continuous increase in \bar{M}_v of the copolymer in situ and copolymer bulk has been observed (Fig. 6) during the entire period of irradiation up to 67 Mrad. In the latter case the \bar{M}_v of the PS in situ decreased, whereas that of PS bulk, showed a marginal increase beyond 15 Mrad. The decrease in \bar{M}_v of PS in situ was attributed to crosslinking of the impregnated PS. It was suggested that the relatively higher molecular weight uncrosslinked PS chains were possibly trapped in the crosslinked PS gel. As a result, the extracted PS was rich in lower molecular weight fractions, and hence a lower value of \bar{M}_v .

Flexural Strength

In the case of PIC-MS (13 : 87) system, the flexural strength of the composite increased exponentially with radiation dose up to 15 days (32 Mrads) of irradiation with a parallel increase in the percent polymer loading (Fig. 8). Thereafter the flexural strength remained constant during subsequent periods of irradiation. On the other hand, in the case of PIC-MS (40 : 60) system the flexural strength of the composites increased up to about 8 days (17 Mrads) of irradiation with parallel increase in the percent polymer loading, and then declined (Fig. 9).

The flexural strengths of PIC-MS (13 : 87) and PIC-MS (40 : 60) composites at a fixed polymer loading (say 7%) is about 21 and 23.5 MPa, respectively, which are about 4.2 and 4.7 times that of the unimpregnated mortar (Figs. 8 and 9). It may be mentioned here that the flexural strengths of PIC-PS¹ and PIC-PMMA² composites at the same polymer loading (i.e., 7%) and using the same base mortar were 15.5 and 19.5 MPa, respectively. This indicates that the flexural strength of PIC-MS composites is higher compared to those of either PIC-PS or PIC-PMMA. Furthermore, it increased

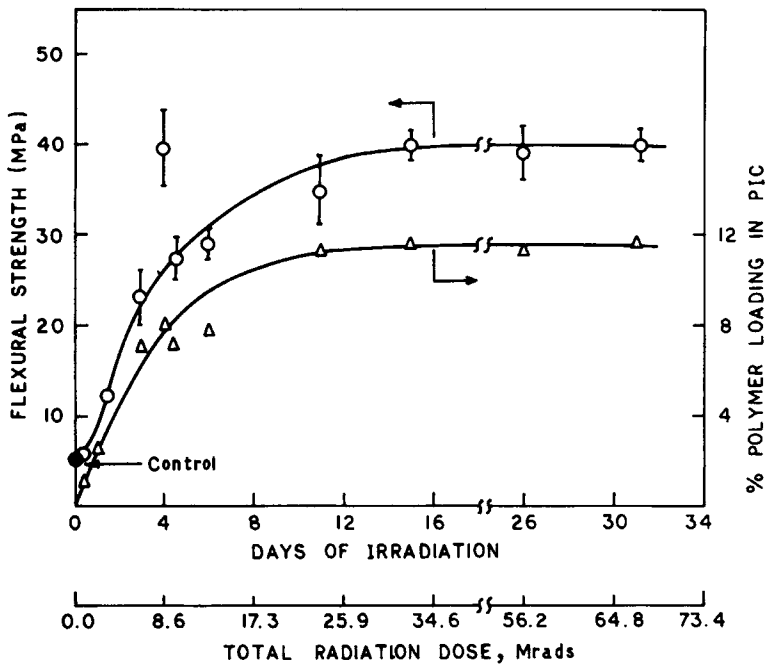


Fig. 8. Variation of flexural strength and % polymer loading in PIC-MSC (13:87) system with days of irradiation.

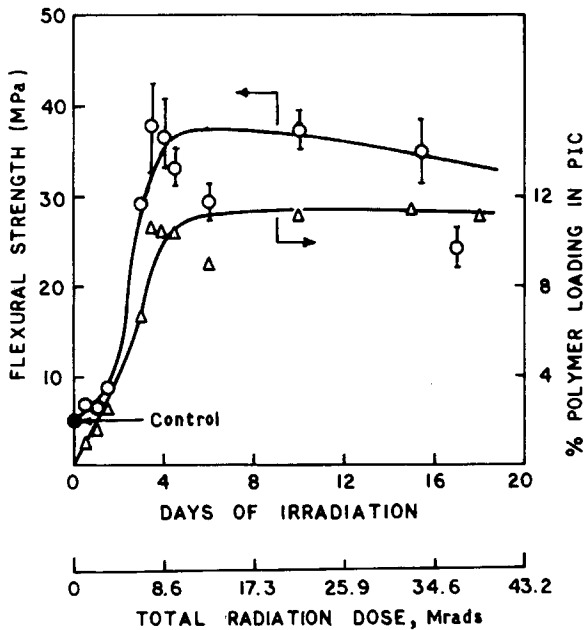


Fig. 9. Variation of flexural strength and % polymer loading in PIC-MSC (40:60) system with days of irradiation.

with increase in MMA content of the copolymer. Similar results have also been reported by Chang et al.³

It is interesting to note that in the case of the PIC-MS (40 : 60) composite a decline in flexural strength is observed beyond 17 Mrad (Fig. 9), which is the same at which a maximum in \bar{M}_v of the copolymer in situ was noted (Fig. 7). This points to a definite relation existing between \bar{M}_v of the impregnated copolymer and the flexural strength of the composite. A similar correlation has also been observed in the case of PIC-PMMA composites.²

In the case of PIC-MS (13 : 87) system, the flexural strength of the composites remained unaffected upon overexposure to gamma radiations (Fig. 8). This may be attributed to cross-linking of the impregnated MS (13 : 87) under the influence of gamma radiation. However, a parallel increase in \bar{M}_v of MS (13 : 87) beyond the optimum radiation dose (Fig. 6) has not been reflected in the flexural strength of the PIC-MS (13 : 87) composites. It may be mentioned that the trend of the flexural strength of PIC-MS (13 : 87) composites is similar to that observed in the case of PIC-PS,¹ although in the latter case a marginal increase in the flexural strength of the composites has been observed upon overexposure to gamma radiation beyond 15 Mrad.

CONCLUSION

Polymerization of S-MMA monomer mixture under the influence of Co-60 gamma radiation is faster in a mortar matrix than in the bulk. Maximum loss of monomer during polymerization and total dose of gamma radiation required for optimum conversion are intermediate between those observed with either monomer, S and MMA. Both the maximum monomer conversion and the maximum polymer loading are, however, greater in the case of mixed monomer feed than those with the component monomers. The flexural strength of the copolymer-mortar composites are higher than that of the component homopolymers. The results suggest that the monomer feed composition of 87% S and 13% MMA offers the best compromise between the advantages and disadvantages of the individual monomers and is characterized by lower monomer loss, highest monomer conversion and polymer loading, and little deterioration of flexural strength on overexposure to radiation.

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