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STUDIES ON GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE IN NATURAL RUBBER LATEX INDUCED BY GAMMA RADIATION

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Abstract—Methyl methacrylate graft natural rubber was prepared by initiating the polymerization of methyl metacrylate in natural rubber field latex using γ rays. The combined effect of radiation and chemical initiation was also studied. Properties of these graft rubbers were compared with those prepared using only redox catalysts.

INTRODUCTION

When polymers are subjected to high energy radiation, free radicals are formed which can be used to synthesize graft and block copolymers.[1] The direct irradiation of natural rubber in latex form or in the solid state in contact with a vinyl monomer is found to result in graft copolymerization. The irradiation of natural rubber swollen with methyl methacrylate has been investigated by Angier and Turner[2] and the graft copolymer was isolated by fractional precipitation and characterized by solution viscosity, ozonolysis and osmometry. Cockbain *et al.*[3] have studied the film forming properties of graft copolymer lattices of methyl methacrylate and natural rubber prepared using γ radiation.

The present study involves standardization of the conditions for graft copolymerization of methyl methacrylate with natural rubber using γ radiation. The effect of incorporating different concentrations of redox initiator in natural rubber field latex on the efficiency of radiation grafting is also studied. The properties of these graft copolymers are compared with those of graft copolymer prepared using redox catalysts.[4]

EXPERIMENTAL PROCEDURE

Materials

Natural rubber field latex preserved with 1% ammonia was used as the starting material. Methyl methacrylate (MMA) was freed from inhibitor by washing first with 10% solution of sodium hydroxide and then with distilled water and finally dried over anhydrous sodium sulphate.

Polymerization by gamma radiation

A gamma chamber Model 900 supplied by the Bhabha Atomic Research Centre, Bombay, was used as the source for γ radiation. Dose rate was 0.36 Mrad/h.

Methyl methacrylate graft natural rubber was prepared using γ radiation as source of initiation and also using redox catalysts. The latter was used as the control. In both cases NR and MMA were mixed in the ratio 1.5:1

Standardization of radiation dose

A 50% emulsion of methyl methacrylate was prepared by mixing the monomer under stirring with equal weight of water containing ammonium oleate as the emulsifying agent. It was then mixed with field latex preserved with 1% ammonia in the ratio of 1:1.5 by dry weight. The mixture was divided into six equal parts and each subjected to a total radiation dose ranging from 0.06 to 0.35 Mrad. The irradiated lattices were kept overnight and then coagulated by slowly pouring into boiling water containing 2% acetic acid. The coagula were washed, dried at 70°C and the percentage yield of the product which was a mixture of graft copolymer, free polymethyl methacrylate and unreacted rubber, was determined in each case. Results are given in Fig. 1.

Incorporation of initiator

Cumene hydroperoxide was added to methyl methacrylate emulsion at concentrations of 0, 0.087 and 0.175 parts per hundred parts (phr) of rubber. These were then separately mixed with ammonia preserved field latex, irradiated at a dose of 0.18 Mrad and the product was isolated as in the previous method. The yields obtained are given in Fig. 2.

The graft copolymer was isolated from the mixture by first extracting the sample with acetone for 48 h to remove the free polymethyl methacrylate. Then the samples were dried and again extracted with petroleum ether for 48 h to remove the free rubber. The results obtained are given in Fig. 3.

Polymerization by redox catalysts

Methyl methacrylate graft natural rubber was prepared by redox catalysts using the procedure reported

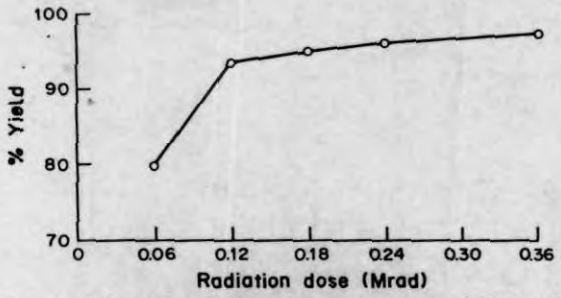

Fig. 1. Effect of radiation dose on percent yield (total solid = graft + homopolymer).

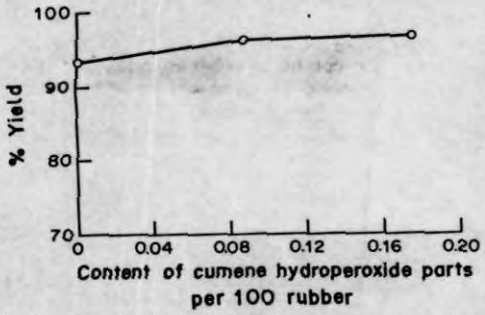

Fig. 2. Combined effect of radiation and cumene hydroperoxide on percent yield.

earlier,[5] with 0.35 phr cumene hydroperoxide (CHP) as initiator and 0.30 phr tetraethylene pentamine (TEP) as activator. Yield of the product and the graft copolymer content in it were determined as described earlier.

Yield and the graft copolymer obtained for the products prepared by the chemical and radiation methods are given in Table 1.

Characterization of the product by infrared studies

Infrared (i.r.) studies were carried out on the products obtained by the above three methods. The graft copolymer purified by solvent extraction was used in each case for taking the i.r. spectrum. The copolymer was dissolved in toluene and cast into a film on a sodium chloride cell and the i.r. spectrum was taken in the frequency range of 4000–625 cm^{-1}. In all cases, absorption peaks were obtained at 1380 and 1730 cm^{-1} respectively to $-CH_3$ group of NR and C=O groups of methyl methacrylate. The presence of these two absorption peaks conclusively proves that

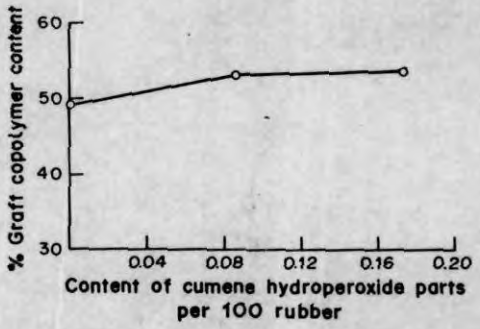

Fig. 3. Combined effect of radiation and cumene hydroperoxide on percent graft copolymer content.

grafting of methyl methacrylate to NR has taken place. The i.r. spectrum for the graft copolymer obtained by radiation initiation is given in Fig. 4. The graft copolymers prepared by chemical initiation and that obtained by the combined chemical and radiation effects were also found to give identical peaks.

Evaluation of physical properties

After studying the effect of radiation dose and incorporation of initiators, about 1 kg each of methyl methacrylate graft NR was prepared at the optimum conditions.

1. By γ irradiation at a radiation dose of 0.18 Mrad with no initiator and activator (I)
2. By γ irradiation at a radiation dose of 0.18 Mrad in presence of 0.087 phr CHP (II)
3. By redox initiation at a concentration of 0.35 phr CHP and 0.30 phr TEP (III)

The properties of the graft rubbers prepared by methods I and II were compared with those prepared by method III, in (a) gum and (b) filled compounds. The recipe used for the comparative study is given in Table 2.

Rubber and the compounding ingredients were mixed on a 6 × 12 in. two-roll mixing mill. The rubber compounds were evaluated for curing characteristics and vulcanizate properties as per the relevant ASTM standards.

Processing and physical properties of the vulcanizates are given in Table 3.

RESULTS AND DISCUSSION

It may be seen from Fig. 1 that the yield of product increased with increase in radiation dose

Table 1. Effect of conditions of grafting on yield and graft copolymer content

Experiment No.	Method of grafting	Yield (%)	Polymethyl methacrylate (%)	Free NR (%)	Graft polymer (%)*
I	Gamma irradiated sample exposed to a radiation dose of 0.18 Mrad	93.8	23	28	49
II	Treatment of the sample with 0.087 phr cumene hydroperoxide and then exposed to a radiation dose of 0.18 Mrad	96	20.5	26.5	53
III	Treatment of sample with 0.35 phr cumene hydroperoxide and 0.3 phr tetra ethylene pentamine	92	11.5	34.5	54

* As percentage of total product—graft + homopolymers.

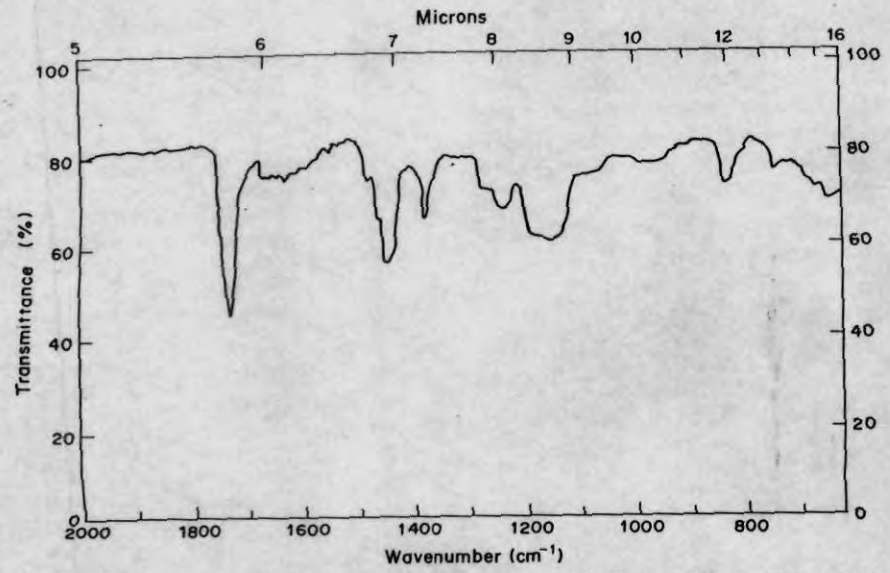

Fig. 4. Infrared spectrum of methyl methacrylate graft natural rubber initiated by γ radiation (0.18 Mrad).

Table 2. Recipe used for compounding graft rubbers

Compounding ingredients	Parts by weight					
	Ia	IIa	IIIa	Ib	IIb	IIIb
Graft rubber*	167.0	167.0	167.0	167.0	167.0	167.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
Styrenated phenol	1.0	1.0	1.0	—	—	—
Phenyl β-napthylamine	—	—	—	1.0	1.0	1.0
SRF Black	—	—	—	30.0	30.0	30.0
Naphthenic oil	—	—	—	4.0	4.0	4.0
Dibenzthiazyl disulphide	1.0	1.0	1.0	1.0	1.0	1.0
Diphenyl guanidine	0.3	0.3	0.3	0.3	0.3	0.3
Sulphur	3.5	3.5	3.5	3.5	3.5	3.5

* Contains homopolymers.

But exposure to γ radiation for dosages above 0.18 Mrad had no favourable effect on grafting. Hence the optimum radiation dose was selected as 0.18 Mrad.

From Fig. 2, it can be seen that incorporation of chemical initiator increased the yield in the case of radiation grafting. But when the initiator concentration was increased to more than 0.087 phr, the effect was not appreciable. Figure 3 showed that the amount of graft copolymer increased with the addition of initiator up to a level of 0.087 phr of cumene hydroperoxide on 100 phr of rubber and above that the effect was not marked. Hence the optimum concentration of initiator was fixed as 0.087 phr cumene hydroperoxide. From Table 1, it could be seen that in irradiated samples graft copolymer content became equal to that in the sample prepared by redox initiators, only when about 25% of the initiator required for redox grafting was present in latex while it was subjected to radiation.

Results in Table 3 showed that properties such as modulus and hardness were superior for samples I and II over the control. Tear strength and rebound resilience were comparable for all three samples. But properties such as tensile strength, elongation at break, compression set and abrasion resistance were slightly inferior for sample I when compared to samples II and III.

Table 3. Physical properties of vulcanizates

Properties	Ia	IIa	IIIa	Ib	IIb	IIIb
Optimum cure time Rheometer at 150 C (min)	8.5	11.0	8.5	8.0	8.5	7.0
Tensile strength (kg/cm²)	190.0	220.0	223.0	183.0	186.0	187.0
Elongation at break (%)	323.0	400.0	460.0	287.0	323.0	353.0
Modulus at 100% elongation (kg/cm²)	90.0	85.0	67.0	106.0	95.0	75.0
Modulus at 300% elongation (kg/cm²)	172.0	171.0	147.0	—	177.0	164.0
Tear strength (kg/cm)	86.0	86.0	86.0	85.0	85.0	86.0
Hardness, Shore A	94.0	94.0	91.0	94.0	94.0	91.0
Compression set, 22 h at 70 C, 25% strain, 30 min recovery	90.2	80.6	78.3	85.3	77.9	76.7
Rebound resilience (%)	41.1	44.5	43.4	40.0	42.2	42.2
Din Abrasion loss (mm³)	—	—	—	184.4	169.3	168.2

CONCLUSION

The study shows that the properties of methyl methacrylate graft natural rubber prepared by radiation initiation are almost comparable to that prepared by chemical initiation. Slightly better properties are obtained for methyl methacrylate graft natural rubber prepared from latex by combination of irradiation and chemical initiation. Use of activator was found unnecessary in this case.

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