Radiation Induced Graft Copolymerization Of Styrene Onto Natural Rubber

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Abstract

Natural rubber was modified by graft copolymerization with styrene using ^{60} Co gamma radiation. The modified rubber (designated as SGNR) was a mixture of free NR, free polystrene and polystrene graft natural rubber. The SGNR was evaluated in comparision with high styrene resins in the production of microcellular solings. Results indicated that SGNR could be used as a substitute for high styrene resins.

Introduction

Modified forms of natural rubber are aimed at extending the areas of applications of the natural product. When vinyl monomers are polymerized in the presence of natural rubber under suitable conditions, some of the new polymeric chains get attatched to the rubber molecules and graft copolymer rubbers are obtained. These graft rubbers posses properties of both natural rubber and the vinyl polymer. In this way the properties of natural rubber can be significally modified according to the type and quantity of the grafted chain.

Various monomers like methyl methacrylate, styrene, acrylonitrile etc. have been used to produce graft copolymers from natural rubber. The most widely used method for grafting vinyl monomers onto natural rubber is redox polymerization. Methyl methacrylate graft natural rubber (Heveaplus MG) is commercially produced in Malaysia using the above technique[1]. The processes of styrene graft NR and acrylonitrile graft NR using redox polymerization, were also reported[2,3]. An alternative method for initiating graft copolymerization is irridation with gamma rays. Irradiation of natural rubber swollen with methyl methacrylate was investigated by Angier and Turner[4]. Cockbain et al[5] studied the film forming properties of graft copolymer latex of methyl methacrylate and natural rubber prepared using γ-radiation. Methyl methacrylate graft copolymerization on NR latex and its extrusion molding were studied by Seiji Ono et al[7]. A study on acrylonitrile graft NR prepared by γ-ray initiation was also reported[8].

This paper reports a process for the production of polysterene graft natural rubber using gamma radiation and its evaluation in the production of microcellular solings. At present different high styrene resins (HSR), which are copolymers of styrene and butadiene are being used for the above purpose. In India about 30000 tonnes of HSR isbeing consumed by the footwear industry per annum, of which about half the quantity is being imported. The suggested method of production of SGNR is comparatively simple and cost effective compared to redox polymerization.

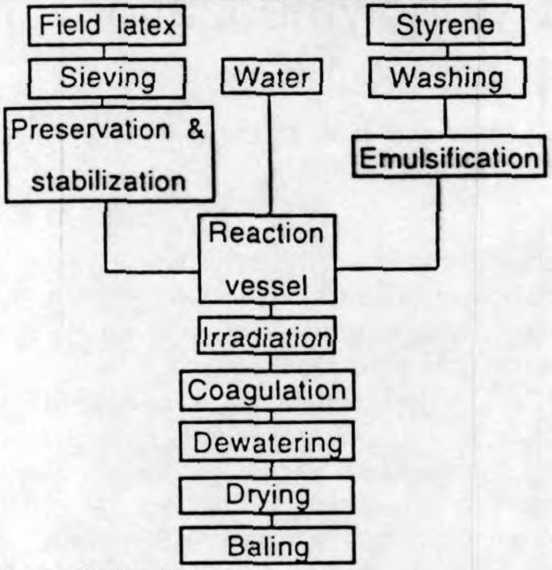
Materials

Natural rubber latex collected from RRII experiment station and commercial grade of styrene (b.p 145°C) were used. Styrene was washed first with 10% sodium hydroxide solution to free it from inhibitor and then with water.

Graft Copolymerizaton

A gamma chamber model 5000 supplied by the Bhabha Atomic Research Centre, Mumbai was used as the radiation source for standardization of the process. The dose rate was 1.3 kGy/h. Large scale trials were conducted in the pilot plant of the Rubber Board (^{60}Co source, capacity 1000 L, dose rate 1.5kGy/h). Field latex (preserved with 1% ammonia and stabilized with 0.4% potassium oleate) and styrene as 50% emulsion were mixed in the ratio, NR:styrene = 1:1. The latex mixture was diluted to 10% DRC, irradiated to the requred dose, coagulated using formic acid, dried and baled. A flow chart showing the sequence of operations is given below.

Production Flow Chart



Charecterization

The modified rubber was first extracted with petroleum ether for 48 h to remove free NR and then with methyl ethyl ketone for 48 h to remove free polystyrene. The isolated graft copolymer was characterized using IR spectroscopy.

Evaluation in microcellular soling

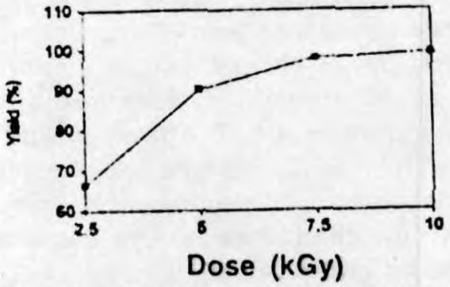
Microcellular solings were prepared using the modified rubber (SGNR) and high styrene resins (SBR 1958 and NIPPON HS 860) and their properties evaluated as per the relevant BIS standards (IS 10702; 1992).

Results And Discussions:

Figure 1 shows the effect of radiation dose on yield of the product. The yield increased with increase in radiation dose. The rate of increase slows down after a radiation dose of 7.5 kGy. Therefore optimum radiation dose was selected as 7.5kGy.

Figure 1

Effect of dose on yield



The experiment was repeated at different dilutions of the latex mixture at a radiation dose of 7.5 kGy.

Figure 2

Effect of dilution on yield

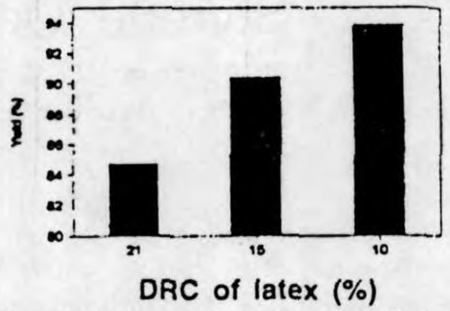
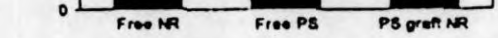


Figure 2 shows the effect of dilution of late mixture on yield of the product. It can be see that as dilution increased yield of the produc increased. Therefore a dilution to 10% DRC ha been selected. Latex contains a rubber phas and an aqueaus phase. When polymerization i rubber latex is intiated by gamma irradiation radicals are generated in both phases[9]. Th hydroxyl radical generated in the aquous phas can react with unsaturated organic compound either by addition to the double bond or by H abstraction, thereby creating more free radica sites. This may be attributed to the increase i yield as dilution is increased.

Figure 3 shows the composition of the modified rubber.

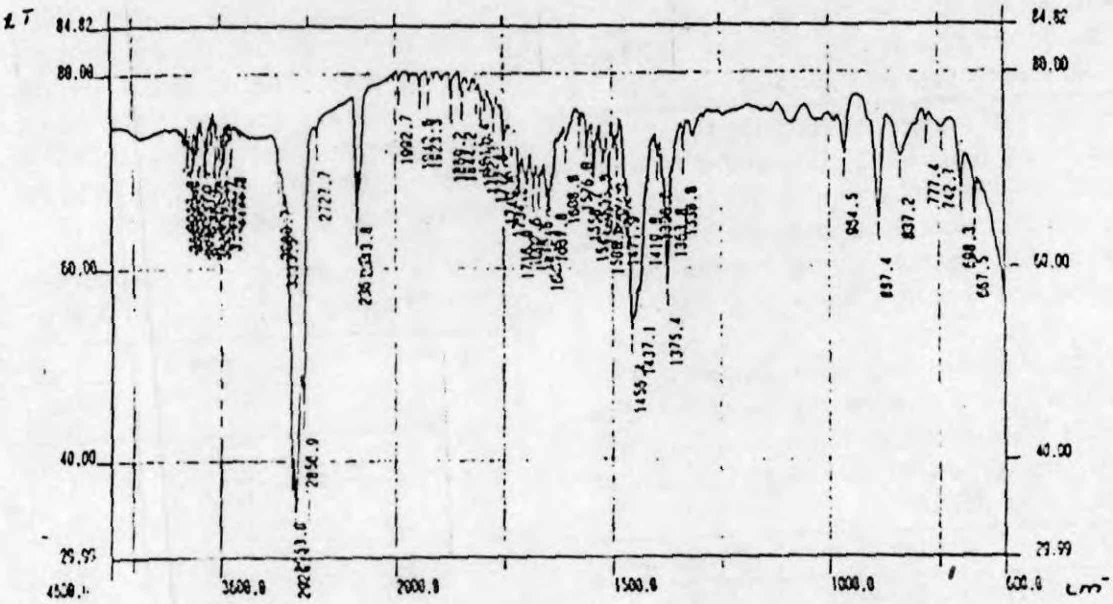
Figure 3

Composition of the modified rubber



The modified rubber is a mixture of fre natural rubber, free polystyrene and polystyren graft natural rubber as shown above.

Figure 4 FTIR Spectrum of isolated graft rubber



gure 4 shows the FTIR spectrum of the isolated raft rubber (after removing free NR and free olystyrene). Peaks at 3026 and 2855 cm^{-1} rrespond to the aromtic C-H stretching in olystyrene. Peaks at 1601 and 1541 cm^{-1} rrespond to the C=C stretching of aromatic ng of polystyrene. Astrong peak at 698 cm^{-1} ands for the monosubstituted benzene ring ong with the characteristic absorptions of NR 837 and 889 cm^{-1}. The peaks at 1452 and 375 cm^{-1} correspond to the aliphatic C-H retching in NR.

The modified rubber contained only 60.75% raft rubber. But for most industrial products a ure graft copolymer is not required and even e presence of 2 to 5% of the graft copolymer sufficient to improve the physical properties of e material, since the presence of a small mount of block or graft copolymer acts as a oap" reducing the tendency to phase eparation. Hence the modified rubber without emoving free NR and free polystyrene, esignated as SGNR, was used for further tudies.

valuation in microcellular soling

About 250 kg of SGNR was prepared in the pilot plant and used for evaluation. Microcellular solings were prepared in the laboratory using SGNR and SBR 1958 as per the formulation given in Table 1 and their properties are given in Table 2.

Table 1. Formulation of the rubber compounds

Ingredients	Parts by weight I	Parts by weight II
NR	70	70
SBR 1958	30	-
SGNR	-	30
Zinc Oxide	5	5
Stearic Acid	6	6
A/o styrenatedphenol	6	6
Titanium dioxide	5	5
China clay	100	100
Precipitated silica	20	20
Calcium silicate	15	15
CI Resin	5	5
Naphthenic oil	10	10
Diethylene glycol	2	2
Vulcafor F	1.2	1.2
DNPT	6	6
Sulphur	2.25	2.25

Table 2. Properties of the microcellular soilings

Properties	I	II
Specific gravity	0.481	0.538
Hardness (ShoreA)	40	41
Compressionset(%)	32.5	25.5
Splittearstrength(kg)	2.9	2.8
DINAbrasionloss(mm)^3	422	489

It is seen that the properties of the M.C soiling prepared using SGNR are comparable to those of the MC soiling containing SBR 1958.

The product was also evaluated by three leading footwear manufacturers in India, whose observation are reported below.

Unit I.

The specifications laid down by the unit for microcellular soiling and the results obtained by using SGNR are given in Table 3.

Table 3. Properties of Microcellular soiling prepared using SGNR

Properties	Requirements	Result obtained
Specific gravity	0.55±0.05	0.56
Hardness (Shore A)	55±5	59
Compression set (%)	25	22.6
RossFlexing 60,000	Nocrack	No crack
Shrinkage at100°C(%)	3	2.9
Abrasion loss (cc)	3	1.6
Thickness (mm)	15+2	15.6

Results show that the microcellular solings prepared using SGNR in place of SBR 1958 are meeting the specified requrements of Unit I.

Unit II

M.C solings preparedusing SBR 1958 and NIPPON HS 860 as controls were compared with that prepared using SGNR. Comparable properties were obtained as is shown in Tables 4 and 5.

Table 4. Properties of M.C soilings prepared using 1958 and SGNR

Properties	SBR1958	SGNR
Specific gravity	0.48	0.46
Hardness (Shore A)	60	60
Compression set (%)	10.8	11.8
Split tear strength (kg)	4.2	3.5
DIN Abrasion loss (mm^3)	233	253
Shrinkage at 100°C (%)	5.5	5.4

When SGNR was compared with NIPPON HS 860, the quantity of SGNR was adjusted so as to equalise the styrene content to that in NIPPON HS 860 (styrene content in SGNR is 47% while that in NIPPON HS 860 is 60%). The above unit compared kneader mixed and mill mixed samples also. The kneader mixed samples showed better properties. This may be due to higher temperature in the mixing chamber which leads to better softening and effectively oncorporation of the resin.

Table 5. Properties of microcellular soilings prepared using Nippon HS 860 and SGNR

Properties	Nippon HS 860	SGNR	
		Kneader mixed	Mill mixed
Specific gravity	0.460	0.525	0.415
Hardness (Shore A)	54	58	52
Compression set (%)	12	8.2	17.5
Split tear strength (kg)	5	4.9	3.2
Abrasion loss (%)	28.9	20.2	-
Shrinkage at 100°C (%)	1.96	1.96	3.97

Unit III

Table 6 shows the properties of M.C soilings prepared using SBR 1958 and SGNR. The properties are comparable.

Table 6. Properties of M.C solings prepared using SBR 1958 and SGNR

Properties	SBR1958	SGNR
Specific gravity	0.491	0.473
Hardness (Shore A)	46	41
Compression set (%)	26.7	20.4
Din abrasion loss (mm^3)	186.5	232.7
Split tear strength (kg)	7.4	6.2
Shrinkage at 100°C (%)	3.9	3.8

These results confirm that polystyrene modified NR could be used as a substitute for high styrene resins in microcellular soling production.

Acknowledgement

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