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RADIATION INDUCED GRAFT COPOLYMERIZATION OF ACRYLONITRILE ON NATURAL RUBBER

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Abstract—Acrylonitrile graft natural rubber was prepared by initiating the polymerization of acrylonitrile in natural rubber field latex using γ-rays. The reaction was carried out at different rubber–monomer concentrations and the properties of the modified rubbers were compared with those of natural rubber and nitrile rubber.

INTRODUCTION

Modification of natural rubber (NR) by graft copolymerization with vinyl monomers has been extensively studied in the past with a view to impart new and desirable properties to NR. Initiation by irradiation is one of the methods for graft copolymerization of vinyl monomers. Brief reports are available on the radiation grafting of acrylonitrile (Ballantine *et al.*, 1956) parachloro and dichlorostyrene (Mesrobian, 1958) on natural rubber. The grafting of methylmethacrylate (Angier and Turner, 1958; Cooper *et al.*, 1959a, b; Cooper and Vaughan, 1959; Cockbain *et al.*, 1958, 1959; Mariamma George *et al.*, 1987) and styrene (Turner, 1959) was investigated in greater detail. Mazam *et al.* (1983) studied the modification of natural rubber in the presence of vinyl monomers like glicidyl methyl methacrylate, hydroxyl ethyl methyl acrylate and diethyl aminomethyl methacrylate by γ-radiation. The present study involves the standardisation of the condition for graft copolymerization of acrylonitrile (AN) on natural rubber in the latex stage using γ-radiation, with a view to impart oil and solvent resistance to the latter. The reaction was carried out at different rubber–monomer compositions and the properties of the modified rubbers so obtained were compared with those of natural rubber and nitrile rubber.

EXPERIMENTAL

Natural rubber latex collected from RRII Experiment Station and acrylonitrile (Reagent grade) after removing inhibitor were used as the starting materials.

Polymerization by γ-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 0.30 Mrad/h.

Method

Fresh natural rubber field latex was sieved through 40 and 60 mesh sieves and stabilised with 1% NH_3 (v/v). The required quantity of acrylonitrile (freed from inhibitor) was added to the latex with stirring. Stirring continued for 30 min. The latex was then exposed to Co^{60} source for a predetermined time. The irradiated latex was coagulated with 1% formic acid and the coagulum pressed, dried at 50°C and the yield was noted.

Standardisation of radiation dose

Forty parts of acrylonitrile was mixed with 60 parts (dry weight) of natural rubber as latex and exposed to radiation ranging from 0.075 to 0.75 Mrad. Dry weight of the product obtained in each case was noted. The results are given in Fig. 1. Like in any graft polymerization reaction the product obtained in this case is a mixture of free natural rubber, acrylonitrile graft natural rubber and free polyacrylonitrile. The actual graft copolymer was isolated from the mixture by extracting first with petroleum ether to remove free NR and then with dimethyl formamide to remove free poly AN. The data on the characterization is given in Table 1.

Effect of monomer concentration

Acrylonitrile was mixed natural rubber latex in different proportions viz.; 20, 30, 40 and 50 parts of

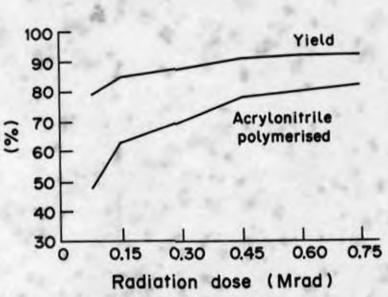

Fig. 1. Effect of radiation dose on yield (dry weight of product) and the amount of acrylonitrile polymerised.

Table 1. Characterization data

Radiation dose (Mrad)	Free NR (%)	Free Poly AN (%)	Graft copolymer (%)
0.075	46.2	9.8	43.9
0.15	39.3	12.9	47.8
0.30	21.2	18.3	60.5
0.45	12.7	18.9	68.4
0.60	8.6	19.5	71.9
0.75	7.4	19.9	72.7

acrylonitrile was mixed with 80, 70, 60 and 50 parts (dry wt) of NR latex respectively and irradiated for 0.45 Mrad followed by coagulation with 1% formic acid. Dry weight of the product and the actual graft copolymer present in each case were also determined. The results are given in Fig. 2 and Table 2.

Technological properties of vulcanizates

Modified NR of varying acrylonitrile content were prepared as described earlier and the polymer mixture as such without extracting free NR and free poly AN were used for studying the technological properties. The formulations are as shown in Table 3. The properties of the vulcanizates were determined as per the relevant ASTM standards.

RESULTS AND DISCUSSION

Figure 1 shows the effect of radiation dose on yield and the amount of acrylonitrile polymerised. As the radiation dose is increased, the total yield and the percentage of monomer polymerised increase. Since there is 100% recovery of NR as indicated by a clear serum, the total yield is dependent on the acrylonitrile present in the product either as graft or as homopolymer. The percentage of acrylonitrile polymerised is calculated as

$$\frac{(\text{Total recovered material} - \text{wt of NR})}{\text{Weight of acrylonitrile added to latex}} \times 100.$$

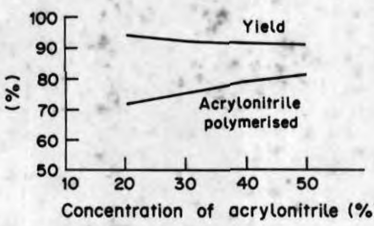

Fig. 2. Effect of concentration of acrylonitrile on yield (dry weight of product) and the amount of acrylonitrile polymerised.

Table 2. Characterization data

NR:AN in the reaction medium	Free NR (%)	Free Poly AN (%)	Graft copolymer content (%)
80:20	18	11	71
70:30	14	17	69
60:40	11	22	67
50:50	7	28	65

Radiation doses above 0.45 Mrad had no remarkable effect in increasing the percentage of acrylonitrile polymerised. Characterisation studies as shown in Table 1 also reveal that the graft copolymer formation increases on increasing the radiation dose and above 0.45 Mrad the increase is only nominal. Therefore for further studies, the radiation dose was fixed as 0.45 Mrad.

Figure 2 shows the effect of acrylonitrile concentration on yield and the amount of acrylonitrile polymerised. As the acrylonitrile concentration is increased the percentage conversion of monomer to polymer increases. Characterization of the products (Table 2) shows that as the monomer concentration is increased, the amount of free polyacrylonitrile increases and free NR decreases and the products contain 65–71% graft copolymer.

Table 3. Compounding recipe

	Parts by weight					
	I	II	III	IV	V	VI
Natural rubber	100	—	—	—	—	—
Modified rubber (AN content 15%)	—	100	—	—	—	—
Modified rubber (AN content 25%)	—	—	100	—	—	—
Modified rubber (AN content 35%)	—	—	—	100	—	—
Modified rubber (AN content 45%)	—	—	—	—	100	—
Nitrile rubber (AN content 30%)	—	—	—	—	—	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1
Phenyl β naphthylamine	1	1	1	1	1	1
SRF black	50	50	50	50	50	50
Naphthenic oil	5	5	5	5	5	—
Dibutyl phthalate	—	—	—	—	—	5
Cyclohexyl benz thiazyl sulphenamide	3.5	3.5	3.5	3.5	3.5	3.5
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5

Table 4. Properties of vulcanizates

	Properties	Compound No.					
		I	II	III	IV	V	VI
1.	Modulus at 200% elongation (N/mm^2)	4.5	6.4	8.7	10.2	—	3.1
	Retention after ageing at 70°C for 96 h (%)	104	118	114	103	—	110
2.	Tensile strength (N/mm^2)	24.3	17.8	14.8	10.6	8.9	9.4
	Retention after ageing at 70°C for 96 h (%)	93	97	97	99	108	105
3.	Elongation at break (%)	746	503	383	220	65	538
	Retention after ageing at 70°C for 96 h (%)	83	92	89	93	385	98
4.	Tear strength (N/mm)	74	60	68	59	42	49
5.	Hardness (Shore A)	51	64	74	86	96	54
6.	Compression set (%)	18	24	30	47	58	28
7.	Abrasion loss (CC/h)	3.7	2.5	2.6	7.2	9.6	3.5
8.	Resilience (%)	61	56	43	40	35	39

In order to compare the properties of the modified NR of varying acrylonitrile content with those of NR and nitrile rubber, compounds were prepared as per recipe shown in Table 3. The properties of the vulcanizates are given in Table 4. Table 4 reveals that as the acrylonitrile content is increased, there is substantial improvement in the modulus and hardness of natural rubber. But a drop in tensile strength, tear strength, elongation at break, resilience and compression set resistance are also observed.

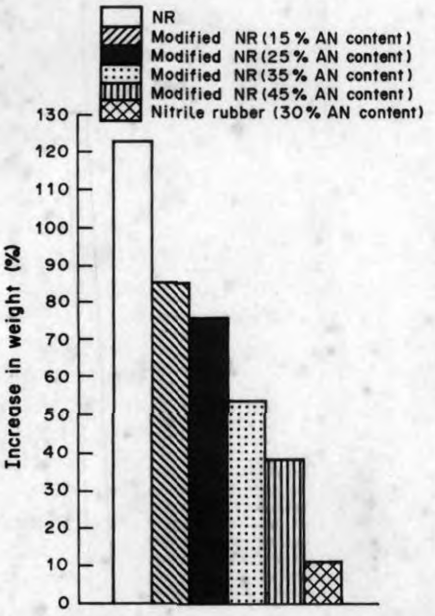

Fig. 3. Effect of immersion in petrol at room temperature for 70 h.

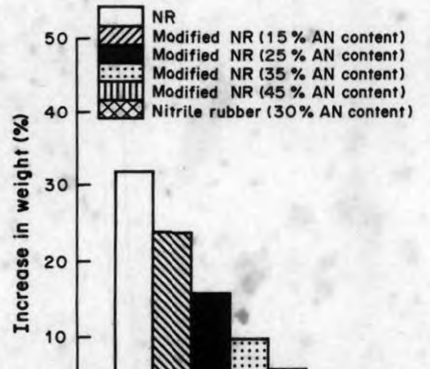

Fig. 4. Effect of immersion in hydraulic oil at room temperature for 70 h.

The effects of immersion of the samples in petrol and hydraulic oil for 70 h at room temperature are depicted in Figs 3 and 4 respectively.

It can be seen that the petrol and oil resistance of NR is substantially improved by grafting with acrylonitrile. As the acrylonitrile content is increased the resistance to swelling in petrol and oil is also increased. But the modified NR of even 45% AN content has only a lower level oil and solvent resistance than that of nitrile rubber of 30% AN content, as shown in Figs 3 and 4.

CONCLUSION

A method for preparing acrylonitrile graft NR using γ-radiation was developed. Modified rubbers of different acrylonitrile content were prepared and their properties studied. The oil and solvent resistance of NR can be substantially improved by graft copolymerization with acrylonitrile. However, the oil and solvent resistance of the modified rubbers are not found to be as good as those of nitrile rubber.

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