156

GRAFT COPOLYMERISATION OF ACRYLONITRILE WITH NATURAL RUBBER

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INTRODUCTION

Graft copolymers are particular kinds of polymers in which a second monomer is copolymerised with an existing polymer. When vinyl monomers are polymerised in presence of natural rubber (NR) under suitable conditions, some of the new polymeric chains formed, get attached to rubber molecules and a graft copolymer is obtained. These graft copolymers have a combination of properties of both natural rubber and the vinyl polymer. In this way the properties of natural rubber can be widely modified according to the nature and quantity of the graft copolymer.

Polymerisation reactions of various vinyl monomers dispersed in natural rubber latex have been reported (Bloomfield et al 1954. Burfield & Ng 1975, Rajammal et al 1980). The most promising graft copolymers based on natural rubber, so far obtained are those derived from methyl methacrylate and styrene. Acrylonitrile (ACN) when grafted with natural rubber, gives a reinforced material with improved resistance to oils and solvents (Naunton 1961). Graft copolymers of natural rubber containing acrylonitrile have been made from latex (Fernando et al 1978).

Polymerisation of acrylonitrile monomer to polyacrylonitrile using potassium persulphate/sodium bisulphite initiator system has been reported (Sorenson & Campbell 1961). This paper discusses the standardisation of a procedure for graft copolymerisation of acrylonitrile with natural rubber in latex stage, using potassium persulphate/sodium bisulphite initiator system. The technological properties of the resultant product have also been evaluated in comparison with, those of natural rubber and nitrile rubber.

MATERIALS AND METHODS

Field latex collected from RRII Experiment Station and acrylonitrile (Reagent Grade) were used as the Starting materials. Other chemicals like sodium lauryl sulphate, potassium persulphate and sodium bisulphite were of AR grade.

Acrylonitrile was graft copolymerised with natural rubber field latex using potassium persulphate/sodium bisulphite initiator system. For evolving the optimum conditions for the graft reaction, the following factors were studied.

Concentration of latex stabiliser

Ammonia is the most suitable preservative for natural rubber latex. But polymerisation of acrylonitrile is inhibited by ammonia (Mark et al 1964) and hence ammonia was not used as the preservative for natural rubber latex in the present study. The suitability of other stabilizers like ethylene oxide condensate (Vulcastab LW) and sodium lauryl sulphate at different concentrations (2·5 to 7·5 phr) was studied. The recipe used for the study was as follows :

Ingredients	*Parts by Weight* *Dry*	 *Wet*
Field latex (35% DRC)	100	286
Acrylonitrile	66·7	66·7
Stabiliser	varying	varying
Potassium persulphate (20%)	5	25
Sodium bisulphite (10%)	2·5	25

Temperature — Room temperature (30°C)

Period of reaction — 24 hrs.

Field Latex was suitably stabilised and acrylonitrile, after removing inhibitor, was added to the latex with stirring. When complete dispersion was effected potassium persulphate as a 20% solution was stirred in. Stirring was continued for 30 minutes. Sodium bisulphite as a 10% solution was then added with stirring. The reaction vessel was closed and kept undisturbed for 24 hrs. The reacted latex was then coagulated using 10% calcium chloride solution. The coagulum was filtered, washed, dried and weighed.

Concentration of initiator

The above reaction condition was used for fixing up the concentration of initiator. Stabiliser used for the study was sodium lauryl sulphate at a concentration of 7·5 phr. The concentration of initiator was varied from 1 to 6 phr of potassium persulphate/0·5 to 3 phr of sodium bisulphite. The yield of the product obtained in each case was noted. Results obtained are given in Table I.

Table 1. *Effect of concentration of initiator on yield*

Concentration of initiator (phr) $K_2S_2O_8/NaHSO_3$	Yield (%)
1·23/0·62	61·0
2·46/1·23	61·5
3·69/1·84	88·6
4·92/2.46	96.0
6·15/3·07	96·5

Period of reaction

The reaction was allowed to continue for various periods of time keeping all other conditions constant, as stated earlier. The concentration of initiator used was 5 phr of potassium persulphate/2·5 phr of sodium bisulphite. The products obtained were extracted with petroleum ether to remove free natural rubber and then with Dimethyl formamide to remove free polyacrylonitrile and the amount of graft product obtained was calculated. Total yield in each case was also noted. The data obtained are given in Table 2.

Table 2. *Effect of time of reaction on yield and amount of graft product*

Time of reaction (hr)	Yield (%)	Free NR (%)	Free poly ACN (%)	Graft product (%)
1	78·0	65·8	22·2	12·0
1½	82·4	62·7	24·0	13·3
2	89·5	57·7	27·3	15·0
2½	90·0	55·8	28·4	15·8
3	92·0	52·8	30·7	16·5
5	92·8	52·9	31·2	15·9
7	91·9	52·7	31·2	16·1
9	95·5	52·3	31·3	16·4
24	96 0	51·5	32·0	16·5

Effect of varying acrylonitrile content

The reaction was carried out by varying the amount of acrylonitrile (NR : ACN = 90 : 10, 80 : 20, 70 : 30, 60 : 40) and the yield of the reaction product was determined in each case. Results are given in Table 3.

Table 3. *Effect of concentration of acrylonitrile on yield*

NR : ACN	Yield (%)
50 : 50	96·2
60 : 40	96·5
70 : 30	96·9
80 : 20	97·5
90 : 10	98·5

Graft reaction was conducted by mixing natural rubber latex and acrylonitrile in the ratio, NR : ACN = 60 : 40, at the selected conditions and the technological properties of the product were compared with those of natural rubber and nitrile rubber (chemaprene N — 3309). Compound recipe is given in Table 4. The tensile Strength, elongation at break, modulus at 100% elongation, ageing resistance, tear Strength, hardness, resilience and compression set were determined as per IS 3400. Percentage swell in petrol and hydraulic oil were determined as per ASTM No : D 471 - 79.

Table 4. *Compound formulation*

Ingredients	Parts by weight I	II	III
Natural rubber	100	—	—
Nitrile rubber	—	100	—
Graft rubber	—	—	100
Zinc Oxide	5	5	5
Stearic acid	1	1	1
SRF black	50	50	50
DBP	—	5	5
Aromatic Oil	5	—	—
CBS	3·5	3·5	3·5
Sulphur	0·5	0·5	0·5
Optimum cure time			
Optimum cure time at 150°C (minutes)	13	20·5	9·5

RESULTS AND DISCUSSION

It was observed that the reaction mixture was stable when sodium lauryl sulphate at a concentration of 7·5 phr was used. The results of the study for fixing up the optimum concentration of initiator, as given in Table 1, Show that upto a concentration of 5 phr. of potassium persulphate/2·5 phr of sodium bisulphite, yield is increasing and after that the increase in yield is not much appreciable. So optimum concentration of initiator was fixed as 5 phr of potassium persulphate/2·5 phr of sodium bisulphite. From Table 2 it is seen that as the time of reaction is increased, the yield of the product is also increased and yield is maximum at about 9 hrs. The maximum amount of graft product obtained is 16·5% and for this a minimum time of 3 hrs is required. In the present study the reaction mixture was kept overnight. The results of the yield obtained by varying Acrylonitrile Content, as given in Table 3, show that under the selected conditions more than 96% yield is obtained for all the concentrations studied.

The physical properties of the vulcanisates prepared from Natural Rubber, nitrile Rubber (ACN Content 33%) and graft rubber (obtained by mixing NR and ACN in the ratio 60 : 40) are given in Table 5. It is seen that hardness and modulus at 100% elongation of the graft rubber are superior to those of natural rubber and nitrile rubber. The resistance to swelling in oils and solvents of the graft rubber is much higher than natural rubber but lower than that of nitrile rubber. There is reduction in properties like tensile strength, elongation at break, ageing resistance, tear strength and resilience for the graft rubber.

Although a high percentage recovery of 96% is obtained as a result of the reaction only 16·5% of the reacted product is existing as graft acrylonitrile. The rest of it may be present as free polyacrylonitrile. The variation in some of the physical properties for the product developed may be due to this.

Table 5. *Physical properties of the vulcanisates*

ST. No.	Physical properties	I	II	III
1.	Modulus at 100% Elongation (kg/cm^2)	15·5	13	50
2.	Elongation at break (%)	610	675	200
3.	Tensile strength (kg/Cm^2)	210.	120	75
4.	After ageing at 70°C for 96 hrs.			
	(a) Retention of Modulus at 100% elongation (%)	100	95·2	100
	(b) Retention of elongation at break (%)	90	95	77
	(c) Retention of Tensile strength (%)	98·5	100	85
5.	Hardness (shore A)	52	57	88
6.	Resilience (%)	57	38·5	32
7.	Compression set (%)	21	30	46
8.	Tear strength (kg/cm)	60	53	37
9.	Swelling in petrol after 70 hrs. (%)	195	21	90
10.	Swelling in hydraulic oil after 70 hrs (%)	40	0·5	12·6

CONCLUSION

A method for the preparation of acrylonitrile graft natural rubber was standardised using potassium persulphate/sodium bisulphite initiator system. Oil and solvent resistance of natural rubber is substantially improved by grafting with acrylonitrile. The physical properties like hardness and modulus are enhanced. Properties like tensile strength, elongation at break, ageing resistance, tear strength and resilience are slightly lowered. The procedure gives around 17 percent of graft rubber.

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DISCUSSION

Q — LAL DE ALWIS, (Chemanex Ltd.) : (1) Have the studies of graft copolymerisation of acrylonitrile with NR been scaled up for commercial production ?

(2) What are its applications and advantages over NR ?

A — N. M. CLARAMMA, (RRII) : (1) Percentage of copolymerisation is only 16·5%. Hence this product is not a substitute for nitrile rubbers where resistance to solvents is concerned.

(2) Further work is in progress to increase the degree of coplymerisation.