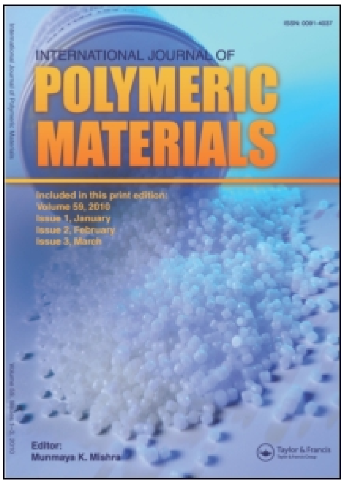

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THERMOPLASTIC IONOMERS BASED ON "STYRENE GRAFTED NATURAL RUBBER"

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Graft copolymer of natural rubber was prepared by polymerizing styrene in natural rubber latex using tertiarybutylhydroperoxide and tetraethylenepentamine through emulsion polymerization. Natural rubber thus reinforced by grafting styrene onto the hydrocarbon backbone was further converted to the ionomer by sulfonating with acetyl sulfate, followed by neutralization of the polymersulfonic acids using zinc acetate in methanol. The "zinc sulfonated styrene grafted natural rubber" designated as x.yZnS-SGNR where x.y shows number of milliequivalents of sulfonic acid/100 g of SGNR, behaves like a thermoplastic elastomer. It shows improved stress-strain properties as compared to the host polymer, styrene grafted natural rubber (SGNR). The modified samples of styrene grafted natural rubber of different sulfonic acid concentrations were prepared and evaluated using X-ray Fluorescence Spectroscopy (XRFS), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICPAES), Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Thermogravimetric Analysis (TGA), and by the measurement of physical properties.

Keywords: ionomers, ionic styrene grafted natural rubber, thermoplastic elastomer

INTRODUCTION

Graft copolymerization of natural rubber with monomers such as styrene produces self-reinforced thermoplastic natural rubber, in which the desired modification is achieved by way of phase-separation of blocks of glassy polymer which have become covalently bonded to the rubber molecules by graft copolymerisation. These graft copolymers

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combine the properties of both natural rubber and the polymer of the monomer grafted. The most promising graft copolymers based on natural rubber so far obtained, arev those derived from methyl methacrylate and styrene. A comprehensive review of the literature describing graft polymerization of natural rubber with various monomers like methyl methacrylate, styrene, acrylonitrile and ethylene methacrylic acid have been made [1–6].

Ionomers are ion containing polymers having hydrophobic backbones and a relatively small amount of ionic groups typically acid groups, neutralized with a metal ion [7–9]. It is well known that such ionic groups tend to form phase-separated ionic aggregates through metal "bridges" in the hydrophobic polymer matrix resulting in physical properties superior to the host polymer [7–12]. These cross-links are labile at processing temperatures, allowing the ionomers to be extruded or molded in conventional equipment. The upper use temperature of the ionomers is limited, as might be expected, because the cross-links begin to "melt out". The primary use of this class of materials is centered on their combination of properties such as high transparency, toughness, flexibility, adhesion and oil resistance. Food packaging, skin and blister packaging, and several shoe uses are examples. Ionomers, therefore, have received a considerable industrial and academic attention in recent years. To date, many types of ionomers have been developed and examined [7–14]. Among them ionomers of EPDM, nitrile rubber, polychloroprene rubber, and ethylene methacrylic acid copolymer are very important. There is no report, so far, on reprocessable ionomers based on either natural rubber or styrene grafted natural rubber.

The aim of the present study includes:

(a) the synthesis of styrene grafted natural rubber,
(b) preparation of zinc sulfonated styrene grafted natural rubber (ZnS-SGNR),
(c) characterization of ZnS-SGNR,
(d) evaluation of the effects of ionic groups on the mechanical properties of the resultant ionomer, and
(e) reprocessability of the modified polymer.

EXPERIMENTAL

Materials

Natural rubber latex was obtained from Rubber Research Institute of India, Kottayam, India. Styrene, sodiumlaurylsulfate, polyvinyl alcohol, tertiarybutyl hydroperoxide and tetraethylenepentamine were of AR grade. Styrene was washed with 10% sodium hydroxide solution to free it from inhibitor, and then with water. Aceticanhydride, zinc acetate and 1,2-dichloroethane (DCE) were obtained from S.D. Fine Chemicals Ltd., Mumbai, India. Concentrated sulfuric acid, methanol, and isopropanol were procured from E. Merck (India) Ltd., Mumbai.

Synthesis of Styrene Grafted Natural Rubber

Styrene was graft copolymerised with natural rubber latex using tertiarybutyl hydroperoxide and tetraethylenepentamine system. The typical formulation for the efficient graft copolymerisation of styrene in ammonia preserved natural rubber latex is shown in Table 1.

Preparation of "Zinc Sulphonated Styrene Grafted Natural Rubber"

The graft copolymer (SGNR) was dried under vacuum at 50°C for 48 hours prior to use. The sulfonating agent acetyl sulfate was prepared *in situ* by the reaction of acetic anhydride and concentrated sulfuric acid. Excess of acetic anhydride was used to scavenge any water that might have been present. Sulfonations were carried out in dichloroethane solution at room temperature. Acetyl sulfate was added dropwise and the reaction was terminated after 10 minutes by adding isopropanol. The polymer sulfonic acid neutralized with zinc acetate in methanol was recovered by steam stripping, and the product was vacuum dried at 50°C.

Characterization

]XRFS Analysis

The estimation of sulfur content of ZnS-SGNR was conducted as per ASTM D-4294 (1995). The measurement was done using Oxford Lab

TABLE 1 Formulation for the Graft-Copolymerisation of Styrene in Natural Rubber Latex

Ingredients	Parts by mass (g)
Natural rubber (as 30 drc latex, 0.4% ammonia)	200
Non-ionogenic stabilizer (as 20% aqueous solution)	9
Styrene	33
Tertiarybutyl hydroperoxide	0.13
Tetraethylenepentammine (as 10% aqueous solution)	0.6
Time of polymerization (h)	24
Polymerization temperature (°C)	55

X-3000 bench top XRF analyzer supplied by Oxford Instruments, U.K., using thin films molded in an electrically heated hydraulic press at 10 MPa.

ICPAES Analysis

Zinc analysis was performed using Inductively Coupled Plasma-Atomic Emission Spectroscope (ICPAES), model Labtam Plasmascan-8410. 0.5 g of the sample digested with 15 ml of 9 : 4 mixture of nitric acid and perchloric acid and diluted to 100 ml was analyzed in ICPAES.

FTIR Spectroscopy

FTIR spectra of the compression-molded films of neat NR, SGNR and ZnS-SGNR were taken in Nicolet Avtar 360 ESP FTIR Spectrometer.

NMR Spectroscopy

NMR spectra of NR, SGNR and ZnS-SGNR were taken in a Bruker Avance DPX 300 FTNMR spectrometer operating at a proton resonance frequency of 300.13 MHz.

Thermogravimetric Analysis (TGA)

TGA thermograms were recorded under nitrogen atmosphere on a Netzsch STA 409 with a data acquisition system 414/1 at a heating rate of 10°C/min.

Physical Properties

Test specimens were prepared by molding in an electrically heated hydraulic press for 5 minutes at 150°C and at a pressure of 10 MPa. The stress-strain properties were determined according to ASTM D 412 (1987) at 25°C using dumbbell test pieces in an lnstron Universal Testing Machine (UTM) model 4206, using cross head speed of 500 mm min^{-1}.

The tear resistance was determined as per ASTM D 624 (1986) using unnicked 90° angle test pieces (die C) at 25°C and cross head speed of 500 mm min^{-1} in an Instron UTM, model 4206.

The abrasion resistance was determined using DIN abrader as per DIN standard 531516. The hardness was determined as per ASTM D 2240 (1986) and expressed in Shore A units.

Reprocessability

The reprocessability of the 25.5 ZnS-SGNR ionomer was studied by masticating the molded samples in the Brabender Plasticorder for 5 minutes at a rotor speed of 60 rpm at 120°C. The sample was molded in an electrically heated hydraulic press for 5 minutes at 150°C, under a pressure of 10 MPa. The process of mastication and molding was repeated up to three cycles. The stress-strain properties of the molded specimen after each cycle were determined.

RESULTS AND DISCUSSION

Sulfur Estimation

Figure 1 shows the variation of the level of sulfonation of SGNR with the meq of sulfuric acid added in the form of acetyl sulfate at the experimental conditions as estimated using XRFS method. The ionic content increases with increase in the concentration of sulfuric acid added. The reagent conversion at a level of 32% was established through the estimation of sulfur present in the sulfonic acid of the ZnS-SGNR using the XRFS analysis.

Zinc Estimation

Figure 2 reveals the level of neutralization of the sulfonic acid content in the ZnS-SGNR. Irrespective of the sulfonic acid content in the sulfonated-SGNR, it has been found that the level of neutralization by the zinc acetate remains the same. ICPAES measurements of the zinc present in the ZnS-SGNR shows that about 96% neutralization of the sulfonic acid groups in the rubber occurs, if 1 : 1 milliequivalent ratio of zinc acetate and sulfonic acid are maintained.

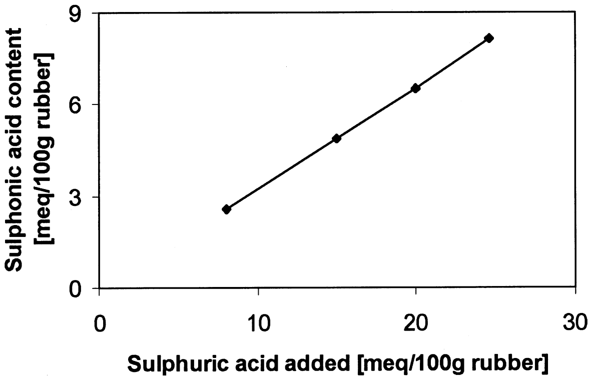


FIGURE 1 Level of sulfonation of SGNR with the amount of sulfonic acid (as acetyl sulfate) added.

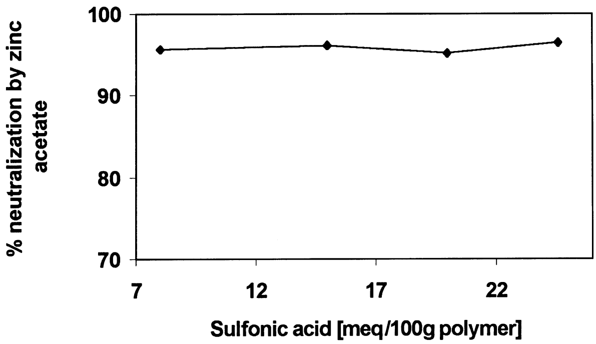


FIGURE 2 Percentage neutralization by zinc acetate *vs.* sulfonic acid content.

FTIR Spectroscopy

IR spectra of the control NR, SGNR and ZnS-SGNR are shown in Figure 3. In the IR spectrum of SGNR the peaks at 3026 and

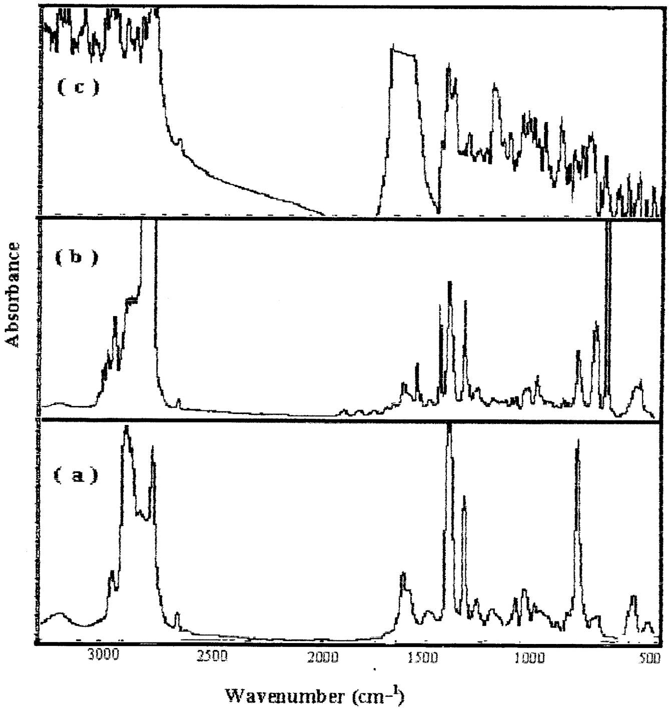
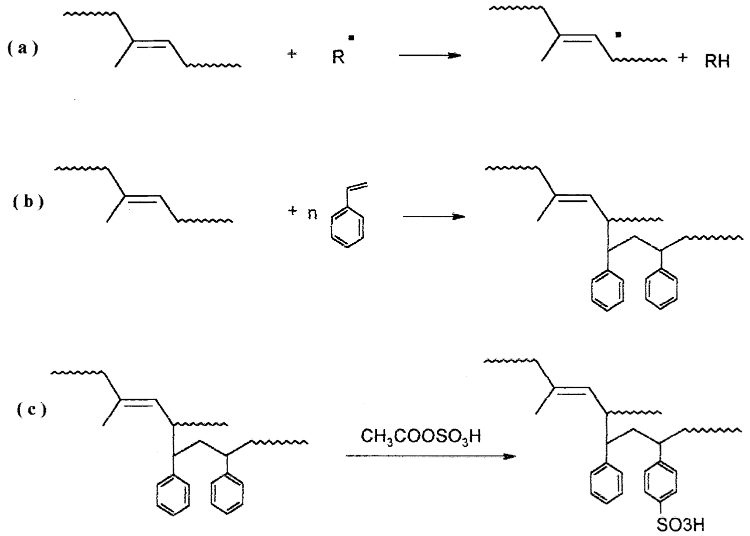


FIGURE 3 Infra Red spectra of (a) natural rubber, (b) styrene grafted natural rubber, and (c) zinc sulfonated styrene grafted natural rubber.

2855 cm^{-1} correspond to the aromatic C–H stretching in polystyrene. Peaks at 1601 and 1541 cm^{-1} correspond to the C=C stretching of aromatic ring of polystyrene. A strong peak at 698 cm^{-1} stands for the monosubstituted benzene ring along with the characteristic absorption of natural rubber at 837 and 889 cm^{-1}. The peaks at 1452 and 1375 cm^{-1} correspond to the aliphatic C–H stretching in natural rubber. The grafting of NR by styrene has, therefore been well established. The IR spectrum of the ZnS-SGNR show peaks at, 1008 cm^{-1} representing the inplane bending vibrations of phenyl group substituted with a metal sulfonate group, 1127 cm^{-1} for the sulfonate anion attached to a phenyl ring, 1042 cm^{-1} for the symmetric stretching vibration of the zinc sulfonate group and the doublet at 1235 cm^{-1} due to symmetric stretching vibration of the sulfonate group [14–17].

The two kinds of reactive sites in the SGNR, such as (i) the phenyl rings in the polystyrene blocks and (ii) the residual C=C in the rubber block are evident from the reactions represented in Scheme 1(a) and (b). Although olefinic unsaturation is inherently more reactive to acetyl sulfate than the phenyl rings, infrared spectroscopy analysis



SCHEME 1 (a) Reaction between natural rubber and peroxide free radical (R°) producing free radical sites at the allylic carbon on natural rubber back bone. (b) Polymerization of styrene followed by grafting in natural rubber latex. (c) Sulfonation of styrene grafted natural rubber using acetyl sulfate, producing sulfonated styrene grafted natural rubber.

confirmed that sulfonation occurred almost exclusively in the polystyrene blocks as per the Scheme 1(c).

NMR Spectroscopy

The n.m.r spectra of the control NR (a), SGNR (b) and ZnS-SGNR (c) are represented in Figure 4. In the spectrum of SGNR, not only the characteristic signals of NR at 1,2 and 5 ppm are retained but a new signal at 7.2 ppm also appears. The new signal at 7.2 ppm is due to the

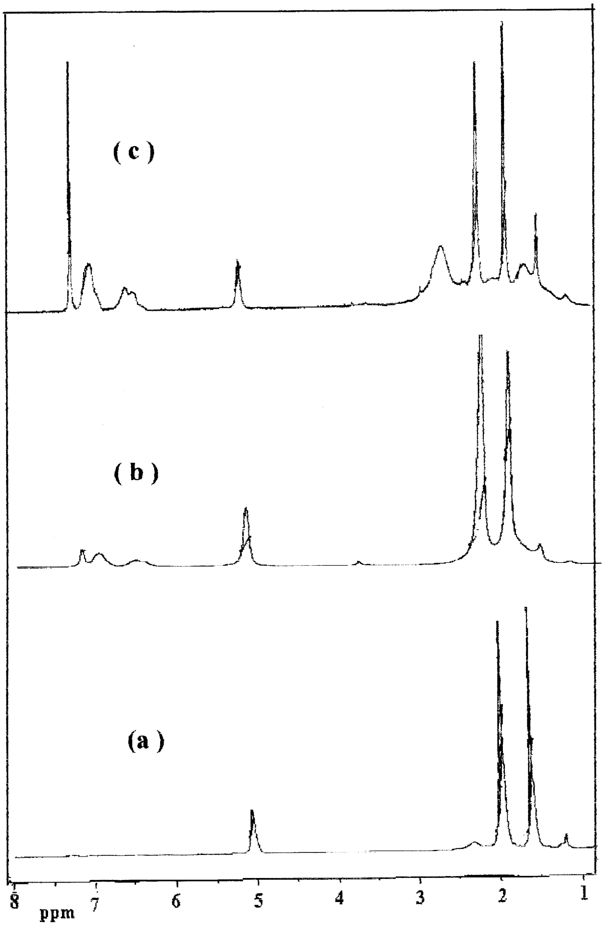


FIGURE 4 Nuclear Magnetic Resonance spectra of (a) natural rubber, (b) styrene grafted natural rubber and (c) zinc sulfonated styrene grafted natural rubber.

benzene ring present in the grafted styrene units. This is evident from the positive chemical shift to the corresponding signals in SGNR spectrum as compared to the NR. The chemical shift of peaks in the modified polymer is due to the local conformational change, which arises due to the grafting of styrene units at the allylic carbon atom in natural rubber.

The environment of the grafted phenyl units has been disturbed in the sulfonated graft polymer. This is clear from the chemical shift of the signals corresponding to the aromatic ring at 7.0277 ppm to 7.2781 ppm. The relatively large shift in the resonance signals of phenyl ring confirms that a strong ionic group such as $-(SO_3)_{1/2}Zn$ is attached to the benzene ring in SGNR. It can therefore be considered as a supplementary evidence for the FTIR spectroscopic observation [14].

Thermogravimetric Analysis (TGA)

Figure 5 shows the degradation behavior observed from the thermogravimetric analysis (TGA) of SGNR (A), 20.2 ZnS-SGNR (B) and 25.5 ZnS-SGNR (C). The results of TGA are summarized in Table 2. It was observed that sample (C) is more stable, because the degradation starts at 375°C, whereas the degradation of sample (A) starts at 350°C. This increase in stability of the ZnS-SGNR is due to the greater stability of the aromatic sulfonate derivative [17]. The higher residual

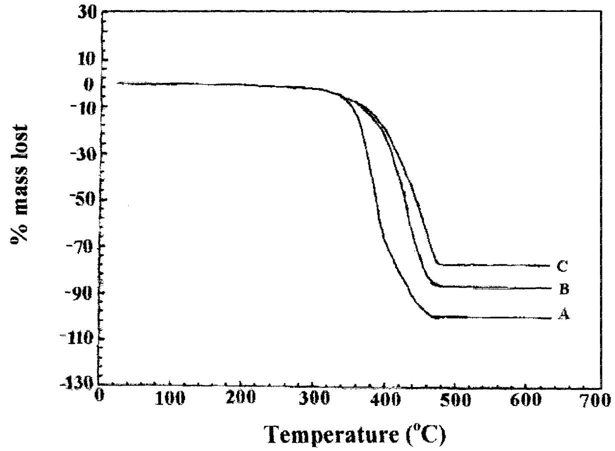


FIGURE 5 TGA thermograms of (a) SGNR, (b) 20.2 ZnS-SGNR, and (c) 25.5 ZnS-SGNR.

TABLE 2 Results of Thermogravimetric Analysis

Sample	Temperature of onset of degradation (°C)	T_{max}(°C)	Residual weight (%)
SGNR (A)	350	380	2
20.2 ZnS-SGNR (B)	370	435	15
25.5 ZnS-SGNR (C)	375	440	22

weight % shown by ZnS-SGNR, as compared to SGNR, could be attributed to the presence of zinc in the former, which presumably forms zinc oxide. The thermal stability increased with increasing sulfonation level. This is evident from the T_{max} values, *i.e.*, the temperature at which the rate of degradation is maximum, shown in Figure 6. The differences in the TGA thermograms between the salts of different ionic content may be due in part to differences in the viscosity of polymers, which affects the diffusion rate of the volatile degradation products of the sample [16].

Physical Properties

The data listed in Table 3 documents the increasing effect of zinc sulfonate groups on the physical properties of SGNR. The 25.5 ZnS-SGNR shows a tensile strength of 9 MPa. The same parameter for the unvulcanised base SGNR is only 1.23 MPa. The physical properties of the ZnS-SGNR at this stage conform well with the requirements of a good thermoplastic elastomer. The elongation at break of the ionomer samples decreased as the level of sulfonation increased. The tear

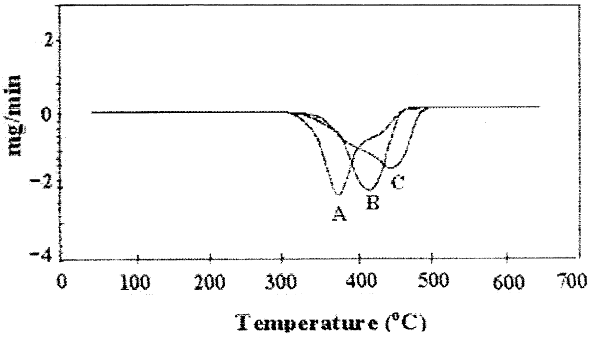


FIGURE 6 DTG thermograms of (a) SGNR, (b) 20.2 ZnS-SGNR, and (c) 25.5 ZnS-SGNR.

TABLE 3 Physical Properties at 25°C

Properties	Samples			
	SGNR	15.1 ZnS-SGNR	20.2 ZnS-SGNR	25.5 ZnS-SGNR
Tensile strength (MPa)	1.23	5.7	7.62	9
Elongation at break (%)	110	201	191	128
Tear strength (N/mm)	35	28.4	54.2	82.5
Hardness (Shore A)	42	78	82	85
Abrasion loss (cm^3/h)	0.92	0.741	0.712	0.528

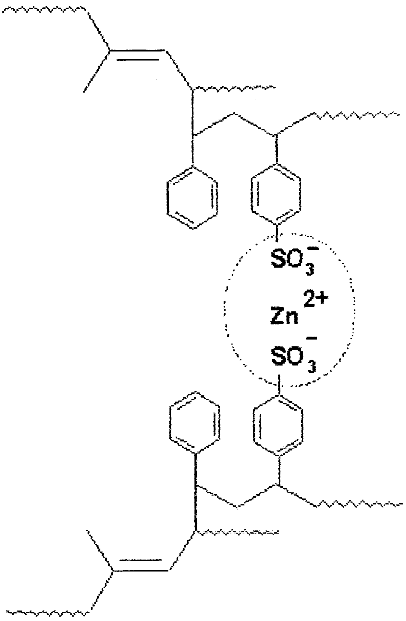
resistance increased as the level of sulfonation increased. The tear resistance of an elastomer is a measure of crack propagation. It is known that tear strength is enhanced by factors which tend to dissipate energy [18]. The ionic domain of ZnS-SGNR may be acting as tear deviators or arrestors. The higher abrasion resistance shown by ZnS-SGNR sample of higher sulfonate levels could be attributed to the strength of the matrix, as evident from the stress-strain behavior. The hardness of ZnS-SGNR increased as the level of sulfonation increased. Hardness is a measure of modulus of elasticity at low strain [19]. The higher hardness may be due to the higher content of ionic aggregate [20].

Reprocessability

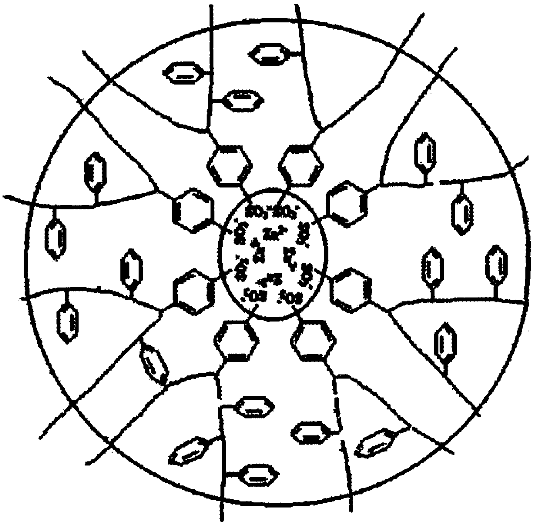
Results of the reprocessability studies are summarized in Table 4. It was observed that the stress-strain properties of the Zn-SNR remain almost constant after repeated cycles of mixing and molding. The morphological structure of ZnS-SGNR is believed to be similar to that of conventional thermoplastic elastomers, that is, a combination of hard domains and soft segments. In agreement with the most important and widely applicable models for ionic aggregates [11, 12, 21], the following structure is proposed for the ZnS-SGNR (Scheme 3).

TABLE 4 Results of Reprocessability Studies of 25.5 ZnS-SGNR

No. of cycles	Stress-strain properties		
	Elongation at break (%)	Tensile strength (MPa)	Tear strength (N/mm)
1	128	9	82.5
2	126	9.1	82.5
3	122	9	80.2



SCHEME 2 Proposed chemical structure of zinc sulfonated styrene grafted natural rubber.



SCHEME 3 Proposed model for the morphological structure of zinc sulfonated styrene grafted natural rubber.

CONCLUSIONS

The studies of ionic styrene grafted natural rubber have allowed us to draw the following conclusions:

- Zinc neutralized sulfonated styrene grafted natural rubber could be prepared by reacting styrene grafted natural rubber with acetyl sulfate followed by neutralization of the sulfonic acid with zinc-acetate.
- The analytical techniques XRFS and ICPAES respectively show that acetyl sulfate reagent conversion is about 32%, and neutralization of the sulfonic acid is 96%.
- FTIR spectra show evidence for the grafting of styrene onto the natural rubber backbone and also for the formation of sulfonated styrene grafted natural rubber.
- NMR spectra confirm the presence of ionic groups in the modified rubber, giving credence to the FTIR spectra.
- Thermogravimetric analysis studies show the improved thermal stability of the ionomer. It also reveals that thermal stability increases with increase in the ionic content of the polymer.
- The modified SGNR has tensile strength about ten times the strength of unvulcanised base graft polymer.
- The thermoplastic elastomeric nature of the compound is evident from the retention of the stress-strain properties even after three cycles of repeated mixing and molding.

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