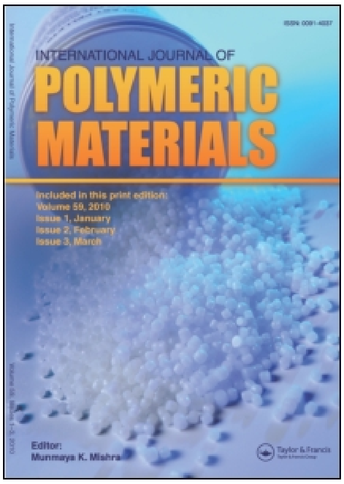

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REPROCESSABLE IONIC ELASTOMERS BASED ON STYRENE-BUTADIENE RUBBER

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Zinc sulfonated SBR prepared by the sulfonation of styrene units in SBR, followed by the neutralization of the resultant SBR sulfonic acids, behaves as ionic thermoplastic elastomer, and shows improved physical properties compared to SBR. Studies include X-ray fluorescence analyses (XRF), FTIR spectroscopy, dynamic mechanical analyses (DMA) and measurement of physical properties.

Keywords: ionomers, Zinc sulfonated SBR, reprocessability

INTRODUCTION

Ionomers are ionic polymers containing low levels of ionic groups [1–3]. Ionic elastomers have the unique ability to behave as cross-linked elastomers at ambient temperatures, and to melt and flow at elevated temperatures, like thermoplastics [4]. Since these materials could be processed by thermoplastic processing techniques avoiding a vulcanization step, they have the potential to emerge as important industrial polymers. The aim of this work is to prepare and investigate the properties of reprocessable ionic elastomers based on styrene butadiene rubber (SBR). The ionomeric SBR's were prepared by sulfonation of the styrene units in SBR followed by neutralization of the resultant SBR sulfonic acids by zinc acetate. Zinc sulfonated SBR's, hereafter abbreviated as ZnS–SBR, show improved physical properties as compared to SBR gum vulcanizate.

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EXPERIMENTAL

Synthesis of the Ionomer

SBR(Synaprene-1502, obtained from Synthetics and Chemicals Ltd., Mumbai, India) was dissolved in 1,2-dichloroethane, and sulfonated using the sulfonating agent, acetyl sulfate, generated *in situ*, from acetic anhydride and concentrated sulfuric acid. The SBR sulfonic acid produced was neutralized by a solution of zinc acetate in methanol. The ZnS–SBR thus produced was steam stripped, and dried in a vacuum oven at 50°C.

Sample Preparation

The ionomers were masticated in Brabender Plasticorder model PL-3S. Mixing was done for 5 minutes at a rotor speed of 60 rpm, and at a temperature of 120°C. Test specimens were prepared by molding in an electrically heated hydraulic press for 5 min at 150°C under a pressure of 10 MPa. The neat SBR was also masticated under the same condition.

The SBR gum compound was mixed as per ASTM D 3185 (1988) on a laboratory mixing mill. The cure curve of the compound was taken on a Goettfert elastograph model 67.85, and the compound was then vulcanized up to its optimum cure time in an electrically heated hydraulic press.

Characterization Techniques

X-ray Fluorescence Measurements

The sulfur content of the ionomers was estimated as per ASTM D 4294 (1995) using Oxford Lab X-3000 benchtop X-ray fluorescence analyzer (XRF) supplied by Oxford Instruments U.K.

FTIR Analyses

Infrared spectroscopic studies of the compression molded thin films were carried out using Nicolet Impact 410 spectrophotometer with a resolution of $4\,\mathrm{cm}^{-1}$.

Dynamic Mechanical Analyses

The dynamic mechanical analyses of the samples were performed in a dynamic mechanical thermal analyzer (DMTA-MK-II) at a frequency of 20 Hz, and a dynamic strain of 16 μ. The measurements were carried out over a temperature range of $-100°\mathrm{C}$ to $+100°\mathrm{C}$ at a heating rate of $2°\mathrm{C\,min}^{-1}$.

Determination of Physical Properties

The stress–strain properties were determined according to ASTM D 412 (1987) using dumb-bell test pieces in an Instron Universal Testing Machine (UTM), model 4206, using a crosshead speed of $500\,\mathrm{mm\,min}^{-1}$.

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

The abrasion resistance was determined using a DIN abrader as per DIN standard 53516.

The hardness was determined as per ASTM D 2240 (1986) and expressed in Shore A units.

Determination of Reprocessability

The reprocessability of the ionomer at the level of sulfonation 30.7 meq $[100\,\text{g polymer}]^{-1}$ (ZnS–SBR-3) 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

Estimation of Sulfur

The results of XRF analyses of the ionomer samples are shown in Table 1. The weight percentage of sulfur in the samples and the corresponding levels of sulfonation in meq $[100\,\text{g polymer}]^{-1}$ are also shown. The ionomer samples became harder as the level of sulfonation increased.

FTIR Characterization

The infrared spectra of neat SBR and the ionomer prepared from it (ZnS–SBR-3) are shown in Figure 1. The spectrum of SBR (Fig. 1a) shows a band at 2912 cm^{-1} corresponding to CH_2 stretching. The weak band around 1600 cm^{-1} is characteristic of C—H stretching in benzene ring [5]. The band at 963 cm^{-1} to C—H out of plane deformation of C=C of butadiene units.

TABLE 1 Results of X-ray fluorescence analyses

Sample	*Amount of sulfur (weight %)*	*Sulfonate content* $[meq(100\,g\ SBR)^{-1}]$
ZnS–SBR-1	0.326	10.2
ZnS–SBR-2	0.634	19.8
ZnS–SBR-3	0.985	30.7
ZnS–SBR-4	1.232	38.5

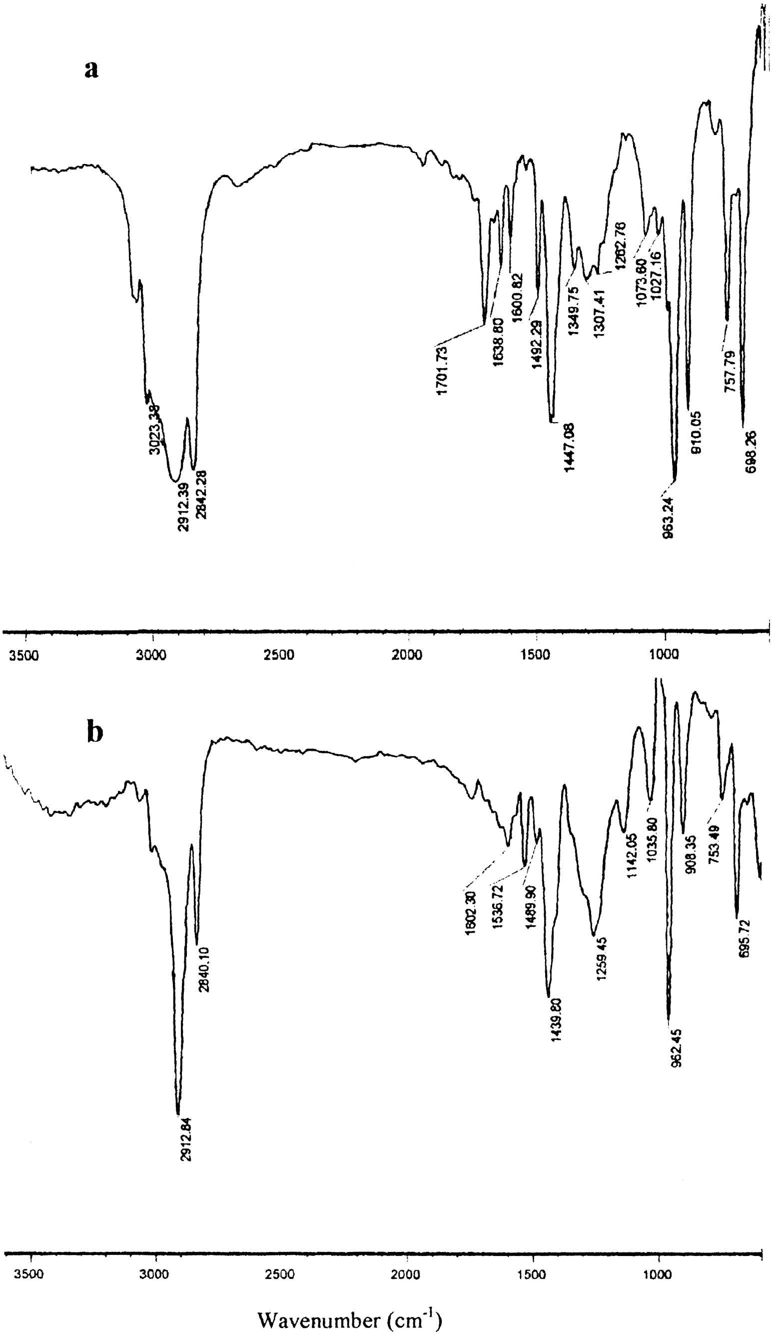

FIGURE 1 FTIR spectra of: (a) SBR, and (b) ZnS–SBR.

In ZnS–SBR (Fig. 1b) the bands at 2912 cm^{-1}, 1602 cm^{-1} and 962 cm^{-1} are also present. S=O stretching (asymmetric) band appears at around 1142 cm^{-1}. The S=O symmetric stretching of sulfonate ion shows a band at 1035 cm^{-1}. The band at 1259 cm^{-1} corresponds to ionic sulfonate groups [5, 6]. It is inferred that the sulfonate groups are attached on the benzene ring. The structure of SBR and the proposed structure of ZnS–SBR are shown in Figure 2.

Dynamic Mechanical Analyses

Figure 3 shows the plot of loss tangent (tan δ) against temperature obtained from the dynamic mechanical analyses of SBR gum vulcanizate (prepared as per the recipe shown in Tab. 2) and ZnS–SBR-3. The glass transition

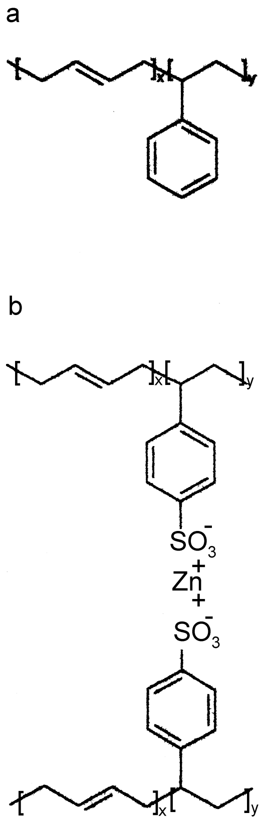

FIGURE 2 (a) Chemical structure of SBR, and (b) proposed structure of ZnS–SBR.

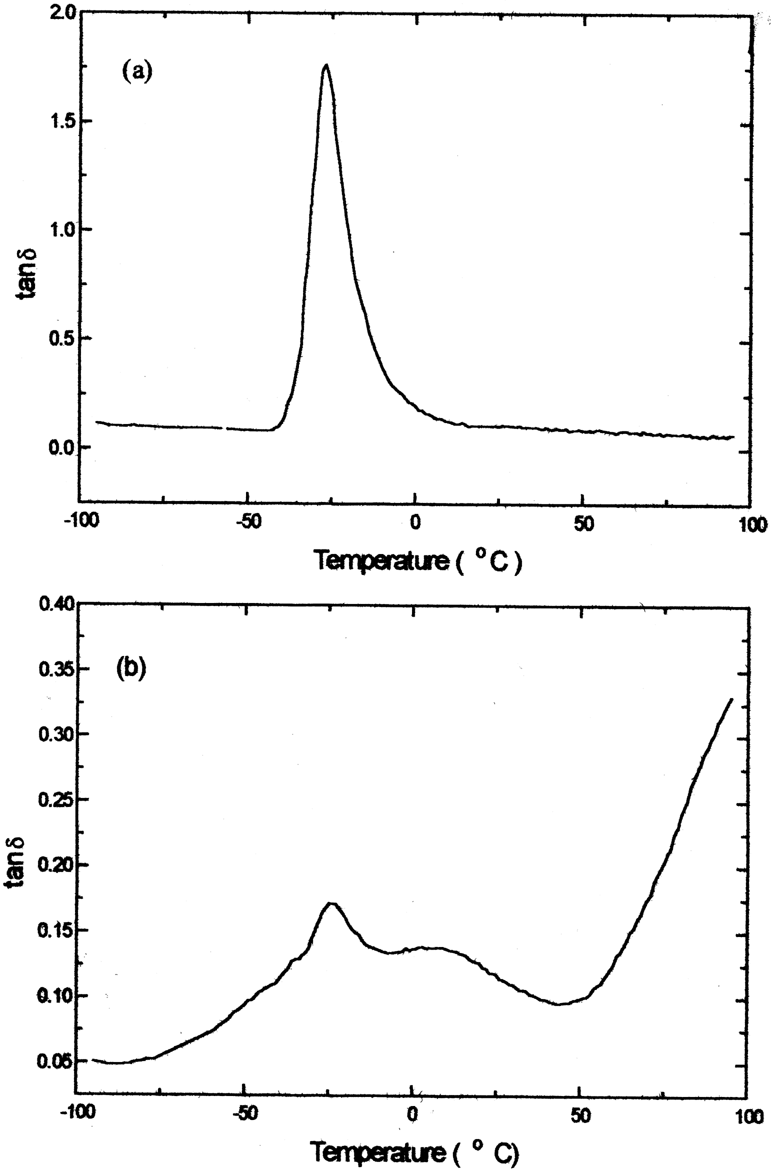

FIGURE 3 Plots of tan δ versus temperature of (a) SBR vulcanizate, and (b) ZnS–SBR.

temperature (Tg) occurred around $-26°C$ in the case of both the polymers. The tan $\delta_{\max}$ (*i.e.*, the tan δ value at Tg) was less in the case of ZnS–SBR than in SBR vulcanizate. This is because of the stiffening imparted by the

TABLE 2 Formulation of SBR gum compound

Component	*Parts*
SBR	100
Sulfur	2.0
MBT	1.25
TMTD	0.20
ZnO	3.0
Stearic acid	2.0
SP(antioxidant)	1.0

ionic domains in ZnS – SBR [7]. ZnS – SBR shows a broad transition in the range of −5°C to +14°C, which is ascribed to the transition due to the ionic aggregates (Ti) [8]. Transition due to ionic aggregates has been found to occur in the same temperature range in the case of rubbery ionomers [8, 9]. In the case of SBR gum vulcanizate, expectedly the broad transition due to ionic aggregates has not been observed. The ionomer as it is not chemically cross-linked became soft at elevated temperatures [4]. The results of dynamic mechanical analyses are summarized in Table 3.

Physical Properties

The physical properties of SBR gum vulcanizate and the ionomer samples are shown in Table 4. The hardness of the ionomer at the level of sulfonation 19.8 meq [100 g polymer]$^{-1}$ (ZnS – SBR-2) was equivalent to that of the SBR vulcanizate. The hardness of the ionomers increased as the level of sulfonation increased. Hardness is a measure of modulus of elasticity at low strain [10]. The increased modulus of elasticity brought about by the increased concentration of ionic aggregates in ZnS – SBR samples may be the reason for their higher hardness.

The modulus at 100% elongation and the tensile strength of the ionomer at the level of sulfonation 10.2 meq [100 g polymer]$^{-1}$ (ZnS – SBR-1) was lower than that of the SBR vulcanizate. However the modulus and tensile strength of the ionomer ZnS – SBR-2 was higher than that of SBR

TABLE 3 Results of dynamic mechanical analyses

Sample	*Tg*[a] (°*C*)	*Tan δ at Tg*	*Transition due to ionic aggregates*[b] *Ti* (°*C*)	*Tan δ at Ti*
SBR gum vulcanizate	−26	1.764	–	–
ZnS – SBR	−26	0.172	−5 to +14	0.139

[a] From (tan $\delta)_{\max}$ in the plot of tan δ *vs.* temperature.

[b] From tan δ *vs.* temperature plot.

TABLE 4 Physical properties of SBR gum vulcanizate and zinc sulfonated SBRs

Sample	*Modulus* 100% (*MPa*)	*Tensile strength* (*MPa*)	*Elongation at break* (%)	*Tear strength* (*kN/m*)	*Abrasion loss* (cm^3/hr)	*Hardness* (*Shore A*)
SBR	1.28	1.89	218	12.39	3.23	35
ZnS−SBR-1	0.98	1.10	518	11.79	4.45	26
ZnS−SBR-2	1.38	2.71	510	15.47	3.12	35
ZnS−SBR-3	5.37	5.38	205	20.5	2.91	74
ZnS−SBR-4	–	6.69	108	26.21	2.72	83

vulcanizate and the values increased with the level of sulfonation. The relation between the level of sulfonation and tensile strength is shown in Figure 4. The elongation at break of the ionomer samples decreased when the level of sulfonation increased.

ZnS–SBR-2 shows higher tear strength compared to the control SBR vulcanizate. The tear resistance increased with the level of sulfonation. It is known that tear strength is enhanced by factors which tend to dissipate energy [11]. The ionic domains of ZnS–SBR may be acting as tear deviators or arrestors. Abrasion resistance follows the same pattern as the tear strength. It is apparent that the ionic aggregates present in ZnS–SBR behave as ultrafine particles of a reinforcing filler, in addition to acting as physical cross-links [11, 12].

Reprocessability

The results of reprocessability studies of ZnS–SBR-3 are shown in Figure 5. It was observed that the tensile strength remains almost constant even after repeated cycles of mixing and molding. This shows that ZnS–SBR behaves as a thermoplastic elastomer, and could be reprocessed by mechanical recycling without deterioration in properties.

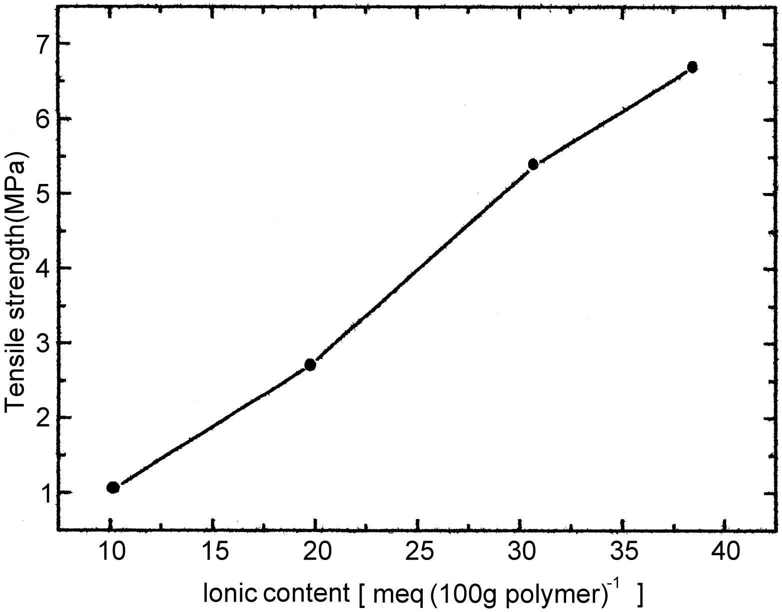

FIGURE 4 Variation of tensile strength of ZnS–SBR with the ionic content.

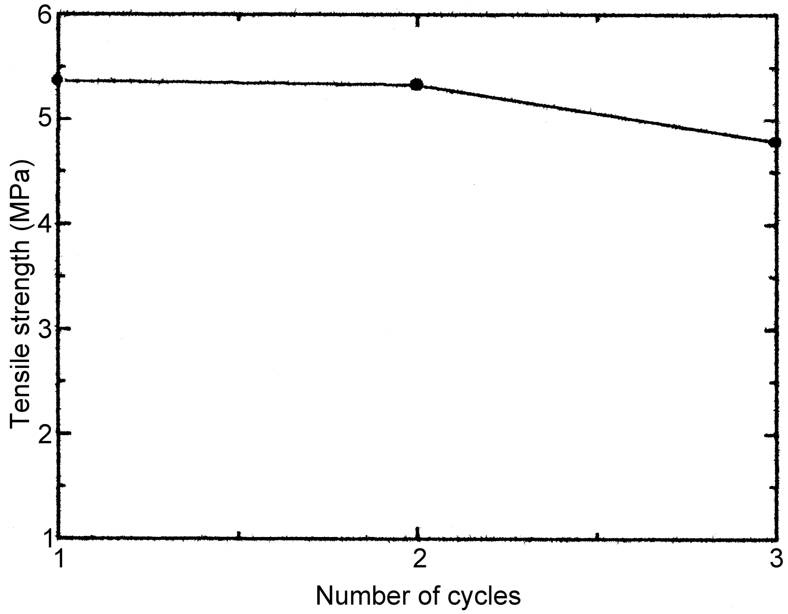

FIGURE 5 Variation of tensile strength of ZnS–SBR-3 at different cycles of processing.

CONCLUSIONS

ZnS–SBR could be prepared by sulfonation of styrene units present in SBR followed by neutralization of the resultant sulfonic acid. XRF studies could be used to estimate the sulfur content in ionomer samples. Infrared spectroscopic studies provide evidence for the sulfonation. Results of dynamic mechanical analyses show the occurrence of an ionic transition in ZnS–SBR, in addition to the glass-rubber transition of SBR. ZnS–SBR shows improved physical properties as compared to SBR gum vulcanizate. Reprocessability studies show that the ZnS–SBR could be reprocessed by mechanical recycling without deterioration in physical properties.

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