5.1 Introduction

The effect of particulate and fibrous fillers on the properties of ionomers is of great interest because fillers could be used very effectively to enhance their ultimate properties [1, 2]. Such studies provide information as to how the thermal and
viscoelastic properties of the ionomer, and its biphasic microstructure, can be modified so as to obtain the best balance of physical properties and processability. The two-phase morphology of ionomers, and the resulting differences in polarity of the two phases, provide possibilities of preferential interaction by different fillers. This is evident from the results of early studies by Lundberg et al [3] on lightly sulfonated polystyrene ionomers. The influences of plasticizer on the microstructure and relaxation properties of poly (methyl methacrylate) ionomers were investigated [4]. Evaluation of the effect of carbon black (HAF) [5], silica [6], and zinc stearate [7] on the properties of EPDM based ionomers were published. The results of our studies are discussed in terms of the multiplet-cluster and EHM model of ionomer microstructure [8].

Typical advantages associated with short fibers as fillers in polymer matrices include design flexibility, high low-strain modulus, anisotropy in technical properties and stiffness, good damping, ease in processing and production economy. Fibers may also improve thermo mechanical properties of polymer matrices to suit specific areas of applications and to reduce the cost of the fabricated articles. Short fiber reinforced rubbers are usually easier to process than those with continuous cord reinforcement. Studies on the incorporation of different short fibers such as rayon, nylon and glass fibers in to natural rubber matrix, and the mechanism of reinforcement have been done extensively. The term ‘short fiber’ means that the fiber length should not be too long, because the fibers may get entangled with each other, causing problems of dispersion, whereas a very small length of the fiber does not offer sufficient stress transfer area to achieve significant reinforcement. Short fiber reinforcement in thermoplastic elastomers (TPEs) has become another area of potential significance. To assess the effect of fillers on the polar and non-polar phases 26.5 ZnS-RISGNR ionomer has been used.

This chapter presents:

1. Differential scanning calorimetry and dynamic mechanical thermal analysis of the effect of particulate fillers such as HAF black, silica, zinc stearate and short fiber fillers such as nylon, and glass on the thermal transitions of the 26.5 ZnS-RISGNR ionomers.

2. FTIR studies.
3. Physical properties.
4. SEM analysis, and
5. Reprocessability studies.

5.2 Characterisation

5.2.1 Differential scanning calorimetry (DSC)

Table 5.1 DSC profiles of ionomer/filler compounds containing 10 phr filler

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tg1 (°C)</th>
<th>Tg2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-64</td>
<td>+85</td>
</tr>
<tr>
<td>2</td>
<td>-63</td>
<td>+83</td>
</tr>
<tr>
<td>3</td>
<td>-63</td>
<td>+100</td>
</tr>
<tr>
<td>4</td>
<td>-62</td>
<td>+68</td>
</tr>
<tr>
<td>5</td>
<td>-62</td>
<td>+68</td>
</tr>
<tr>
<td>6</td>
<td>-66</td>
<td>+52</td>
</tr>
</tbody>
</table>

Samples are 1 = neat ionomer; 2, 3, 4, 5 and 6 represent ionomer filled with HAF black, Silica, Nylon, Glass and Zinc stearate respectively.

Fig. 5.1 DSC profiles of the ionomer and its 10 phr filled compounds.

Samples are 1 = neat ionomer; 2, 3, 4, 5 and 6 represent ionomer filled with HAF black, Silica, Nylon, Glass and Zinc stearate respectively.
The DSC results of HAF black, silica, nylon, glass, and zinc stearate filled compounds of the 26.5 ZnS-RISGNR ionomer are presented in table 5.1. The DSC profiles as shown in figure 5.1 reveal that all these fillers have influenced both the $T_g1$ and $T_g2$ of the 26.5 ZnS-RISGNR ionomer. The interaction of the active sites on the filler surface with both the matrix and the ionic domains in the ionomer may be responsible for the change in the thermal transitions (Fig. 5.1) on filler incorporation.

### 5.2.2 Dynamic mechanical thermal analysis (DMTA)

Results of dynamic mechanical thermal analyses for the 26.5 ZnS-RISGNR ionomer and their filled compounds have been summarized in the table 5.2.

**Table 5.2 Results of dynamic mechanical thermal analyses**

<table>
<thead>
<tr>
<th>Materials $^*$</th>
<th>Thermal transitions</th>
<th>Tan $\delta$ corresponds to</th>
<th>Log $E'$ (Pa) corresponds to</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g1$ ($^\circ$C)</td>
<td>$T_g2$ ($^\circ$C)</td>
<td>$T_g1$ 25$^\circ$C ($^\circ$C)</td>
</tr>
<tr>
<td>1</td>
<td>-21</td>
<td>+87</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>-20</td>
<td>+99</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>-20</td>
<td>+76</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>-20</td>
<td>+99</td>
<td>0.09</td>
</tr>
<tr>
<td>5</td>
<td>-20</td>
<td>+99</td>
<td>0.09</td>
</tr>
<tr>
<td>6</td>
<td>-20</td>
<td>+99</td>
<td>0.09</td>
</tr>
</tbody>
</table>

$^*$Materials: 1 = neat ionomer; 2 = HAF black; 3 = Silica; 4 = Nylon; 5 = Glass; 6 = Zinc stearate

Incorporation of (HAF) carbon black into the neat ionomer increases its $T_g1$ ($-21^\circ$C) to $-20^\circ$C. Reinforcement of the matrix and the cluster phase is evident from the tan $\delta$
values at $T_g1$ and $T_g2$ (Table 5.2 and Figs. 5.2 & 5.3). The $\tan \delta$ at 25°C for the neat ionomer lowered on black loading, whereas the corresponding storage modulus increased. This may be due to the strong interactions involving the backbone chains [10, 11] and the clusters. The $\tan \delta$ at $T_g2$ was increased for all the fillers except for silica. The incorporation of silica caused a slight increase in the $T_g1$, which may be due to the stiffening of the backbone chain.

Incorporation of silica results in a further decrease in $\tan \delta$ presumably due to the formation of an adsorbed polymeric shell on the active filler surface. Apart from $T_g1$, the ZnS-RISGNR neat ionomer and its silica filled compound show a second transition ($T_g2$) around $+87$ and $+76$ °C respectively. The incorporation of silica caused a marginal reduction in $\tan \delta$ at the high-temperature ionic transition ($T_g2$), thus suggesting that the formation of the hard phase is reduced in the presence of silica. The silica seems to facilitate the dipolar relaxation of the polymer, which may be the reason for the reduction in the ionic transition for the silica filled ionomer when compared to the neat ionomer. The silanol groups in silica seem to interfere in the formation of ionic aggregates. Scheme 5.1 shows the representation of the probable mechanism of interaction between the silanol groups of the filler and the ionic aggregate.

![Fig. 5.2 DMTA spectra of the 10 phr filled compounds of 26.5 ZnS-RISGNR ionomer.](image)

1 = HAF black; 2 = Silica; 3 = Nylon; 4 = Glass; and 5 = Zinc stearate.
The stiffening of the polymer backbone and a weakening of the ionic transition in the presence of silica may be inferred from our observations.

Fig. 5.3 Temperature dependence storage modulus of the 10 phr filled compounds of 26.5 ZnS-SGNR ionomer. 1 = HAF black; 2 = Silica; 3 = Nylon; 4 = Glass; and 5 = Zinc stearate

The lower storage modulus of the silica filled ionomer at Tg2, when compared to the value at Tg1, suggest that the filler weaken formation of both the multiplets and clusters present in the ionomer.

According to these results, it may be deduced that at the elevated temperatures the fillers act as facilitators for a stronger inter cluster attraction, which results in an increase in the cluster transition temperature and the corresponding tan δ. The silica, at higher temperature, may be disrupting the ionic multiplets and clusters to reduce their concentration to the minimum with a reduction in their Tg2 as shown in table 5.2. At 25 °C, except for zinc stearate, all other fillers show a reduction in the tan δ. The higher value of tan δ at Tg2 for the zinc stearate is probably due to the plasticization of the ionic domains in the ionomers [2].
Based on these results it is assumed that the polymer – filler interactions in the case of filled ZnS-RISGNR are of two types: (i) filler–nonpolar polymer backbone, which is similar to the interaction involving diene rubbers and reinforcing fillers, as manifested in the lowering of tan δ at Tg1, and (ii) ionic groups of the ionomer–polar groups present on the surface of the filler particles (–OH, >C=O, -NH-CO- etc.), which is manifested in an increase in tan δ at Tg2. While the rubber–filler interaction involving the non-polar polymer backbone is of weak van der Waals' type; the same due to ionic aggregates can be of much stronger type. The increase in the Tg1 as well as Tg2 for the filled compounds of ZnS-RISGNR shows that carbon black, silica, nylon fiber, and glass fiber act as reinforcing fillers. The decrease in the intensity of the peak at low temperature further supplements our view that the fillers are reinforcing. Appearance of both the low temperature as well as high temperature transitions for the filled zinc sulphonated ionomer samples, similar to the neat ionomer ZnS-RISGNR, may be considered as an evidence for the retention of the micro phase and the "physical cross-links" as characteristic of ionomers. The Log E'(Pa)–temperature plot reveals that the "network" persists even at the highest experimental temperature. From the values of the storage modulus at Tg1, at 25 °C and at Tg2, it has been
observed that the silica filled ionomer is somewhat balanced with respect to the storage modulus.

The incorporation of zinc stearate in to ZnS-RISGNR ionomer increases its glass-rubber transition (Tg1) from -21°C to -20°C. The dual role exhibited by zinc stearate in ionomers based on RISGNR may be evident from the intensity of tan δ peaks (Table 5.2) for the 10-phr-zinc stearate filled ionomer at two transitions. At Tg1, zinc stearate acts as reinforcing filler (low intensity tan δ peak) where as at the higher temperature (high intensity tan δ peak) it plasticises the ionic domains. It was found that at 120-130°C, zinc stearate starts to melt, weakens the strong ionic association prevailing in ionomers based on RISGNR. In the case of ionomers based on RISGNR, zinc stearate has a dual effect. The thermal profile of the zinc stearate filled RISGNR ionomer resembles the investigations of Weiss [12]. Appearance of multiple transitions for the zinc stearate compound of the RISGNR ionomer along with the detection of the anomalous melting behavior of the zinc stearate in the thermal profiles may be considered as evidence of interactions between zinc stearate and sulfonate groups in RISGNR ionomers.

5.2.3 Fourier transform infrared spectroscopy

The FTIR spectra of the neat ionomer and its compounds filled with HAF carbon, silica, nylon fiber, glass fiber, and zinc stearate are shown in the figure 5.5. The fillers have influenced the intensities of the characteristic peaks of the ZnS-RISGNR ionomers. The variation of the peak intensities of the ZnS-RISGNR with different fillers has been represented using figure 5.4. The interaction between the functional groups on the surface of the filler particles and the zinc sulfonate groups of the ionomer may be responsible for this variation. Higher the interaction between the ionic groups and the functional groups on the filler, greater will be the intensity of the peak responsible. It has been found that the ionomer reinforced with HAF carbon black gives the maximum peak intensity. This is in agreement with their physical properties.
Fig.5.4 Comparison of the FTIR spectra of the neat ZnS-RISGNR with their 10 phr filled compounds

Fig.5.5 Variation of peak intensities in the IR spectrum of neat ZnS-RISGNR caused by different fillers
FTIR spectra of ionomer-zinc stearate (10 phr) compound (Fig. 5.4) and the neat ionomer reveal that the intensity of the characteristic peaks of the neat ionomer has been lowered to 10 – 15 % with the incorporation of 10 phr zinc stearate. The peaks at 2923, 2854, 2361 cm\(^{-1}\) for the neat ionomer have been showing peak intensities of 0.299, 0.255 and 0.0627 respectively. However, in the IR spectrum of RISGNR ionomer filled with 10-phr-zinc stearate as shown in figure 5.4 the peak intensities are 0.035, 0.018, and 0.039. This shift in the peak intensities upon zinc stearate filling may be due to the ion-ion interaction arising out of coulombic forces between zinc stearate and the ionic aggregates, which result in marked changes in the environment of the sulfonate groups in the zinc stearate filled ionomer.

![FTIR spectrum of the HAF black filled ZnS-RISGNR](image)

**Fig.5.6** FTIR spectrum of the HAF black filled ZnS-RISGNR

### 5.2.4 Physical properties

#### 5.2.4 (a) Carbon black (HAF)
Studies on the physical properties of the neat polymers and (HAF) carbon black filled ionomer compounds show that zinc salt of RISGNR shows higher tensile strength (Fig. 5.7) and lower elongation at break (Fig. 5.8) in comparison with the neat base polymer.

**Fig. 5.7** Tensile strength of the ZnS-RISGNR ionomer / HAF black compound with the carbon content

**Fig. 5.8** Tear strength of the ionomer / HAF black compound with the carbon content
It has been observed that the hardness of the ionomer increased with increase in the carbon content (Fig. 5.9). The carbon black filled samples of the ionomer showed improved resistance towards abrasion loss (Fig. 5.10). This may be due to the
presence of ionic aggregates, which act as physical cross-links. Both the tear strength and hardness have been found to be increasing with the carbon content. Hardness is a measure of modulus of elasticity at low strain.

5.2.4 (b) Silica

Table 5.3 Hardness and abrasion loss of the ionomer/silica compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Hardness (Shore A)</th>
<th>Abrasion loss (cm$^3$/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
<td>0.738</td>
</tr>
<tr>
<td>2</td>
<td>86</td>
<td>0.384</td>
</tr>
<tr>
<td>3</td>
<td>88</td>
<td>0.294</td>
</tr>
<tr>
<td>4</td>
<td>89</td>
<td>0.272</td>
</tr>
</tbody>
</table>

1, 2, 3 and 4 show ionomer compounds with 0, 5, 10 and 20 phr silica.

Fig. 5.11 Tensile strength of ionomer/silica compounds with silica content.

Samples: 1 = neat ionomer; 2, 3, and 4 represent ionomer/silica compounds containing 5, 10 and 20 phr silica.
Measurement of the physical properties of the neat polymer and its compounds containing 5, 10, and 20-phr silica show that the hardness of the base ionomer increased and its abrasion loss decreased up on adding silica (Table 5.3). The tensile strength increased with the silica loading (Fig. 5.11). The incorporation of silica caused a decrease in the elongation at break (Fig. 5.12).

**Fig. 5.12** Elongation at break of the ionomer / silica compound with silica content.
Samples: 1 = neat ionomer; 2, 3, and 4 represent ionomer/silica compounds containing 5, 10 and 20 phr silica.

**Fig. 5.13** Tear strength of the ZnS-RiSGNR/silica compound with silica loading
The higher tear strength and lower abrasion loss of the silica filled ionomer may be due to the reinforcement of the matrix with the silica particles. The interaction between free – OH groups on silica with the polar centers of the ionomer may be the reason for the reinforcement.

5.2.4 (c) Short fibers (Nylon & glass)

Table 5.4 Hardness and abrasion loss of the ionomer /nylon fiber compounds

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hardness (Shore A)</th>
<th>Abrasion loss (cm³/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
<td>0.738</td>
</tr>
<tr>
<td>2</td>
<td>86</td>
<td>0.591</td>
</tr>
<tr>
<td>3</td>
<td>87</td>
<td>0.546</td>
</tr>
<tr>
<td>4</td>
<td>88</td>
<td>0.436</td>
</tr>
</tbody>
</table>

1, 2, 3 and 4 show nylon compounds of ionomer with 0, 5, 10 and 20 phr nylon fiber

The physical properties of the short fiber (nylon and glass) filled ionomers as compared to the neat ionomer (Table 5.4 and figures 5.14 and 5.15).

Fig. 5.14 Tensile strength of ionomer /nylon fiber compound with the fiber content.

Samples 1 = neat ionomer; 2, 3 and 4 represent the compounds containing 5, 10 and 20 phr nylon fiber.
Fig. 5.15 Elongation at break of the ionomer / nylon fiber compound with the fiber content. Samples 1 = neat ionomer; 2, 3 and 4 represent their compounds containing 5, 10 and 20 phr nylon fiber.

Nylon fibers of 0.4-0.6-mm lengths were used to facilitate good dispersion. The improvement in the physical properties of the ionomer – fiber compounds may be due to the relatively good fiber – matrix adhesion. The stress transfer, in this case, may be occurring through shearing at the fiber – matrix interface. Maximum tensile and tear strength for the composite was observed at a nylon loading of 20 phr. Incorporation of nylon fibers becomes very difficult beyond 20-phr.

Table 5.5 Physical properties of the ionomer and glass composites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hardness (Shore A)</th>
<th>Abrasion loss (cm³/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
<td>0.738</td>
</tr>
<tr>
<td>2</td>
<td>86</td>
<td>0.396</td>
</tr>
<tr>
<td>3</td>
<td>88</td>
<td>0.328</td>
</tr>
<tr>
<td>4</td>
<td>89</td>
<td>0.294</td>
</tr>
</tbody>
</table>

Samples 1, 2, 3 and 4 show ionomer / glass fiber compounds with 0, 5, 10 and 20-phr glass fiber
An improvement in the shore A hardness and abrasion loss was rendered to the ionomer at this optimum nylon fiber loading. Presence of the polar NH-CO groups on the nylon fibers interacting with polar centers in the ionomer may be the causative for...
the reinforcement of the ionomer. The physical properties of the fiber – ionomer compounds have been found to be lower at low fiber content, which may be due to (1) dilution of the matrix and (2) reinforcement of the matrix by the fibers increases only as the fiber volume fraction increases. At low fiber content, the matrix is not restrained by enough fibers and highly localized strains occur in the matrix at low strain levels, causing the bond between fiber and matrix to break, leaving the matrix diluted by non – reinforcing, debonded fibers. At high fiber concentrations, the matrix is sufficiently restrained and the stress is more evenly distributed, thus the reinforcing effect outweighs the dilution effect. As the concentration of the fibers is increased to a higher level, the tensile properties gradually improve to give strength higher than that of the matrix. The concentration of fibers beyond which the properties of the compounds improve above the original matrix strength value is known as the optimum fiber concentration (OFC). This OFC is quite often found to lie between 20 and 30 phr. At very high fiber concentration (40 phr) of nylon 6 the strength again decreases, because there is insufficient matrix material to adhere the fibers together.

The elongation at break for the glass fiber /

![Graph](image)

**Fig. 5.18** Tear strength of ionomer / glass fiber compounds with glass fiber content

Ionomer compounds (Fig. 5.17) decreased where as the tear strength (Fig. 5.18) increased as the glass fiber content increased.
5.2.4 (d) Zinc stearate

Table 5.6 Physical properties of the ionomer / zinc stearate compounds

<table>
<thead>
<tr>
<th>Samples</th>
<th>TS (MPa)</th>
<th>E.B (%)</th>
<th>Hardness (Shore A)</th>
<th>Abrasion loss (cm³/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2</td>
<td>248</td>
<td>42</td>
<td>1.92</td>
</tr>
<tr>
<td>2</td>
<td>8.70</td>
<td>124</td>
<td>85</td>
<td>0.738</td>
</tr>
<tr>
<td>3</td>
<td>9.72</td>
<td>112</td>
<td>86</td>
<td>0.696</td>
</tr>
<tr>
<td>4</td>
<td>11.58</td>
<td>102</td>
<td>87</td>
<td>0.576</td>
</tr>
<tr>
<td>5</td>
<td>10.96</td>
<td>96</td>
<td>89</td>
<td>0.596</td>
</tr>
</tbody>
</table>

Samples 1 = neat RISGNR; 2 = neat ionomer; 3, 4 and 5 show, ionomer / zinc stearate compounds with 10, 20 and 30-phr-zinc stearate

The physical properties of RISGNR, ZnS-RISGNR and the zinc stearate filled ionomer are shown in the table 5.6. The ionomer shows higher tensile strength but lower elongation at break than RISGNR. This is due to the presence of physical cross-links arising from the ionic aggregates in the ionomer.

Fig. 5.19 Tear strength of the ionomer/zinc stearate compound with the zinc stearate

Addition of up to 20-phr-zinc stearate increases the tensile strength but decreases the elongation at break, and at further loading, both tensile strength and elongation at
break decrease. At high loading zinc stearate may be diluting the matrix and acting as an inert filler, thus decreasing polymer – filler interaction. Improvement in the tear strength and resistance to abrasion loss of the ionomer was lowered with the addition of the zinc stearate, beyond filler loading of 20 phr. However, hardness of the ionomer increased up on the incorporation of zinc stearate.

5.2.4.e. Comparison of the physical properties

Among the fillers used for the study the properties were observed to be in the order HAF black > nylon > silica > glass > zinc stearate as shown in Table 5.7. The tensile strength was maximum for the HAF filled ionomer and minimum for the zinc stearate/ionomer system (Fig. 5.20).

Table 5.7 Physical properties of 10 phr each of HAF black, silica, nylon, glass, and zinc stearate filled compounds of the 26.5 ZnS-R1SNGR ionomer

<table>
<thead>
<tr>
<th>Samples</th>
<th>E.B. (%)</th>
<th>Hardness (Shore A)</th>
<th>Abrasion loss (cm³/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>124</td>
<td>85</td>
<td>0.738</td>
</tr>
<tr>
<td>2</td>
<td>108</td>
<td>86</td>
<td>0.646</td>
</tr>
<tr>
<td>3</td>
<td>118</td>
<td>88</td>
<td>0.294</td>
</tr>
<tr>
<td>4</td>
<td>112</td>
<td>87</td>
<td>0.546</td>
</tr>
<tr>
<td>5</td>
<td>112</td>
<td>88</td>
<td>0.328</td>
</tr>
<tr>
<td>6</td>
<td>112</td>
<td>86</td>
<td>0.698</td>
</tr>
</tbody>
</table>

1 = neat ionomer; 2, 3, 4, 5 and 6 show ionomers filled with HAF black, Silica, Nylon, Glass and Zinc stearate respectively having 10 phr filler in each case
**Fig. 5.20** Comparison of the tensile strength of the neat ionomer (1) with their filled compounds of HAF black (2), silica (3), nylon (4), glass (5) and zinc stearate (6)

**Fig. 5.21** Comparison of the tear strength of the neat ionomer (1) with their filled compounds of HAF black (2), silica (3), nylon (4), glass (5) and zinc stearate (6)
Fig. 5.22 SEM micrograph of the cryogenic fractured surface of the ionomer / silica (10 phr) compound.

Fig. 5.23 SEM micrograph of the cryogenic fractured surface of the ionomer / silica (10 phr) compound with magnification
The elongation at break (Table 5.7), however, had its lowest value for the HAF filled system in comparison with the other filled systems of the ionomer such as silica, nylon, glass and zinc stearate.

Both HAF and silica filled systems have shown higher tear strength (Fig. 5.21). The shore A hardness of the silica and glass fiber reinforced compounds was higher than the other filled compounds of ionomers. Abrasion loss was minimized in the silica and glass filled systems.

**5.2.5. Scanning electron microscopy**

In the case of silica filled ionomers, the SEM micrographs of the cryogenic fractured surface in which the fillers look very much wetted and embedded in the matrix (Fig. 5.22) These show that the fillers can be identified and the particle size and shape have been preserved (Fig. 5.23). The SEM micrographs of the microtomed surface of the glass fiber filled ionomer showed that the glass fibers are seen embedded in the
ionomer matrix (Fig. 5.24), which shows a better adhesion between the ionomer and the fibers. The fibers are seen oriented in all directions (Fig. 5.25).

Fig. 5.25 SEM micrograph of the cryogenic fractured surface of the ionomer / glass fiber compound

The SEM micrographs of the prestretched nylon filled ionomer surface made with a knife (microtomy) at room temperature (Fig. 5.26) shows that the cut fiber ends are clearly seen and most of them are aligned in one direction. The better adhesion between the fiber and the matrix is almost clear. The enhanced physical properties of the nylon filled ionomer based on RISGNR may be due to this intact interfacial bonding, which seems to be pointing to a stronger bond at the interface. The improved physical properties of the nylon filled ionomers may be due to this strong adhesion between the nylon fibers and the ionomer matrix as shown by the SEM micrographs. The nylon fibers have been found to be in every direction. These observations are found to be in good agreement with their physical properties.
Fig. 5.26 SEM micrograph of the microtomed surface of the ionomer / nylon compound.

5.2.6 Reprocessability studies

Table 5.8 Results of reprocessability studies ionomer / filler compounds

<table>
<thead>
<tr>
<th>Samples</th>
<th>E.B. at cycles (%)</th>
<th>Tear strength at cycles (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>124  122  120</td>
<td>84.5  83.8  83.2</td>
</tr>
<tr>
<td>2</td>
<td>108  107  105</td>
<td>124.4 123.1 122.4</td>
</tr>
<tr>
<td>3</td>
<td>118  116  112</td>
<td>124.6 123.4 122.7</td>
</tr>
<tr>
<td>4</td>
<td>112  110  109</td>
<td>118.6 117.3 116.4</td>
</tr>
<tr>
<td>5</td>
<td>112  111  107</td>
<td>122.4 120.2 118.3</td>
</tr>
<tr>
<td>6</td>
<td>112  109  107</td>
<td>102.4 101.6 101.2</td>
</tr>
</tbody>
</table>

1- neat ionomer; 2, 3, 4, 5 and 6 show ionomers filled with 10 phr each of HAF black, Silica, Nylon, Glass and Zinc stearate respectively
It has been observed that (Fig. 27), the tensile strength of the filled ionomer compounds at all the filler loadings under study remain almost constant even after repeated cycles of mixing and molding.

![Graph showing tensile strength over number of cycles](image)

**Fig. 5.27 Tensile strength of the ionomer composites at different cycles of processing.** 1 = neat ionomer; 2, 3, 4, 5 and 6 show ionomers filled with 10 phr each HAF black, Silica, Nylon, Glass and Zinc stearate respectively

This shows that the ionomer composites behave as thermoplastic elastomers and it could be reprocessed at 120°C by mechanical recycling without deterioration in its physical properties. The changes in elongation at breaks and tear strength remain minimum during reprocessing (Table 5.8).

### 5.3 Theory of filler – ionomer interaction

The interaction of the filler and the ionomer imparts an increase in stiffness and strength to the ionomer. In order to produce significant reinforcement, particle size must be less than about a micron. As specific surface area increases (i.e., as particle size decreases), strength of filled vulcanizates generally increase. It is instructive to determine how particle size influences particle-to-particle spacing in a particulate-
filled ionomer compounds. Spherical particles of diameter 'd' distributed on a three-dimensional square lattice are considered.

Scheme 5.2 Schematic representation of the ionomer-filler interaction showing the restricted mobility shell ('t') around the filler. Dotted line shows the shell limit.

Although this is a simple model, which neglects structure, it nonetheless, illustrates the essential importance of particle size. The nearest neighbor particle spacing 's' for a volume fraction 'υ' of filler is given by:

\[ S = d \left[ 0.806 / \left( \frac{1}{\sqrt[3]{\nu}} - 1 \right) \right] \]

Particle spacing is the same order of magnitude as particle diameter. If it is assumed that there is a shell of thickness 't' around particles in which chain mobility is hindered as a result of interaction with the particles, then the volume fraction 'υ_t' of the rubber phase within 't' is given by:

\[ υ_t = υ \left[ \frac{1}{1 + 2t/d} - 1 \right] / 1 - υ \]

\[ 2t < s \]

All of the network chains will have relaxational motions restricted by at least one filler particle as shown in the proposed model in scheme 5.2. Restricted chains have increased resistance to molecular separation, which is a precursor to crack initiation and growth. Large particles provide stiffening, and act as stress-raising inclusions.
which promote fracture in essentially unmodified bulk rubber. However, as filler particles are made sufficiently small, it becomes inappropriate to view the composite simply as rigid inclusions embedded in a matrix, which behaves like bulk gum rubber. Matrix mobility at large strain is reduced because of close proximity to filler surfaces, and this is expected to hinder crack initiation and growth.

In the case of the fracture in uniaxial tension of a hypothetical perfectly brittle elastomeric network, in which irreversible chain ruptures across the fracture plane are the only mechanism of energy dissipation. Because of the complex topology, network chains will bear different forces when the material is continuously deformed. In addition, an inadvertent discontinuity (flaw) may further magnify chain forces locally. Regardless, some region will experience the highest forces and a network strand there will reach a critical force and break. This is the start of the molecular fracture, which is a precursor to crack formation (i.e., macro-fracture). The load this chain was bearing quickly will be transferred to surrounding chains, which will become overloaded and break. Once a single molecular fracture is initiated, surrounding chains rupture quickly. A cascading process leads to facile crack initiation and immediate catastrophic propagation of a single crack across the specimen. Strength is very low, and fracture energy is equal to the energy lost by recoiling chains, which broke to create the fracture surface. Such behavior may be approximately shown by ionic cross-linked polymers.

In the case of the fracture behavior of vulcanisates containing rigid filler, since inclusions amplify matrix stress; one might expect strength to be decreased. Indeed, a gum vulcanisate containing a single rigid macro – inclusion has reduced strength, the reduction being greater for larger inclusions. However, in a micro-composite containing a significant volume fraction, say 25 %, of rigid filler particles, though crack initiation is facilitated in essentially bulk like matrix, the inclusions do provide some interference to propagation, as the crack path must deviate around filler particles. The effects trade – off, and the strength of the micro composite rubber is not much different than that of the unfilled matrix. This is the ‘break- even point’ for rubber reinforcement. Crack deflection and energy dissipation are minimal, and there is still a single crack tip, which grows through the largely unhindered matrix. Furthermore, catastrophic crack growth follows rather quickly after crack initiation. In the case of
highly reinforced rubber a crack may split when it meets very fine particles, presumably because strength anisotropy reaches a critical value. A crack does not simply propagate around the barrier and continue more or less perpendicular to the deformation direction. Aligned and restricted matrix chains surrounding particles inhibit continued lateral crack growth. Instead, two new crack form, which grow longitudinally in opposite directions towards closely spaced adjacent particles. Particle spacing is critical to crack splitting.

5.4 Conclusion

- Both DMTA and DSC support the retention of the ionomer properties for the carbon black filled compound.
- DMTA plot shows that both the Tg1 and Tg2 are retained even in the silica filled ionomers. The value of the thermal transitions suggests that silica reinforces the backbone chain and weakens the ionic associations. The room temperature storage modulus for the silica filled ionomer is the highest among the selected fillers.
- The short fibers of nylon as well as glass have been found to be interacting with both the matrix-phase and the cluster-phase.
- Zinc stearate acts as an ionic domain plasticizer, presumably by the incorporation of some ionic head groups of the zinc stearate in to the sulfonate multiplets, which lowers the Tg. Appearance of multiple transitions for the zinc stearate compound of the ionomer along with the detection of the anomalous melting behavior of the zinc stearate in the DSC profiles may be considered as evidence of interactions between zinc stearate and sulfonate groups in RISGNR ionomers.
- Physical properties of the filled systems show improvement over the neat ionomer. Both particulate fillers such as HAF black, silica, zinc stearate and short fibers such as nylon, and glass reinforce with the ionomers based on styrene grafted natural rubber.
- FTIR results give support to these observations
5.4 References