5A.1 Introduction

Short fiber reinforced composites are relatively a new class of materials that find applications in most general purpose and speciality products ranging from belts, hoses, diaphragms and seals to tyres. Since short fibers can be incorporated directly into the rubber compound along with other additives, the resulting composites are amenable to the standard rubber processing steps of extrusion, calendering and the various type of molding operations such as compression, injection and transfer molding [1]. Properties of short fiber elastomer composite critically depend upon the interfacial bonding between fiber and the matrix [2-6]. Conventionally, a tricomponent system based on hexamethylenetetramine (hexa), resorcinol and fine particle hydrated silica
(HRH system) is used to achieve good adhesion between short fiber and the rubber matrix. This is because, the constituents of the dry bonding system can be added to the rubber matrix like any other compounding ingredients and extra process like dipping and the drying can be avoided. Fiber-matrix adhesion in short fiber rubber composites has been a field of extensive research. Dunnom [7] observed a marked difference in the adhesion between the matrix and the fiber by adding silica to a compound containing resorcinol and hexa. Rajeev et al. [2], Sreeja et al. [5], Derringer [8], and De and co-workers [9-10] have described the various aspects of short fiber adhesion to rubber in the presence of the dry bonding system. In all these studies they have used conventional precipitated silica [2, 8, 10-13]. The role of silica is to improve wetting of the fiber surface [7-9, 12]. As small particles have higher surface area, nanosilica can be more effective in improving wettability of the fibers.

In this work the effect of nanosilica based tri-component dry bonding system on short Nylon 6 fiber - natural rubber composite is reported. The mechanical properties of Nylon 6 short fiber/natural rubber composites are presented.

5A.2 Experimental

NR-N6 composites were prepared using the prepared nanosilica and commercial silica based HRH bonding system. Formulation of the test mixes are given in the table 5.A.1. Natural rubber used in this study was ISNR-5 and Nylon 6 fiber, obtained from SRF Ltd., Chennai, India, was chopped to approximately 6 mm length. Fiber loading was varied from 0 to 30 phr. Hexa:Resorcinol:Silica (HRH) ratio was maintained as 2:2:1. HRH loading was adjusted as 16% of the fiber loading.
Table 5 A.1. Formulation of the mixes

<table>
<thead>
<tr>
<th>Ingredients (phr)†</th>
<th>Nanosilica HRH bonding</th>
<th>Commercial silica HRH bonding</th>
<th>Without HRH bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tr>
<tr>
<td>Hexa</td>
<td>- 0.67 1.33 2</td>
<td>- 0.67 1.33 2</td>
<td>- - - -</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>- 0.67 1.33 2</td>
<td>- 0.67 1.33 2</td>
<td>- - - -</td>
</tr>
<tr>
<td>Nanosilica</td>
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<td>- - - -</td>
<td>- - - -</td>
</tr>
<tr>
<td>Commercial silica</td>
<td>- - - -</td>
<td>0.33 0.66 1</td>
<td>- - - -</td>
</tr>
<tr>
<td>Nylon 6 fiber</td>
<td>0 10 20 30</td>
<td>0 10 20 30</td>
<td>0 10 20 30</td>
</tr>
</tbody>
</table>

† phr- parts per hundred rubber.

Natural rubber-100 phr, Zinc oxide-5 phr, Stearic acid-2 phr, \( \text{N-(1,3-dimethylbutyl)N'-phenyl-p-phenylenediamine} \) -1 phr, CBS-0.6 phr, TMTD- 0.2 phr and sulphur-2.5 phr were common to all mixes.

The details of preparation of the mixes, molding and testing are given in chapter 2.

**5A.3 Results and Discussion**

Figure 5A.1 shows the variation of tensile strength with fiber loading in longitudinal direction for all mixes. The tensile strength increases with fiber content with an initial minor drop at 10 phr. This drop may be due to the dilution effect of the fibers at lower loadings [14-15]. At higher fiber loadings, however, the reinforcing effect takes over, resulting in an improved ultimate strength.
Chapter 5A

The improvement in tensile strength of the composite containing 30 phr fiber loading with nanosilica as HRH bonding is 39 % compared to the gum compound. But the same mix containing commercial silica as HRH bonding shows only about 26 % improvement than the gum compound. The improvement in tensile strength of composite containing no HRH bonding system is only about 8 %. This implies that nanosilica is very effective in improving the efficiency of HRH bonding system in short nylon fiber – Natural rubber composites. Nanosilica contributes to effective interaction between the fiber and the matrix due to its small particle size and hence improves the interfacial adhesion between the fiber and the matrix. SEM studies of the tensile fractured samples also support this view.

Figures 5A.2 is the SEM picture of the tensile fracture surface of the composite containing nanosilica based HRH system. Fiber-surface is not smooth as the matrix is adhered on to the fiber. Fiber ends are seen to be broken. This indicates that there is a strong bond existing between the fiber and the matrix.
Figures 5A.3 is the micrograph of the tensile fracture surface of samples containing commercial silica based HRH bonding system. The fibers are pulled out from the matrix. No resin is adhered on to the fiber surface, as the bond is not as strong as in the case of nanosilica. The micrographs of the tensile fracture surface
of samples without HRH bonding system also shows that the fibers are pulled out from the matrix (Fig.5A.4).

![Scanning Electron Micrographs of composite without HRH](image)

**Figure 5A.4.** Scanning Electron Micrographs of composite without HRH

![Tensile Strength Variation](image)

**Figure 5A.5.** Variation of tensile strength with fiber loading in transverse direction
The variation of tensile strength of the composites with fiber loading in transverse direction is shown in figure 5A.5. The strength drops drastically with 10 phr fiber. With further increase in fiber loading, the strength is not improved as in the case of longitudinal orientation of fibers. This is because the load is not effectively transmitted to the fibers as they are oriented across the direction of load. In this configuration growing crack can easily pass through the fiber-matrix interfaces facilitating the easy failure of the sample.

![Figure 5A.6. Variation of tear strength with fiber loading in longitudinal direction](image)

The variation of tear strength in longitudinal direction with fiber loading is shown in figure 5A.6. Tear strength increases with fiber loading. The higher tear strength of the composites is due to the obstruction of tear path by longitudinally oriented fibers. The composite containing synthesized nanosilica HRH system shows an improvement in tear strength from 43 N/mm for gum to 106 N/mm with 30 phr fiber loading. The composite containing commercial silica shows an improvement to 93 N/mm with the same fiber loading. Without HRH bonding
system the corresponding value is 82 N/mm. The composite containing nanosilica shows a greater extent of improvement in tear strength than the other two types of composites. This may be attributed to the lower particle size of the synthesized silica. Due to this it improves the wettability of the fibers to the matrix.

![Graph showing tear strength variation with fiber loading](image)

**Figure 5.A.7. Variation of tear strength with fiber loading in transverse direction**

Figure 5 A.7 shows the variation of tear strength with fiber loading in transverse direction. The increase in tear strength with increase in fiber loading is not as high as that in longitudinal direction. We can see that the composite with nanosilica HRH system shows an improvement from 43 N/mm for gum to 87 N/mm with 30 phr fiber loading. With commercial silica HRH system, the improvement is 83 N/mm with the same fiber loading. But the composites containing no HRH bonding system shows very little improvement in the presence of 30 phr fiber.

Figure 5A.8 and Figure 5A.9 show the variations of elongation at break with fiber loading in longitudinal and transverse directions, respectively. In both the cases there is a sudden drop in elongation at break with 10 phr fiber loading and
after that it remains more or less constant with increase in fiber loading. The decrease in elongation at break of the composite with fiber loading may be due the restraining effect of the fibers.

![Graph showing variation of elongation at break with fiber loading in longitudinal direction](image1.png)

**Figure 5A.8. Variation of elongation at break with fiber loading in longitudinal direction**

![Graph showing variation of elongation at break with fiber loading in transverse direction](image2.png)

**Figure 5A.9. Variation of elongation at break with fiber loading in transverse direction**
The variation of Modulus at 50 % elongation for the composites with fiber loading in longitudinal direction is shown in figure 5A.10. There is marked improvement in modulus with increasing fiber content.

Figure 5A.10. Variation of modulus with fiber loading in longitudinal direction

Figure 5A.11. Variation of modulus with fiber loading in transverse direction
The composite with synthesized nanosilica shows an improvement from 0.438 N/mm² for gum to 26 N/mm² with 30 phr fiber loading. With commercial silica the modulus is improved to 19 N/mm² at similar fiber loading. The corresponding improvement for the composite without HRH bonding system is to 15 N/mm². The lower particle size of the nanosilica helps in improving the adhesion of the fiber and matrix. A similar trend is observed in transverse direction also (Fig. 5A.11).

The variation of abrasion loss with fiber loading is shown in figure 5A.12. Abrasion loss of all the composite samples is less than that of the gum compound. Samples with nanosilica show considerable decrease in the abrasion loss. In the case of samples without HRH bonding system, there is only marginal decrease in the abrasion loss. During abrasion test the matrix as well as the reinforcing fiber are worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In this case, the presence of strong interfacial adhesion between the fiber and matrix makes the matrix stiffer and lowers the abrasion loss.

![Figure 5A.12. Variation of abrasion loss with fiber loading](image-url)
Figure 5A.13 shows the variation of compression set of all the mixes with fiber loading. Compression set increases with fiber loading. As the fiber loading increases the elastic property of the composite decreases. The composites containing nanosilica with 30 phr fiber loading shows higher compression set than the composite with commercial silica-HRH bonding and the composite without HRH bonding.

![Compression Set vs Fiber Loading](image)

**Figure 5A.13. Variation of compression set with fiber loading**

The variation of rebound resilience with fiber loading is shown in figure 5A.14. A continuous decrease in resilience is observed with fiber loading. As more energy is dissipated at the fiber-matrix interface the resilience is reduced. The composite containing nanosilica shows lower resilience than other two types of composites. Because in that composites the fiber-matrix adhesion is very strong.
Figure 5A.14. Variation of resilience with fiber loading

Figure 5A.15. Variation of percentage retention in tensile strength with fiber loading
Figure 5A.16. Variation of percentage retention in tear strength with fiber loading

Figure 5A.17. Variation of percentage retention in modulus with fiber loading
Ageing of the composite at 70°C for 72 hours causes a marginal increase in mechanical properties in the presence of HRH dry bonding system. (Fig. 5A.15- Fig. 5A.17). This may due to the improved fiber-matrix attachment by ageing. Similar result in the case of NBR composites has been reported earlier [16]. The percentage retention in ageing is higher for nanosilica bonded composites than that of commercial silica for the entire fiber loading.

5A.4 Conclusions

Dry bonding system comprising of resorcinol, hexamethylene tetramine, and silica causes significant improvement in the mechanical properties of the NR-short Nylon 6 fiber composites. The efficiency of HRH bonding system in NR-Nylon 6 short fiber composite is increased in the presence of synthesized nanosilica with particle size lower than the commercially available silica. Tensile strength, tear strength, modulus and abrasion resistance are increased by the use of nanosilica in HRH system which shows that the interfacial adhesion between the fiber and the matrix is improved. Compression set and resilience are adversely affected by the introduction of nanosilica. The composites show anisotropy in mechanical properties. Ageing of the composite at 70°C for 72 hours causes an increase in the tensile strength, tear strength and modulus in the presence of the dry bonding system. The retention in ageing is better for nanosilica composites.

5A.5 References


Chapter 5A


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138
### 5B.1 Introduction

Styrene-butadiene rubber (SBR), a general purpose synthetic rubber is widely used in products such as tyres and belts, is much superior to NR with respect to ageing and ozone resistance. SBR exhibits significantly lower resilience than NR so that it has higher heat buildup on flexing. The oil resistance of SBR is poor and it is not resistant to aromatic, aliphatic or halogenated solvents. But the extrusion properties of SBR are superior to those of NR and its stocks have fewer tendencies to scorch in processing. The abrasion resistance of SBR is as good as that of NR or slightly better. The gum vulcanizates of SBR are generally weak and it is essential to use reinforcing fillers to produce products of high strength. Reinforcing SBR with short Nylon fibers will improve its mechanical properties. Interfacial bond is known to play an important role in short fiber composites since this interface is critical in transferring the load from the matrix to the fiber. Several methods are used to improve fiber matrix adhesion. The dry bonding system commonly used in rubbers is the HRH system consisting of hydrated silica, resorcinol.
and hexamethylene tetramine to create adhesion between the fiber and the rubber matrix. It has been reported by many authors that the HRH bonding system significantly improves the adhesion of various natural and synthetic fibers to rubber matrices [1-7]. In this work the effect of nanosilica based tri-component dry bonding system on the mechanical properties of short Nylon 6 fiber / styrene butadiene rubber composite is reported.

5B.2 Experimental

SBR/short Nylon 6 composites were prepared by using the newly prepared nanosilica and commercial silica based HRH bonding system. Styrene butadiene rubber (SBR) used was Techlen SBR 1502 grade and Nylon 6 fiber obtained from SRF Ltd., Chennai, India, was chopped to approximately 6mm length. Fiber loading was varied from 0 to 30 phr. Hexa:Resorcinol:Silica (HRH) ratio was maintained as 2:2:1. HRH loading was adjusted as 16% of the fiber loading. Formulation of the test mixes are given in the table 5B.1.

Table 5B.1. Formulation of the mixes

<table>
<thead>
<tr>
<th>Ingredients (phr)*</th>
<th>Nanosilica HRH bonding</th>
<th>Commercial silica HRH bonding</th>
<th>Without HRH bonding</th>
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<tbody>
<tr>
<td>Hexa</td>
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<td>Resorcinol</td>
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<tr>
<td>Commercial silica</td>
<td>- - - - 0.33 0.66 1</td>
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<td></td>
</tr>
<tr>
<td>Nylon 6 fiber</td>
<td>0 10 20 30</td>
<td>0 10 20 30</td>
<td>0 10 20 30</td>
</tr>
</tbody>
</table>

* phr- parts per hundred rubber.
SBR-100 phr, Zinc oxide-5 phr, Stearic acid-2 phr, N-(1,3- dimethylbutyl) \( N' \)-phenyl-\( p \)-phenylenediamine) -1 phr, CBS-0.8 phr, TMTD- 0.2 phr and sulphur-2 phr were common to all mixes.

The details of preparation of the mixes, molding and testing are given in chapter 2.

5B.3 Results and Discussion

The variations of tensile strength with fiber loading in both the directions are shown in figure 5B.1 and figure 5B.2. Tensile strength varies linearly with the fiber loading. At any fiber content the tensile strength is higher for the nanosilica HRH bonded composites.

![Graph showing variation of tensile strength with fiber loading](image)

Figure 5B.1. Variation of tensile strength with fiber loading in longitudinal direction
Figure 5B.2. Variation of tensile strength with fiber loading in transverse direction

The introduction of 10 phr fiber in the gum compound increases the tensile strength by 400% for nanosilica HRH bonded composites (Fig.5.B.1). The commercial silica HRH bonded composite shows an improvement of 300 % for the same mix. The corresponding improvement for the composite without HRH bonding system is only 200%. Similar improvements are also observed in 20 phr and 30 phr fiber loaded samples. This implies that the nanosilica has better interaction with the matrix and hence improves wettability of the short fibers, resulting in higher tensile strength. SEM studies of the tensile fractured samples also support this view. Figures 5.B.3 shows the tensile fracture surfaces of the composite with nanosilica HRH bonded system. Fiber surface is not smooth. Matrix is adhered on to the fiber surface. Broken fiber ends are also seen. This indicates that there is a strong bond existing between the fiber and the matrix.
Figures 5B.4 is the micrographs of the tensile fracture surface of composite containing commercial silica HRH bonding system. The fibers are pulled out from the matrix. No resin is adhered on to the fiber surface, as the bond is not as strong as in the case of nanosilica. The micrographs of the tensile fracture surface of samples without HRH bonding system shows that all the fibers are pulled out from the matrix (Fig.5 B.5). Comparing figures 5 B.1 and 5 B.2 it is clear that tensile strength is higher in longitudinal direction. This is because the transverse orientation of fibers is not effective in supporting the load as the growing crack can easily pass through the fiber-matrix interfaces facilitating easy failure of the composite.
Figure 5B.4. Scanning Electron Micrographs of Commercial silica HRH bonded Composite

Figure 5B.5. Scanning Electron Micrographs of composite without HRH

Tear strength increases linearly with fiber loading for all the mixes (Fig.5 B.6 and 5 B.7). Tear strength increases to 111 N/mm from 14 N/mm in the presence of 30 phr fibers in the composite containing nanosilica based HRH bonding system. The corresponding values for the commercial silica based HRH system and without HRH are 106 N/mm and 101 N/mm, respectively. Like NR composite here also the tear strength is higher for the nanosilica HRH bonded composites.
Figure 5B.6. Variation of tear strength with fiber loading in longitudinal direction

Figure 5B.7. Variation of tear strength with fiber loading in transverse direction

The decrease in particle size of nanosilica improves dispersion of silica in the matrix and helps the better adhesion of the fiber and the matrix through the silica surface. A similar trend is observed in the transverse direction also (Fig. 5 B.7). The
tear strength values are higher in the longitudinal direction than the transverse direction. This is because transversely oriented fibers being parallel to the propagating crack front offers less resistance to propagating tear resulting in lower tear strength values.

The elongation at break decreases with fiber loading (Fig. 5B.8). The elongation at break undergoes a sharp fall on introduction of 10 phr of fibers in all the mixes. This is because the fibers inhibit the orientation and flow of molecular chains and hence the ultimate elongation decreases substantially on introduction of low concentration of fibers. With further fiber loading, the ultimate elongation remains almost constant. Since nanosilica improves the wettability of short fibers, there is better interaction between the matrix and the fiber occurs. Therefore composites having nanosilica-HRH bonding will have lower elongation at break. In transverse direction also elongation at break decreases with fiber loading and it is lower for composites containing nanosilica based HRH bonding system (Fig. 5B.9).

![Figure 5B.8. Variation of elongation at break with fiber loading in longitudinal direction](image)
**Figure 5B.9. Variation of elongation at break with fiber loading in transverse direction**

Figures 5 B.10 and 5 B.11 show variation of modulus with fiber loading in the longitudinal and the transverse directions, respectively.

**Figure 5B.10. Variation of modulus with fiber loading in longitudinal direction**
The modulus increases with fiber loading for all the mixes in both the directions. But the improvement in modulus is low in the case of transverse direction. Here also the composite with nanosilica based HRH system gives the highest value. This implies that the nanosilica has better interaction with the matrix and hence improves the modulus values.

Figure 5B.11 show that abrasion loss decreases with fiber loading. This may be attributed to the fact that as the fiber loading increases, reinforcement increases. The decrease in abrasion loss for 30 phr fiber loaded composites are 63.4%, 58.49% and 38.64% respectively for the composite with nanosilica, commercial silica and without HRH, respectively. Samples with nanosilica show a considerable decrease in the abrasion loss than the sample containing commercial silica. This is because of more restrained matrix of the composite. During abrasion test the matrix as well as the reinforcing fiber is worn out by the abrading surfaces. A stiffer matrix has lower abrasion loss. In this case the presence of strong interfacial adhesion between the fiber and the matrix renders the matrix stiffer and lowers the abrasion loss.
Figure 5B.12. Variation of abrasion loss with fiber loading

Figure 5B.13 shows the variation of compression set with fiber loading. The compression set increases with fiber loading.

Figure 5B.13. Variation of compression set with fiber loading
This is because as fiber loading increases, the elastic characteristic of the matrix is reduced, giving high compression set values. The increases in compression set for 30 phr fiber loaded composites are 72%, 67% and 61% respectively for nanosilica based HRH bonding System, commercial silica based system and without HRH. Nanosilica bonded samples show a higher value of compression set. This may be due to probable breakage of fiber-matrix interfacial bond when subjected to prolonged effect of temperature and compressive force to the system.

Figure 5B.14. Variation of resilience with fiber loading

Figure 5B.14 shows that there is a reduction in resilience with fiber loading. The dissipation of energy at fiber-matrix interface results in lower resilience value. For the 30 phr fiber- loaded composites, resilience shows a reduction of 39% for nanosilica based HRH system, 26% for commercial silica system and 19% for non-HRH system. Resilience, which is an indication of material elasticity is lowest for nanosilica composites. In presence of nanosilica, there is strong adhesion between the matrix and the fiber.
Ageing of the composite at 70° C for 72 hr. causes a marginal increase in mechanical properties in presences of HRH dry bonding system. (Fig.5 B.15, Fig.5 B.16 and Fig.5 B.17). This is due to the improved fiber-matrix attachment by ageing.

**Figure 5B.15. Variation of percentage retention in tensile strength with fiber loading**

**Figure 5B.16. Variation of percentage retention in tear strength with fiber loading**
Similar effect in the case of melamine fiber reinforced EPDM rubbers has been reported in earlier [8]. The percentage retention in ageing is higher for nanosilica bonded composites than that of commercial silica for the entire fiber loading. This shows that the efficiency of nanosilica HRH bonding system is better than that of commercial silica HRH dry bonding system in SBR / short Nylon 6 fiber composites.

![Graph showing variation of percentage retention in modulus with fiber loading](image)

**Figure 5B.17. Variation of percentage retention in modulus with fiber loading**

### 5B.4 Conclusions

HRH bonding system in SBR / Nylon 6 short fiber composites causes a significant improvement in the mechanical properties of the composites. The efficiency of HRH bonding system in SBR / Nylon 6 short fiber composite is increased in the presence of synthesized nanosilica. Tensile strength, tear strength, modulus and abrasion resistance are increased by the use of nanosilica HRH system which shows that the interfacial adhesion between the fiber and matrix is improved in the presence of nanosilica. Compression set and resilience are adversely affected by the use of nanosilica based HRH bonding system. The composites show anisotropy in mechanical properties. Ageing of the composite at
70°C for 72 hr causes an increase in the tensile strength, tear strength and modulus in the presence of the dry bonding system. The improvement in properties by ageing is due to the improved fiber-matrix attachment. The retention in ageing is better for nanosilica composites.

5B.5 References