9.1 Introduction

Nanofillers, at low concentration, improve the mechanical and physical properties, electrical conductivity and flame retardancy of the rubber vulcanizates. Improvement in air impermeability and good filler dispersion gives more surface finish and fewer rejections in large scale production of thin walled goods like thin films, gloves, balloons, medical items etc. [1]. Thin walled polymer products are usually produced by dipping process. Latex dipping processes are classified as simple or straight dipping, coagulant dipping, heat-sensitized dipping and electro deposition. Natural rubber latex is the major raw material for dipped goods. Synthetic latices are used for some special properties. Due to the protein allergy of natural rubber latex, examination gloves are manufactured in XNBR latex. Fillers are usually used in gloves to reduce the manufacturing cost. Fillers upto 15% are usually tolerable, anything above that can become detrimental to the performance and quality of the glove.

In the foregoing sections of this work, reinforcing effect of nanokaolin and vinylsilane grafted nanokaolin in XNBR and SBR latices were studied by casting latex films in glass trays. In this Chapter nano clay
reinforced nitrile gloves were made by dipping process, in the normal production line. The work was done at Primus, a well reputed glove manufacturing company in Cochin. Mechanical properties of the latex gloves were studied and the samples were characterized by SEM analysis.

**Brief description of glove manufacturing process.**

The manufacturing process is a multi stage process and includes mainly latex compounding, maturation, dipping, testing and packing

**Latex compounding:**

Concentrated latex as per BIS standards, was mixed with all the ingredients including accelerators, antioxidants etc. The compounded latex was then maintained undisturbed for maturation and then sent to the dipping tank through pipes.

**Dipping Process**

The process of coagulant dipping took place in a continuous chain dipping line. The pre heated, cleaned, hand shaped formers were first dipped in a coagulant tank containing dry coagulant based on calcium nitrate tetrahydrate and then in the latex compound. Dwell time was adjusted to get the required thickness for the product. Then it was send to the drying chamber were the temperature was maintained at 85°C. When half dried, bead rolling was done, while the article was still on the former. Thus a serrated edge was formed on the open end of the glove which helped in better fitting. Then the latex coated former was immersed in a water bath to wash out all water leachable materials. This is called ‘wet gel leaching’ or ‘pre vulcanization leaching’. Vulcanization temperature was in the range 120°C. The vulcanized sample was then given a dry leaching,
also called ‘post vulcanization leaching’. The gloves were then dusted with corn starch to prevent adhesion and to facilitate the stripping of gloves from the former. Then the gloves were stripped from the former manually and turned inside out. After stripping they were fed into tumble driers where complete drying took place. Then they were given lot numbers for identification, sent for inspection and later to the packaging unit. A flow chart of the dipping process is given in Fig. 9.1.

![Flow chart of the dipping process](image)

**Fig. 9.1. Flow chart of the dipping process**

### 9.2 Experimental

**Materials**

XNBR latex is Synthomer 6311. Specifications are given in Table 9.1

<table>
<thead>
<tr>
<th>Component</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids</td>
<td>45%</td>
</tr>
<tr>
<td>pH</td>
<td>8.5</td>
</tr>
<tr>
<td>Viscosity @ 23°C, Brookfield LVT</td>
<td>75 mPa.s</td>
</tr>
<tr>
<td>Particle size</td>
<td>130nm</td>
</tr>
<tr>
<td>Specific Gravity @ 25 °C</td>
<td>1.00</td>
</tr>
<tr>
<td>Surface Tension LVT</td>
<td>31mN/m</td>
</tr>
<tr>
<td>Acrylonitrile Content Level</td>
<td>Medium</td>
</tr>
</tbody>
</table>
Nanokaolin is Nanocaliber100, supplied by English Indian Clays Ltd., Veli, Thiruvananthapuram. Vinylsilane grafted nano kaolin is Nanocalibre-100V, supplied by English Indian Clays Ltd., Veli, Thiruvananthapuram. Nanokaolin is referred as ‘C’ and vinylsilane grafted nanokaolin as ‘V’

**Method**

The compounding ingredients S, ZDC, ZnO and TiO₂ along with nanokaolin /vinylsilane grafted nanokaolin were added to XNBR latex by continuous stirring. The fillers were added in varying concentration, ranging from 1-10 phr. This compounded latex was used in the production of gloves. Further studies were done using ball billed and sonicated samples of clay. Mechanical properties of the gloves were determined using Shimadzu Model AGI Universal Testing Machine and SEM analysis of the tear fractured surface of gloves were determined using JEOL Model JSM-6390LV.

**9.3 Results and Discussion**

**9.3.1 Mechanical properties**

Effect of nanoclays (‘C’ and ‘V’) on the mechanical properties of XNBR latex was studied. Variations of tensile strength/elongation at break and modulus/tear strength of XNBR-C and XNBR-V nanocomposites are given in Fig 9.2 and 9.3 respectively. Tensile strength increased up to 20% for XNBR-C nanocomposite (3phr) and after that decreased. XNBR-V nanocomposite gave 32% increase in tensile strength at 5phr. Tensile strength is a measure of the force required to stretch a glove sample until it breaks. So higher the tensile strength, greater will be the strength of the glove.
Elongation at break gives a measure of how long the glove stretches, as percentage of original sample length, before it breaks. Elongation at break increased for XNBR-C nanocomposite and showed 14% increase at 5phr concentration. Modulus is a measure of the comfort. Lower modulus reflects softer, more comfortable gloves. Comfort depends on proper fit and to some extent on the glove thickness. Here incorporation of nanokaolin increased the tensile strength, elongation at break and reduced the modulus at 300% elongation. Tear strength of both the samples, were greater than that of the nitrile gloves without filler.
Fine particle size and uniform distribution of filler in XNBR latex contributed to the reinforcement. Increase in properties indicated improved product performance.

Further studies were conducted using sonicated and ball milled nanokaolin. Fig.9.4. gives a comparison of mechanical properties of gloves made with sonicated nanokaolin and ball milled nanokaolin. From the figure it was observed that the sonicated nanokaolin gave better increase in mechanical properties when compared to the ball milled sample.

Fig.9.4. Variation of A. Tensile strength, B. Elongation at break, C. Modulus and D. Tear strength of ball milled and sonicated clay filled nitrile gloves against clay concentration.
Table 9.2. gives the percentage increase in properties of sonicated clay filled gloves compared to the ball milled samples. The property improvement for samples with sonicated clay might be attributed to the reduction in the size of the aggregates by sonication.

Table 9.2. Percentage increase in mechanical properties of sonicated nanokaolin filled nitrile gloves in comparison to the ball milled samples.

<table>
<thead>
<tr>
<th>Clay loading (phr)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Modulus at 300% elongation (MPa)</th>
<th>Tear strength (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74</td>
<td>12</td>
<td>31</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>65</td>
<td>17</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>14</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>-</td>
<td>18</td>
<td>9</td>
</tr>
</tbody>
</table>

9.3.2 Scanning electron microscopy (SEM)

Fig. 9.5. A and B. shows the SEM micrographs of the tear fractured surfaces of gloves containing sonicated and ball milled nanokaolin (3phr) respectively. Sample containing sonicated clay showed multiple crazing along different directions. More roughness on the tear fractured surface showed greater resistance to crack propagation. This proved better stress transfer from the rubber matrix to the nanoclay and greater adhesion of the sonicated clay to the rubber matrix [2]. The reduction in the size of the clay particles on sonication increased the surface area of the particles and might have helped in better interaction. But in the ball milled samples the clay flakes were more conspicuous and were sparingly distributed. They seem to be thrown out of the matrix. This might be the reason for the
reduction in the property of the ball milled nanokaolin when compared to the sonicated sample.

![Fig.9.5. SEM images of tear fractured surface of gloves containing A. 3phr sonicated nanokaolin and B. 3phr ball milled nanokaolin](image)

### 9.4 Conclusions

Mechanical properties of nitrile gloves could be improved by the addition of nanokaolin and vinylsilane grafted nanokaolin. Gloves made with sonicated clay showed greater increase in mechanical properties compared to those made with ball milled clay.
Studies on the mechanical properties of nanoclay filled XNBR latex gloves

References
