Effect of organo clay on curing, mechanical and dielectric properties of NR/SBR blends

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Abstract. Natural rubber (NR) and styrene butadiene rubber (SBR) based elastomeric blends reinforced with organically modified Sodium bentonite clay were prepared by two roll mills. Vulcanization parameters such as minimum and maximum torque values scorch and cure times are measured by Oscillating Disc Rheometer. Mechanical properties such as Tensile strength, modulus at 100%, 200% and 300% elongation and elongation at break and Hardness were measured by Universal testing machine and Durometer Shore A hardness meter respectively. Dielectric properties such as dielectric constant ($\varepsilon'$), dissipation factor (tan\(\delta\)) and volume resistivity ($\rho_v$) were measured at room temperature. The curing studies show that torque values are increasing in NR/SBR blends by increase NR content. The scorch and optimum cure time in NR/SBR blends reinforced organo modified clay was found through increase in the SBR content. This may be due to better processing safety of the NR/SBR blends reinforced with organo modified clay. Mechanical properties show that addition of SBR in blends, tensile strength, elongation modulus increases, but 100% modulus slightly increases and no change was observed in Hardness. Dielectric studies show that dielectric constant of NR and SBR rubbers are almost same, it may due to their non-polar nature. But addition of SBR in NR/SBR blend, dielectric constant gradually increases and maximum value observed at 50/50 ratio. But no considerable change was observed in dissipation factor. Frequency dependant resistivity shows that volume resistivity was not changed with respect to frequency up to 3.5 kHz and beyond that the frequency dependence resistivity was found.

1. Introduction
NR/SBR blends reinforced with carbon black has been widely used in the rubber industry to manufacture moulded goods and tyre tread. Use of carbon black produces black colour products and also pollutes the environment. In recent years replacement of carbon black with white colour filler such as organo modified clay is gaining importance. Also, incorporation of very small fraction of the organo modified clay would give significant improvements in the mechanical properties.

Clay reinforced polymer blends and composites have been attracting considerable attention among researchers in view of their excellent mechanical, electrical and dielectric properties. Organo modified clay reinforced polymers have proved themselves to be environmentally and economically superior to polymer reinforced with conventional carbon black filler, providing better mechanical strength in intercalated and exfoliated state [1,2].

Dielectric elastomer, a new class of material reinforced polymer with layered clay are becoming popular and useful for understanding the basics of elastomers and their various applications in electrical and
electronics industry [3,4]. This study carries investigation of curing, mechanical and dielectric properties of NR/SBR blends reinforced with of organo modified clay.

2. Experimental

2.1. Materials
Natural Rubber (NR) ISNR-5 grade obtained from Rubber Research Institute of India, Kottayam, Kerala, having Mooney viscosity {ML (1+4)} at 100°C = 85.3. Styrene Butadiene Rubber (SBR) BSK-1502 grade with Mooney viscosity {ML (1+4)} at 100°C = 46-58 and other rubber additives such as activators zinc oxide and stearic acid, accelerator CBS (N-cyclohexyl-2-benzothiozole sulphonamide) and vulcanizing agent Sulphur were used in this study were supplied from rubber industries, Chennai. Na+-Bentonite clay of Indian origin with cation exchange capacity 80 meq/100 gms, were supplied by Ashapura Group, India. Octadecyl amine was supplied by Sigma Aldrich was used as an organic modifier of the clay.

2.2. Preparation of organo-modified bentonite clay
5 grame of Na+ Bentonite clay, 5 grame of Octadecylamine and 0.466 mi Hydrochloric acid (0.01N) were dispersed into 500 ml of hot water (80°C). The solution was vigorously stirred for 4 hrs to flocculate the clay. The precipitate was collected on a filter, centrifuged and dried to yield the organoclay [5].

2.3. Preparation of NR/SBR Blends Reinforced Organo Modified Clay
The formulations of the natural rubber and styrene butadiene rubber blends organo modified clay are given in Table 1. Mixing was done by using two roll mixing mills at room temperature with rotor friction ratio of 1:1.4. SBR was added to the mixing mill and after smooth band formation the rubber was cut and taken out. Then NR was masticated and SBR sheet added and blended thoroughly with NR. The organo modified clay was added followed by the addition of remaining ingredients.

| Ingredients    | NR (ISNR-5) | SBR (BSK-1502) | ZnO | Stearic Acid | Organo Clay | CBS | Sulphur |
|----------------|-------------|----------------|-----|--------------|-------------|-----|---------|
| phr            | 100         | 75             | 50  | 25           | 0           | 1.5 | 1.5     |

3. Characterization and testing
Vulcanization characteristics of filler reinforced rubber blend were measured using an Oscillating Disc Rheometer (ODR) with amplitude of 3° arc at temperature 150°C. Vulcanization parameters such as minimum (M_L) and maximum torque (M_H), scorch time (t_S2) and optimum cure time (t_90) were measured from the rheograph.

Tensile sheets for the evaluation of mechanical properties were compression moulded at 150°C and at a pressure of 140 Kg/cm² in an electrically heated hydraulic press. A computer controlled precision Universal testing machine (Shimadzu Autograph AGS-2000G Model) was employed at a cross head speed of 500mm/min, for measuring mechanical properties. Tensile strength, modulus at 100%, 200% and 300% elongation and elongation at break of the moulded vulcanizates were measured according to
the ASTM D-412 standard using specimens of dimensions overall length 125 mm, width 25mm, thickness 3mm, centre width 6mm and centre length 33 mm. Hardness measurement was done by using a Durometer Shore A hardness meter as per ASTM D 2240.

ASTM D 150 [6] was used to evaluate the dielectric properties such as dielectric constant (\(\varepsilon'\)), dissipation factor (\(\tan \delta\)) and volume resistivity (\(\rho_v\)) of rubber were measured at various frequency from 50Hz to 5MHz ranges by using LCR meter supplied by Hioki High Tester model No IM3532 and text fixture 9262. Two disc shaped brass electrodes were used to in this study.

The dielectric constant (\(\varepsilon'\)) was calculated from the capacitance using the equation

\[
\varepsilon' = \frac{(C_p \times t)}{(\varepsilon_0 \times A)}
\]  

(1)

The volume resistivity (\(\rho_v\)) was calculated using the equation,

\[
\rho_v = \frac{(R_p \times A)}{t} \ \Omega \text{m}
\]  

(2)

Where \(C_p\) is the capacitance in parallel, \(R_p\) is the Resistance in parallel, \(t\) is thickness of sample, and \(A\) is the area of electrode.

4. Result and discussion

4.1. Vulcanization characterization

The curing characteristics, expressed in terms of the minimum torque(ML), maximum torque(MH), torque difference (MH-ML), scorch time(\(t_{50}\)) and optimum cure time (\(t_{90}\)) for NR/SBR blends reinforced with organo modified clay are shown in Figures 1 and 2 respectively. From Figure 1, it is observed that the minimum and maximum torques values are found to increases in NR/SBR blends reinforced with 5phr organo modified clay by increasing the NR content and decrease in SBR content. Maximum torque (MH) can be regarded as a measure of the stock modulus which is increased in this case due to clay/rubber interactions including intercalation. It was speculated that this acceleration effect is related to zinc (Zn\(^{2+}\)) complexing in which sulphur and amine groups of the organo modified clay participates. This effect is essentially attributed to the amine groups present in the silicate structure which comes from the organophilization of the clay. This argument is supported by the fact that amine compounds are widely used in sulphur-rubber recipes as accelerators for which various mechanisms were already proposed [7]. The minimum torque (ML) value is directly related to the viscosity of the composites. Initially rubber has minimum viscosity at the chosen temperature and degree of oscillation. After a certain time, the viscosity of the sample begins to increase. It is attributed that the vulcanization process has initiated [8].
Figure 1. Minimum and Maximum torques of NR/SBR blends reinforced organo modified clay

Torque difference (MH - ML) which indicates the extent of cross linking and is a measure of dynamic shear modulus, which indirectly relates to the cross linking density of the composites [9]. MH –ML increases with the addition of SBR, which implies the increase in the cross linking density in presence of organo modified clay in NR/SBR blends.

Figure 2. Cure and Scorch time of NR/SBR blends reinforced organo modified clay

From Figure 2, it can be seen that increasing the SBR content and reducing NR content sharply increase the scorch time and optimum cure times of NR/SBR reinforced with organo modified clay which show the processing safety of the NR/SBR compounds. From these it can be assumed that organo modified
clay behaves as an effective vulcanizing agent for NR/SBR compounds, giving a significant increase in the elastomer vulcanization rate [10].

4.2. Mechanical properties
A remarkable increment in the tensile property is been seen when composites are obtained with the addition of organo modified clay. Tensile strength, elongation at break and modulus at 100%, 200% and 300 % elongation of NR/SBR blends reinforced with organo modified clay are shown in Tables 2.

On increase in SBR content, decrease in NR in NR/SBR blends reinforced with organo modified clay, the tensile strength and elongation at break decreases whereas the modulus does not show any significant change. The decrease in tensile strength and elongation at break is due to the addition of SBR content where SBR is not a self-reinforcing rubber compared to NR. All improvements in the tensile properties of rubber blends reinforced with organo modified clay were mainly due to the intercalation of rubber chains into layered silicate galleries, which provides interaction between rubber matrix and organo modified clay and this strong interaction was often seen by the increase of the $T_g$ towards higher temperature [11]. Usually increasing reinforcement should be accompanied by a decrease in ultimate elongation. But in the case NR/SBR blends reinforced with organo modified clay showed increased elongation at break along with increased stiffness. The unexpected high elongation at break is likely due to the encapsulation of individual clay layers and tactoids in a more cross linked rubber fraction than the bulk itself [12]. The enhanced elongation at break for NR/SBR (50:50) is due to the lubricating effect of the onium salts present in the organo modified clay. Their contribution to the formation of dangling chains, improved the dispersion since the breakage depends on the amount of weak spots or inhomogeneities in the filled blends [1]. The hardness properties of the NR/SBR blends reinforced with organo modified clay show moderate increases as SBR loading increases.

Table 2. Mechanical properties of NR/SBR blends reinforced organo modified clay

| Blend ratio NR/SBR | Tensile strength (MPa) | Elongation at Break (%) | 100% Modulus (MPa) | 200% Modulus (MPa) | 300% Modulus (MPa) | Hardness (Shore-A) |
|--------------------|------------------------|-------------------------|--------------------|--------------------|--------------------|-------------------|
| 100/0              | 23                     | 883                     | 1.1                | 1.5                | 1.9                | 43                |
| 75/25              | 18                     | 874                     | 1.0                | 1.4                | 1.7                | 45                |
| 50/50              | 8                      | 729                     | 1.2                | 1.5                | 1.8                | 46                |
| 25/75              | 2                      | 412                     | 1.3                | 1.5                | 1.7                | 45                |
| 0/100              | 1.6                    | 404                     | 1.3                | 1.4                | 1.5                | 46                |

4.3. Dielectric properties
The dielectric properties such as dielectric constant, loss factor and volume resistivity of NR/SBR blends reinforced with 5phr organo modified clay was measured using by Hioki Hi Tester LCR meter (Model No IM3532) at room temperature (30°C) in a wide frequency range from 50 Hz to 5 MHz. The samples were taken in between two brass electrodes.

Figure 3 depicts the dielectric constant ($\varepsilon'$) of NR/SBR blends reinforced with 5phr organo modified clay at room temperature (30°C). Both NR and SBR are non polar rubbers and have a very low dielectric constant due to the dipoles formed by carbon and sulphur bond [13].

The increase in dielectric constant of clay filled NR and SBR can be explained by higher conductivity of fillers. This is due to the presence of polar groups in layered silicates. The value of $\varepsilon'$ of filled system depends on the various factors namely size and shape of the fillers, distribution, orientation and adhesion between the matrix and the filler particles. As the size of the filler decreases, the surface
area available for conductive contacts increases resulting in the formation of conductive pathways. If the polymer-filler interaction increases, the $\varepsilon'$ also increases [4]. Generally, the dielectric constant decreases by increasing frequency; it can be attributed by the lagging of dipoles. At very high frequency, induced dipoles do not have sufficient time to orient in the direction of applied electric field and at very high frequency electronic polarization alone exists in the materials. The dielectric constant of these NR/SBR blends reinforced with organo modified clay at 50:50 ratio can be explained as following. The increasing the dielectric permittivity by increased in heterogeneity and leads to the Maxwell-Wagner or Maxwell-Wagner-Sillars (MWS) polarization at NR and SBR interfaces [14]. It is found that dielectric constant decreased for 25/75 of NR/SBR blends reinforced with 5phr organo modified clay.

![Graph](image)

**Figure 3.** Dielectric permittivity of NR/SBR blends reinforced organo modified clay

The electrical power loss in a dielectric is the function of frequency (f), applied electric field (E) and tan $\delta$. For any dielectric as insulation application, low loss tangent is needed to ensure low power loss. Usually polymer composites filled with conducting or dielectric fillers show some increment in tan $\delta$, which is due to the increase in electrical conductivity of filled system. Figure 4 shows the frequency dependant tan $\delta$ of NR, SBR and NR/SBR blends reinforced with 5phr organo modified clay. It is interesting to note that NR/SBR 50:50 blend shows relatively low dielectric loss tangent value.
Figure 4. Tan δ of NR/SBR blends reinforced organo modified clay

Figure 5 shows the variation in resistivity (\(\rho_{ac}\)) as a function of frequency of NR/SBR blends reinforced with 5 phr organo modified clay. Frequency dependence resistivity or conductivity of polymer gives interesting features of different conducting mechanism such as electrode effects (active at low frequencies), (ii) dc plateau (at intermediate frequencies) and (iii) defect process and also various types of polarization courses in polymers [15,16]. SBR rubber shows better economic and environmental advantage than NR but very low mechanical strength limits its application in electrical insulation. Frequency dependant resistivity of NR, SBR and NR/SBR blends reinforced with organo modified clay shows that volume resistivity was not changed with respect to frequency upto 3.5 kHz and beyond that the frequency dependence resistivity was found to obey the conventional formula which is already reported in the literature [17]. From this investigation, it is concluded that NR/SBR 50/50 blend reinforced with organo modified clay has better dielectric properties with improved mechanical strength.

Figure 5. Resistivity of NR/SBR blends reinforced organo modified clay
5. Conclusions

Main results of the work are listed below:
NR/SBR blends reinforced with 5phr organo modified clay were prepared through a conventional two roll mixing mill at different blending ratios like 100/0, 75/25, 50/50, 25/75 and 0/100. The curing studies showed minimum (ML) and maximum (MH) torque values increasing in NR/SBR blends reinforced with 5phr organo modified clay through increase in the NR content and decrease in SBR content. This may have attributed to changes in modulus and viscosity of blend. Reduction in both scorch time and optimum cure time in NR/SBR blends reinforced organo modified clay was found through increase in the SBR content. This may be due to better processing safety of the NR/SBR blends reinforced with organo modified clay.

The mechanical properties were found to be improved for NR/SBR organo modified clay composites. It may due to intercalation of rubber chains into layered silicate galleries. Hardness of the NR/SBR blends shows moderate increases as SBR loading increases.

NR and SBR are non polar rubbers and have very low dielectric constant due to the dipoles formed by carbon and sulphur bond and addition of 5 phr organo modified clay shows better dielectric constant values for NR, SBR and NR/SBR blends. Maximum dielectric constant was found for NR/SBR (50/50) blend ratio. This can be attributed to higher heterogeneity leading to interfacial polarization. Decreases in dielectric constant of NR/SBR were seen blending 25/75 ratio and tan δ value for 50/50 blend ratio found decreased.

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