

## CURE CHARACTERISTICS AND RHEOLOGICAL PROPERTIES OF MODIFIED KAOLIN - NATURAL RUBBER VULCANIZATES

### Abstract

Metal salt of rubber seed oil (RSO-Na) was modified with Natural Rubber (NR) by melt intercalation to produce vulcanizates with various compositions (2 - 10 Parts per hundred rubbers). Characterization of the modified kaolin using X- ray diffraction revealed increase in d-spacing from 7.15 to 14 Å. Torque minimum ( $M_L$ ), torque maximum ( $M_H$ ) which is correlated with hardness increased with increasing organoclay loading. The storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $\eta_{complex}$ ) increased with increase in modified kaolin thus showing remarkable improvements of the vulcanizates.

**Keywords:** Intercalation, torque maximum, Natural rubber, kaolin, complex viscosity

### Introduction

Polymer reinforcement with nano-sized particles has proved to be a promising technique that is capable of producing materials with remarkable performance but without involving expensive synthetic procedures. The concept of polymer layered silicate nanocomposites was first introduced by researchers at Toyota [1] who discovered the possibility of building a nanocomposite from polyamide 6 and organophilic clay. These are materials in which the particle size of the dispersed phase was nanometer sized at least in one dimension.

Although the chemistry of intercalation of polymers when mixed with appropriately modified layered silicate and synthetic layered silicates are not new developments [2, 31] the field of polymer layered silicate nanocomposites has gained much momentum in recent past. In an attempt to achieving nanoscale dispersion of silicate in a polymer matrix, the silicates are generally treated with alkylammonium or alkylphosphonium ions to produce an organoclay [3]. This treatment becomes necessary so as to open up the gallery of the silicate, and the organoclay can then be easily dispersed in the polymer matrix and form nanocomposite with an intercalated or exfoliated structures.

A number of research works on nanocomposites have been focused on either the thermoplastics or thermosets matrices [4, 5, and 6]. Other studies have been carried out on organomodified clay rubber nanocomposites which involved the use of various elastomers such as natural rubber [7, 8, 9,10,11,12], styrene butadiene rubber [13], polychloroprene rubber, polysiloxane rubber [14,15], ethylene propylene diene rubber [16, 17], chlorobutyl rubber [18] etc.

The use of clay as filler for natural rubber over the years, however had led to poor reinforcing effect; this is largely due to the large particle size and low surface activity. To overcome this, there is need for successful exploitation of the organoclay to achieve good adhesion with the polymer matrices. This study therefore reports the cure characteristics and rheological behaviour of modified kaolin-natural rubber vulcanizates.

## 2 Experimental

### 2.1. Materials

Rubber seed oil (RSO) was obtained from the National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram. Kaolin, grade BCK was obtained from M/s English, India clays Ltd, Veli, Thiruvananthapuram, Kerala, India. Natural rubber was of the Indian standard ribbed smoke sheet (grade RSSV); sodium hydroxide (LR Fischer), hydrazine hydrate (Aldrich), zinc oxide, stearic acid, sulphur and mercaptobenzothiazole (MBT) were obtained from the open market.

### 2.2 Modification of Kaolin surface

Sodium salt of rubber seed oil (RSO-Na) was prepared by contacting 2.8 g of RSO with approximately 10 ml of 20% NaOH in an ice bath with constant agitation for 24 h. The pH of the resulting solution was maintained at 8–9. RSO–Na was then introduced into a separating funnel and washed with water to remove excess base. This solution was then oven-dried to remove any moisture and powdered. 2 g of RSO–Na was reacted with 9.8 g kaolin, 7 ml of hydrazine and 50 ml water under vigorous agitation at 20 °C. The mixture was homogenized using an ultra Schallprozessor (HIELSCHER, GmbH, UP 100 H) and the sample was dried in a freeze drier (HetroTrap-CT600e, JOUAN) and powdered.

### 2.3 Characterization

The IR spectroscopy of both the modified and unmodified samples was determined using the Fourier Transform Infra red spectrometer (MAGNA, 560, NICOLET). In a typical experiment, about 10mg of sample was thoroughly mixed with finely ground KBr and made into pellet to obtain a transparent disc.

The X-ray diffraction of the samples was determined using a Philips -1710 X-ray diffractometer using monochromatic Ni-filtered Cu K alpha radiation 1.5418Å at 40Kv and 20mA. All the readings were taken at room temperatures. The d-spacing was calculated using Braggs equation,  $n\lambda = 2d \sin\theta$ , where  $\lambda$  is the wavelength of the monochromatic x-ray source, d is the spacing between two similar planes,  $\theta$  is the angle at which x-ray falls on the sample, and n is the order of reflection.

### 2.4 Compounding

A conventional vulcanization system was used for compounding. Table 1 shows the composition of the rubber compound. Natural rubber and modified kaolin were mixed in a two roll open mill for 5–10 min according to the recipe (Table 1). Vulcanizate sheets of dimension 90 mm × 90 mm × 1.5 mm were prepared by compression molding of the mixes at 140°C for 10 min on an electrically heated, semi-automatic laboratory press (model PFA15) at 3 torr pressure.

**Table 1.** Kaolin filled (UTK) and organo-kaolin filled (MRK) nanocomposite

| Ingredients (phr) | Pristine   | Modified   |
|-------------------|------------|------------|
| Natural Rubber    | 100        | 100        |
| Zinc Oxide        | 5          | 5          |
| Stearic acid      | 2          | 2          |
| Unmodified        | 2,4,6,8,10 | -          |
| Modified          | -          | 2,4,6,8,10 |
| MBT               | 2          | 2          |
| Sulphur           | 2          | 2          |

### 3.0 Results and Discussions

#### 3.1 Modification of Kaolin surface

##### 3.1.1 FTIR Spectroscopy:

The IR spectra of unmodified and RSO-Na modified kaolin are depicted in figure 1. The unmodified kaolin spectrum shows a band at 3620 and 3695 $\text{cm}^{-1}$ . These bands are characteristics of inner hydroxyls and vibrations of outer surface hydroxyls respectively [19, 20], but for modified sample, there is the occurrence of bands at 2923 $\text{cm}^{-1}$  and 2852 $\text{cm}^{-1}$  indicating the occurrence of intercalation of RSO-Na on kaolin surfaces [21]. Intercalation involves the rupture of some hydrogen bonds between the kaolinite layers and the formation of new hydrogen bonds (involving the inner hydroxyl groups) with inserting molecule. The FTIR spectrum of RSO-Na modified kaolin also shows clear perturbation in the OH-stretching region (above 3620  $\text{cm}^{-1}$ ), and this is characterized by a reduction in transmittance. The implication of this is that there is

possible grafting of the organic moiety of rubber seed oil onto the clay surface. This process of intercalation decreases the electrostatic attraction between the lamellae by causing an increase in the dielectric constant when the compound penetrates between the layers of the kaolinite.

### 3.1.2 X-Ray Diffraction:

The XRD patterns of the neat or pristine kaolin and RSO-Na modified kaolin are shown in figure 2. The d- spacing was determined from the diffraction peak position in the XRD using the Braggs equation. The basal distance of the neat kaolin and the d- spacing of RSO-Na organokaolin are shown in the peaks corresponding to 7.15 Å obtained by previous workers [33], and 14 Å for the current study. Evidently there is an increase in the d-spacing of the modified kaolin, hence the intercalation of organic modifier enlarges the distance of the kaolin layers thus suggesting the successful preparation of organokaolin using rubber seed oil derivative. The peak value of RSO-Na modified kaolin is greater than the d-spacing (13.89Å<sup>o</sup>) reported for caesium acetate- kaolinites intercalate [19] and sodium montmorillonite (12.5-12.6Å<sup>o</sup>) [22, 30] .

### 3.2 Cure Characteristics

The cure characteristic of the modified NR vulcanizate is shown in figure 3. Torque minimum ( $M_L$ ) increases steadily with increase in filler concentration for vulcanizates. Since the torque minimum can be regarded a measure of stock viscosity, the addition of the organoclay of a smaller size tends to impose extra resistance to flow due to a higher restriction to molecular motion of the nanocomposite [23]. The implication of this is that incorporation of modified kaolin increases the viscosity of the vulcanizate. This may be explained with the Einstein, Guth, and Gold equation (Blow, 1971) [24]:

$$\eta_f = \eta_u (1 + 2.5c + 14.1c^2) \quad 1$$

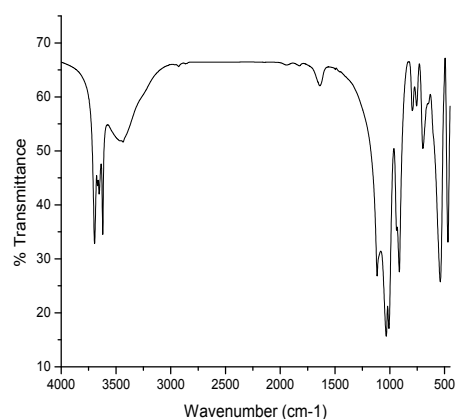
Where the  $\eta_f$  and  $\eta_u$  are the viscosities of modified and unmodified natural rubber nanocomposites and c is the volume fraction of the organoclay. The torque maximum ( $M_H$ ) which is correlated with hardness also increases with increasing organoclay loading. Since the modulus of organoclay is higher than the rubber matrix; the incorporation of modified kaolin will increase the stiffness of the nanocomposite. Similar trend was observed for the torque difference ( $M_H - M_L$ ) and this indicates the extent of cross linking and rubber-filler interaction of the

nanocomposite. Torque difference is a measure of the shear dynamic modulus, which indirectly relates to the crosslink density of the nanocomposites [25, 26]. The increment of  $M_H - M_L$  values may suggest that the organomodified kaolin particles also act as crosslinking agent in the NR matrix [27]. The presence of the modified kaolin has therefore resulted in increase in the torque value caused by the formation of a higher number of crosslinks, which could be attributed to the confinement of the elastomer chains within the silicate galleries and, consequently, to better interaction between the filler and the natural rubber.  $M_H$  can be regarded as a measure of composite modulus. The significantly increased values in  $M_H$  with filler are indirect evidence for improved interaction behaviour and good adhesion between organoclay and natural rubber matrix. This efficiency can also be attributed to the role of the organomodifier in the NR vulcanizates.

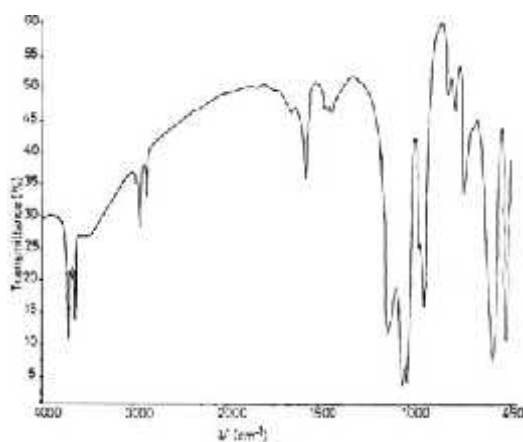
### 3.3 Rheological Properties

The storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $\eta_{complex}$ ) resulting from the dynamic frequency scans of the natural rubber vulcanizates for RSO-Na modified NR vulcanizates relative to the unmodified at different filler loading are presented in figure 4. Rheological behaviour of polymeric material is usually controlled directly by molecular structure, crystallinity, crosslinking and polydispersity. The storage modulus is a measure of the ability of material to store energy while loss modulus is a measure of ability to dissipate energy. From this study, it was observed that there is a general increase in the storage modulus and loss modulus with increase in modified kaolin loading for RSO-Na modified natural rubber. In other word, there is enhancement of these parameters for RSO-Na modified natural rubber over the unmodified. The complex viscosity values for the modified NR vulcanizates are also higher than the unmodified. The general improvement in these rheological properties of the organomodified filled natural rubber nanocomposites may be explained on the basis of the interfacial interaction between the intercalated/exfoliated silicate layers and the natural rubber matrix. According to Li et al [28] (2003), the interfacial adhesion between the clay tactoid and the matrix is dramatically improved due to the formation of partially exfoliated structures, in this case intercalated structures. It is also evident that the complex viscosities of the modified filled nanocomposites are higher than the unmodified filled composite which is also in agreement with the storage modulus. This may also be due to partially exfoliated and intercalated silicate layers which

hinder the melt flow of the NR and organoclay. According to Boucard et al; [29] 2003), at low shear rates, the silicate platelets of high aspect ratio are well separated and this strongly increases the melt viscosity. On the contrary, at higher shear rates, the clay platelets are oriented in the flow direction which consequently leads to reduction in viscosity.



A



B

Fig. 1. FTIR spectrum of A) unmodified and B) RSO-Na Modified kaolin

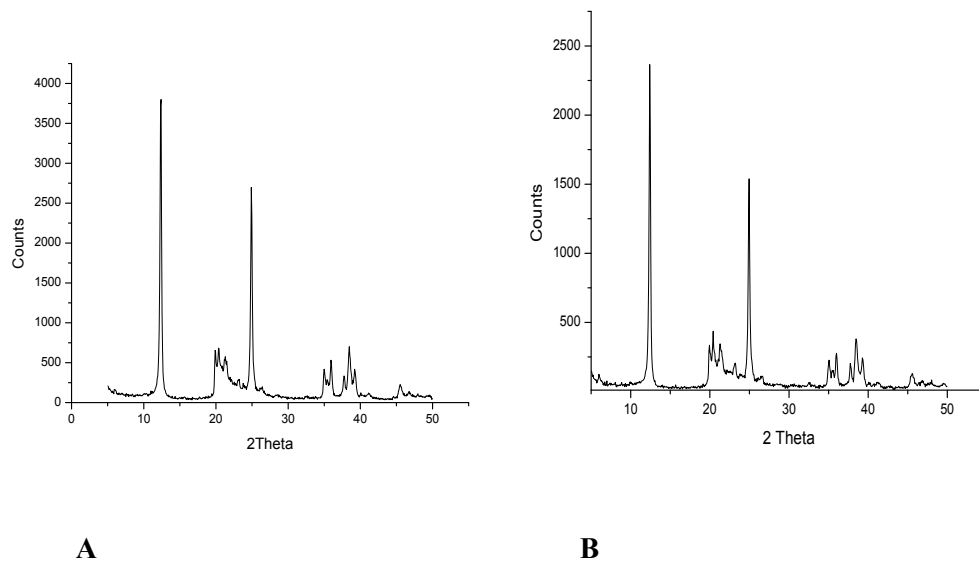


Fig. 2. XRD Pattern of A) Unmodified and B) modified kaolin

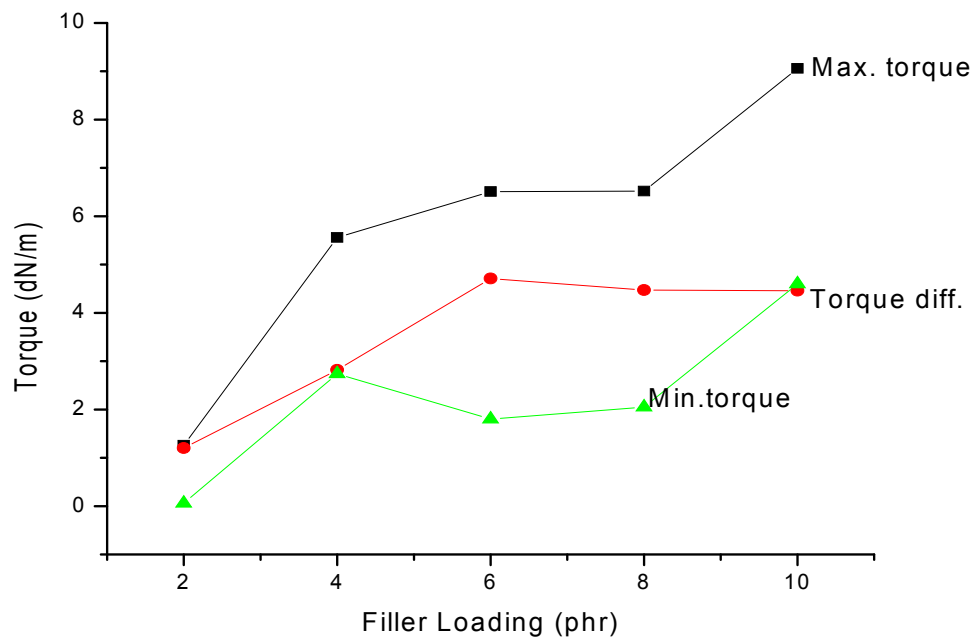
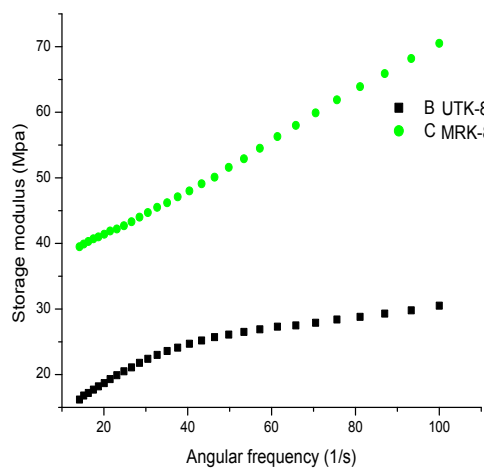
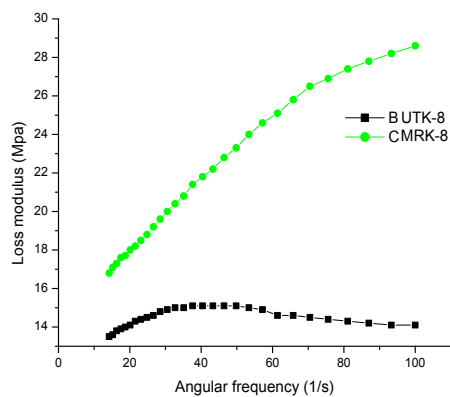


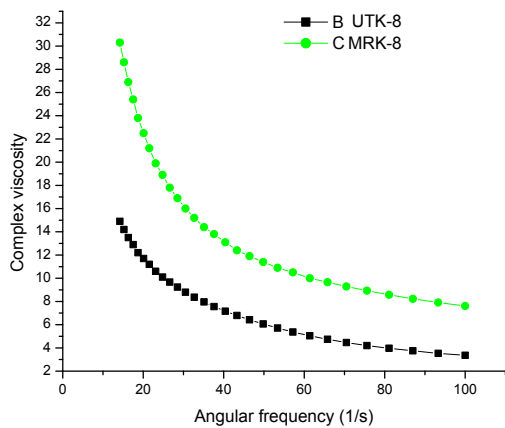
Fig. 3. Cure characteristics of RSO-Na modified NR vulcanizates



**A**



**B**



**C**

Fig. 4 Storage modulus (A), Loss modulus (B), Complex viscosity (C) of RSO-Na modified NR vulcanizate at 8phr

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