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# Cure Characteristics and Rheological Properties of Modified Kaolin-natural Rubber Composites

L. E. Yahaya<sup>1\*</sup>, K. O. Adebowale<sup>2</sup> and B. I. Olu-Owolabi<sup>2</sup>

<sup>1</sup>Cocoa Research Institute of Nigeria, Ibadan, Nigeria.

<sup>2</sup>Chemistry Department, University of Ibadan, Nigeria.

## Authors' contributions

*This work was carried out in collaboration of all authors. Authors LEY, KOA and BIO designed the study, managed the analyses of the work, interpreted the results and prepared the manuscript. All authors read and approved the final manuscript.*

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## ABSTRACT

**Aim:** This study seeks to examine the cure characteristics and rheological properties of modified kaolin – Natural rubber vulcanizates.

**Methodology:** Metal salt of rubber seed oil (RSO-Na) was used to modify kaolin and was then introduced into Natural Rubber (NR) by melt intercalation to produce vulcanizates mixed with various compositions of pristine and modified kaolin (2 - 10 Parts per hundred rubbers).

**Results:** 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 are 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.

**Conclusion:** The results from the study indicate that the modified filled kaolin has a dramatic improvement on the NR composite compared to the pristine.

*Keywords: Intercalation; torque maximum; natural rubber; kaolin; complex viscosity.*

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\*Corresponding author: Email: [eugeneyah@yahoo.co.uk](mailto:eugeneyah@yahoo.co.uk)

## 1. 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 [2,3] 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 [4]. Ordinarily, kaolins as silicate have been used as filler in polymer reinforcement, but for better improvement in compatibility of polymers and organoclay layers which consequently leads to increased interlayer spaced, the kaolin for the nanocomposite need to be organomodified. 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 [5,6,7]. Other studies have been carried out on organomodified clay rubber nanocomposites which involved the use of various elastomers such as natural rubber [8,9,10,11,12,13], styrene butadiene rubber [14], polychloroprene rubber, polysiloxane rubber [15,16], ethylene propylene diene rubber [17,18], chlorobutyl rubber [19] etc.

The use of kaolin 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. MATERIALS AND METHODS

### 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 RSS- 5); 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 reacting 2.8 g of RSO with 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 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. Formulation ingredients for pristine kaolin- filled and modified-kaolin filled nanocomposite**

Ingredients (phr)	Pristine kaolin	Modified kaolin
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

### 2.4 Characterization

The IR spectroscopy of both the modified and unmodified samples was carried out 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.

### 2.5 Rheological Measurement

The rheology of the mixes was studied on a Paar Physica rheometer (MCR 150) – Physica VT 2 at 120°C over a range of angular frequencies.

## 2.6 Cure Characteristics

This was investigated using an oscillating Disc Rheometer (ODR) model 4308, Zwick, Germany. The measured parameters included Torque minimum ( $M_L$ ) and torque maximum ( $M_H$ ).

## 3. RESULTS AND DISCUSSION

### 3.1 Modification of Kaolin surface

#### 3.1.1 FTIR spectroscopy

The IR spectra of unmodified and RSO-Na modified kaolin are depicted in Fig. 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 [20,21], 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 [22,23]. 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 are 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.

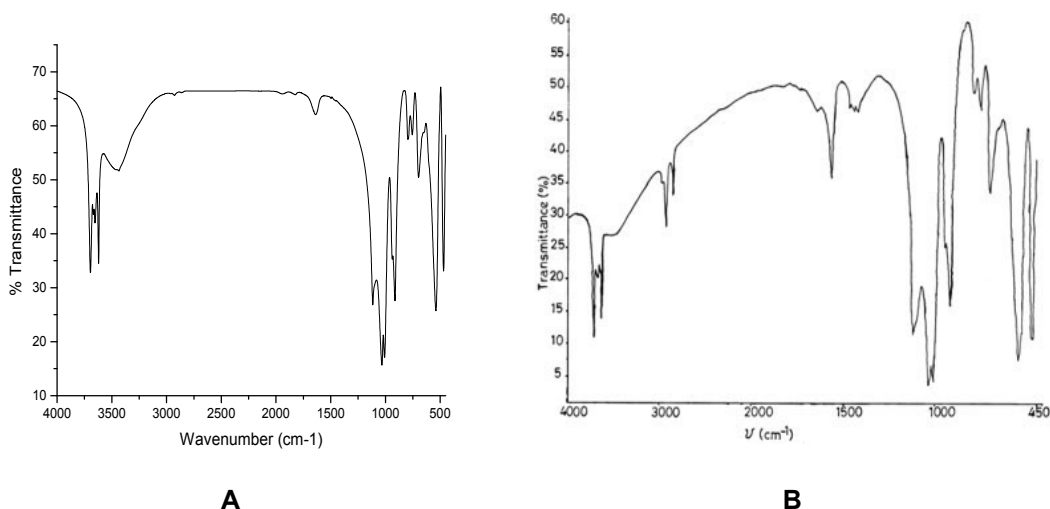


Fig. 1. FTIR spectrum of (A) unmodified and (B) RSO-Na modified kaolin

#### 3.1.2 X-Ray diffraction

The XRD patterns of the neat or pristine kaolin and RSO-Na modified kaolin are shown in Fig. 2. The d- spacing was determined from the diffraction peak position in the XRD using the Bragg's equation. The basal distance of the neat kaolin and the d- spacing of RSO-Na organokaolin are shown in the peaks corresponding to  $7.15 \text{ \AA}$  and  $14 \text{ \AA}$  respectively.

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) reported for caesium acetate-kaolinites intercalate [19] and sodium montmorillonite (12.5-12.6Å) [24,25].

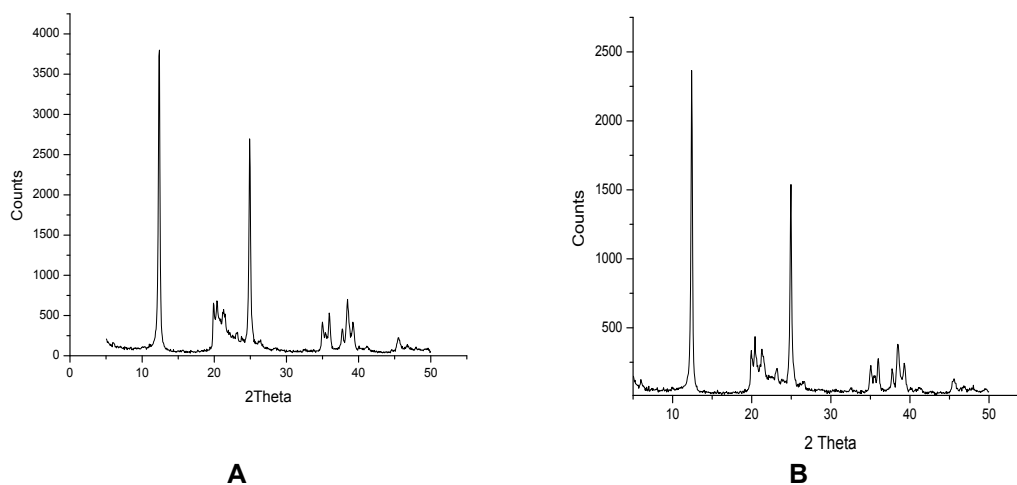


Fig. 2. XRD Pattern of (A) unmodified and (B) modified kaolin

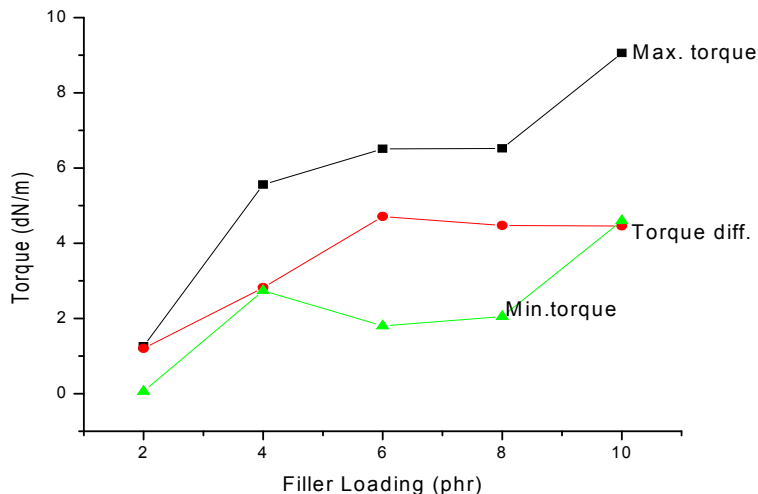
### 3.2 Cure Characteristics

The cure characteristic of the modified NR vulcanizate is shown in Fig. 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 [26]. 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 [27]:

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

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 [28,29]. 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

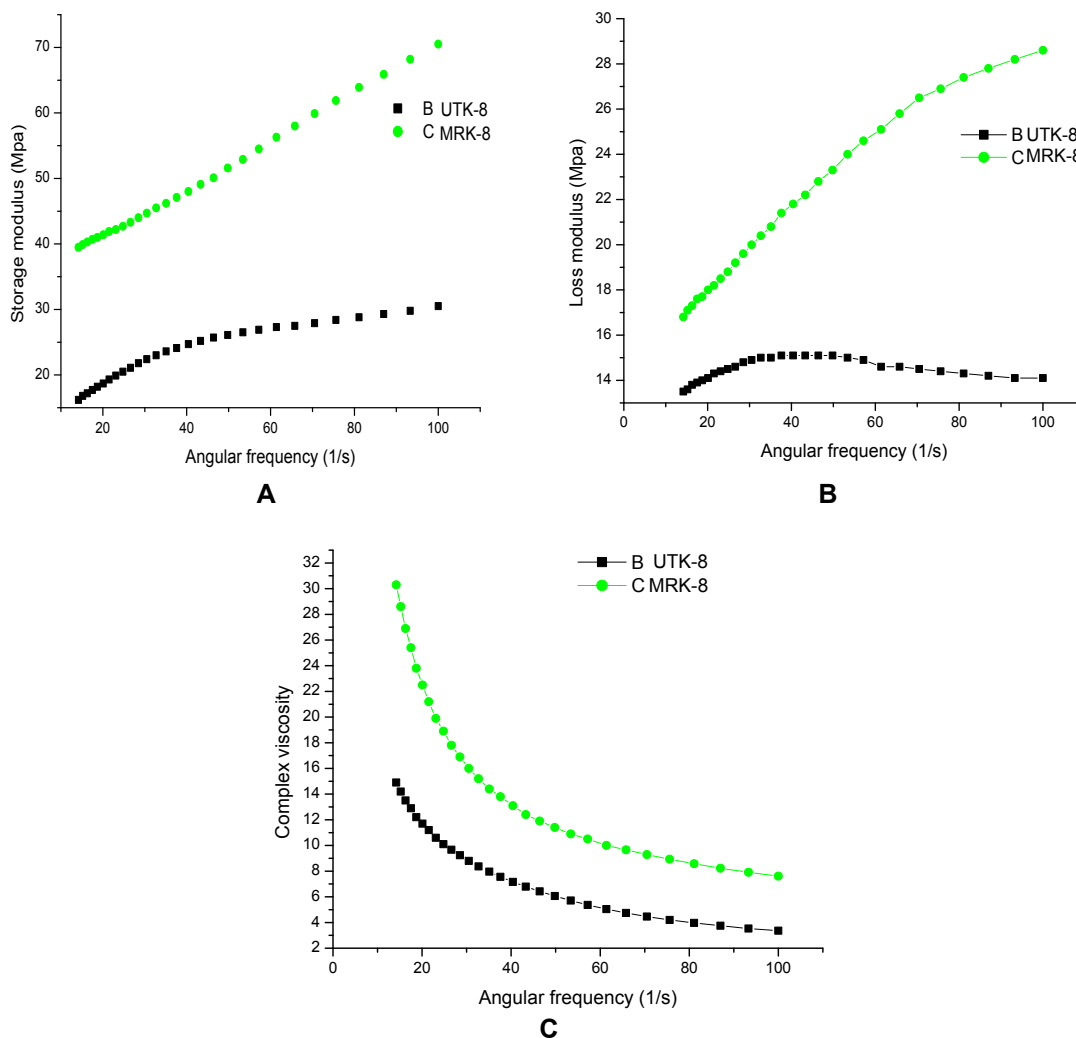
for improved interaction behaviour and good adhesion between organoclay and natural rubber mixes. This efficiency can also be attributed to the role of the organomodifier in the NR vulcanizates.



**Fig. 3. Cure characteristics of RSO-Na modified 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 Fig. 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 words, 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. [30], 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. [31], 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.



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

#### 4. CONCLUSION

The cure and rheological characteristics of modified kaolin- NR vulcanizates was investigated. Results indicated an improvement in these properties of the modified filled NR over the pristine –filled rubber.

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## COMPETING INTERESTS

Authors declare no conflict of interest.

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