ARID ZONE JOURNAL OF ENGINEERING, TECHNOLOGY & ENVIRONMENT
AZOJETE March 2020. Vol. 16(1):58-64
Published by the Faculty of Engineering, University of Maiduguri, Maiduguri, Nigeria.
**Print ISSN: 1596-2490, Electronic ISSN: 2545-5818**
www.azojete.com.ng

ORIGINAL RESEARCH ARTICLE

# PERFORMANCE STUDIES OF NATURAL RUBBER/ORGANOMODIFIED KAOLIN VULCANIZATES DEVELOPED FOR TIRE SIDEWALL APPLICATIONS

**C. O. Mgbemena[1] and C. E. Mgbemena[2]**

*([1]Department of Mechanical Engineering, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria*
*[2]Department of Industrial and Production Engineering, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria)*
** Corresponding author's email address: mgbemena.ogonna@fupre.edu.ng*

**ARTICLE INFORMATION**

Submitted 21 October, 2018
Revised 01 November, 2019
Accepted 05 November, 2019

**Keywords:**
Natural rubber
Organomodified
Kaolin
nanocomposites.

**ABSTRACT**

*This study aims at evaluating the performance of Natural Rubber/organomodified kaolin vulcanizates to ascertain its suitability for tire sidewall applications. The cure characteristics, filler dispersion, tensile and tear properties and De-Mattia flex fatigue characteristics of natural rubber (NR) filled with 2-10 phr of Rubber Seed Oil (RSO), and Tea Seed Oil (TSO) modified kaolin developed specifically for tire sidewall applications were assessed. The NR compounds containing RSO and TSO modified kaolin showed lower optimum cure time (t90 at 150°C) as against that containing the same dosage of unmodified kaolin. The results show significant increases in tensile modulus, tensile strength and tear strength for the NR vulcanizates containing the organomodified kaolins, compared to vulcanizates containing unmodified kaolin. TSO modified kaolin vulcanizates at 6phr showed better resistance to crack initiation and flex fatigue failure. The SEM and AFM micrographs of the vulcanizates containing organomodified kaolins also showed an excellent uniform dispersion of the filler particles in the NR matrix. The results obtained for Natural Rubber/Tea Seed Oil modified kaolin vulcanizates at 10phr shows a short optimum cure time, high maximum torque, better tear strength, excellent resistance to crack initiation and flex fatigue behaviour. These indicate that the Natural Rubber/Tea Seed Oil modified kaolin vulcanizates are preferred materials for tire sidewall applications.*



## 1.0 Introduction

Rubber Clay Nanocomposites (RCNs) have emerged as novel advanced materials, attracting the interests of the academia and industry (Bhowmick et al., 2010). One of the unique features of RCNs is the exceptional improvement in their physical and mechanical properties, such as barrier properties (impermeability to gases), thermal stability, storage modulus, tensile properties, wear resistance and flame resistance at low filler concentrations. In a pioneering study, it was shown that the mechanical properties of NR with 10 phr of organo-montmorillonite are comparable to one containing 40 phr of carbon black (Arroyo et al., 2003).

A review of related publications on RCNs shows that apart from natural rubber (NR), various synthetic rubbers have been used along with clays such as montmorillonites, bentonites, saponite, fluorohectorites with and without organomodifiers which are mostly petrochemical-based and are quite expensive. Studies on the use of nano kaolin for vulcanised rubber

nanocomposites are limited (Dai, 1999; Liu et al., 2008; Mgbemena et al., 2016; Puşcă et al., 2010; Sookyung et al., 2014; Yahaya et al., 2009).

For large scale industrial applications, it is imperative that RCN compositions be tailored to meet the required technical specifications. The selection of low cost renewable natural resources such as kaolin and organomodifiers such as RSO and TSO for RCNs could be an ideal proposition.

Earlier studies have shown that derivatives of RSO and TSO could be used as organo-modifiers for kaolin to function as 'reinforcing nano-fillers' for natural rubber at very low dosages (Mgbemena et al., 2013; Sukumar and Menon, 2008; Yahaya et al., 2009). Recent findings also support the above observations (Mgbemena et al., 2016).

The purpose of this study is to evaluate the properties of Natural Rubber/Organomodified kaolin nanocomposites to determine its suitability for vehicle tire sidewall applications.

## 2. Materials and Method

Kaolin (grade BCK) was obtained from M/s. English Indian Clays Ltd., Thiruvananthapuram. TSO was obtained from Nigeria. RSO, NR (grade RSS5) and rubber chemicals were obtained from local suppliers. The organomodified kaolins were prepared by modification of kaolin with sodium salts of the oils (RSO & TSO) and hydrazine hydrate according to (Ihueze and Mgbemena, 2016, Mgbemena et al., 2013, Mgbemena et al., 2016 and Yahaya et al., 2009). Rubber mixes, as shown in Table 1 were prepared by mixing on an open, two-roll mixing mill at room temperature of 25℃.

Table 1. Composition of mixes

| Mix code* | Ingredient | (phr) |
|---|---|---|
| URK2 | Unmodified kaolin | 2 |
| URK6 | Unmodified kaolin | 6 |
| URK10 | Unmodified kaolin | 10 |
| MRK2 | RSO modified kaolin | 2 |
| MRK6 | RSO modified kaolin | 6 |
| MRK10 | RSO modified kaolin | 10 |
| MTK2 | TSO modified kaolin | 2 |
| MTK6 | TSO modified kaolin | 6 |
| MTK10 | TSO modified kaolin | 10 |

* Base mix: NR 100, ZnO 5, Stearic acid 2, sulfur 2, Mercapto Benzothiazole 2

### 2.1 Characterizations of the materials

The cure characteristics at 150°C of the mixes were tested with an oscillating disk rheometer (ODR) [MV-ODR brand; Micro-Vision Enterprises, India] according to ASTM D 5289 – 1979. The essential data deduced from the rheographs are as follows: the minimum torque (ML), maximum torque (MH), Scorch time (ts2), optimum cure time (t90) and cure rate index (CRI). The tensile properties of the vulcanizates were according to IS: 3400 (Part 1) – 1977. The resistance to flex cracking of the vulcanizates was measured on a Goodrich flexometer according to IS: 3400 (Part 7) – 1985 and IS: 3400 (Part 8) – 1983. The tear strength of the vulcanizates was measured with a Universal Testing Machine (Hounsfield H5 KS; United Kingdom) according to standard ASTM - D624-86. The fracture surfaces of the vulcanizates were

*Corresponding author's e-mail address: mgbemena.ogonna@fupre.edu.ng*

observed under a scanning electron microscope (SEM model -JSM 5600LV; Jeol, USA) after sputter coating with gold. 3D images of the failure surfaces of the vulcanizates were obtained using an atomic force microscope [AFM model – NT-MDT, Russia] using the tapping mode probe.

## 3. Results and Discussion

### 3.1 Cure characteristics and Scanning Electron Microscopy

Table 2 shows the results on the cure characteristics of the rubber compounds at 150°C, as obtained from ODR.

Table 2. Cure characteristics at 150°C of NR compounds containing Unmodified and Organomodified kaolin

| Mix code | Scorch time, $ts_2$ (s) | Optimum cure time, $t_{90}$ (s) | Minimum torque $M_L(dNm)$ | Maximum torque $M_H(dNm)$ | $(M_H - M_L) = \Delta M(dNm)$ | $CR=\left(\frac{100}{t_{90}-t_{s2}}\right)$ (min) |
|---|---|---|---|---|---|---|
| URK2 | 113 | 274 | 0.58 | 4.71 | 4.13 | 37.17 |
| URK6 | 99 | 273 | 0.51 | 5.16 | 4.65 | 34.48 |
| URK10 | 93 | 255 | 0.80 | 5.51 | 4.71 | 37.04 |
| MRK2 | 82 | 222 | 0.60 | 5.20 | 4.60 | 42.92 |
| MRK6 | 86 | 205 | 0.71 | 5.56 | 4.85 | 46.51 |
| MRK10 | 78 | 222 | 1.07 | 5.58 | 4.51 | 41.67 |
| MTK2 | 91 | 250 | 0.65 | 5.19 | 4.54 | 37.74 |
| MTK6 | 84 | 234 | 0.87 | 5.65 | 4.78 | 40.00 |
| MTK10 | 63 | 216 | 0.84 | 6.80 | 5.96 | 38.46 |

The observed reduction in scorch time and optimum cure time of the mixes as above is similar to that reported by Liu et al. (2008). Liu et al. (2008) has reported that the smaller value of minimum torque (ML) is related to slightly large size of kaolinite flakes and weaker interactions between kaolinite particles. Thus, the higher values of ML for the mixes containing RSO modified kaolin and TSO modified kaolin could be an indication of smaller sizes of kaolinite flakes and more interaction between them, as evidenced by SEM images of vulcanizates containing NR/Unmodified kaolin at 10 phr in Figure 1; NR/RSO modified kaolin in Figure 2 and NR/TSO modified kaolin in Figure 3.

However, the increases in cure rate index (CRI), maximum torque (MH) and delta torque ($\Delta M$) of the mixes containing RSO and TSO modified kaolins as against that of the unmodified kaolin indicate an overall increase in the ultimate state of cure and crosslinking efficiency in presence of the organomodified kaolins. A previous report also shows a higher cure rate and state of cure for NR containing RSO modified kaolin (Sukumar and Menon, 2008).

*Corresponding author's e-mail address: mgbemena.ogonna@fupre.edu.ng*

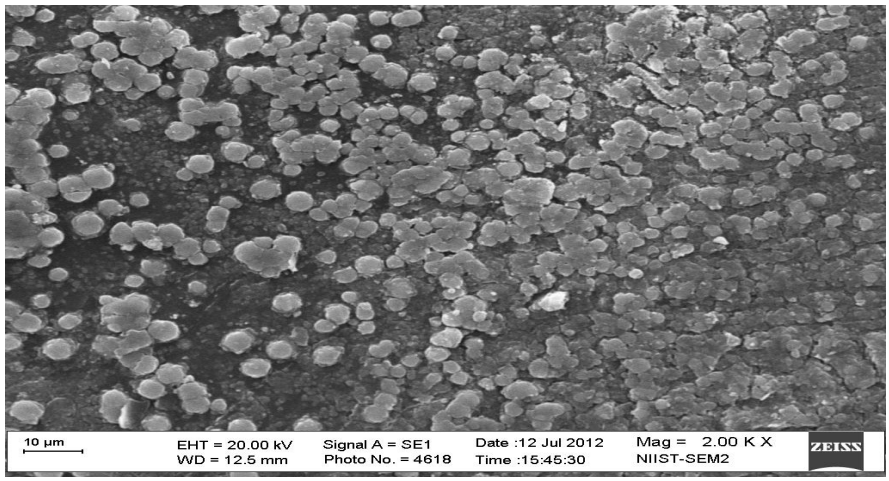


Figure 1: SEM Micrograph for NR/Unmodified kaolin (10 phr)

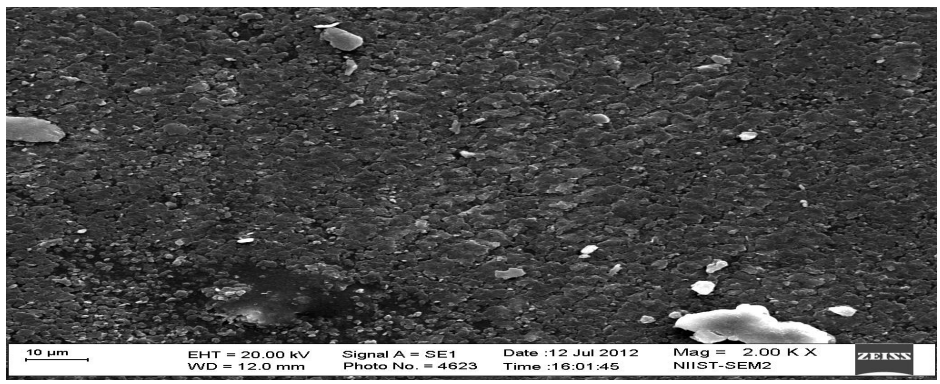


Figure 2: SEM Micrograph for NR/RSO modified kaolin (10 phr)

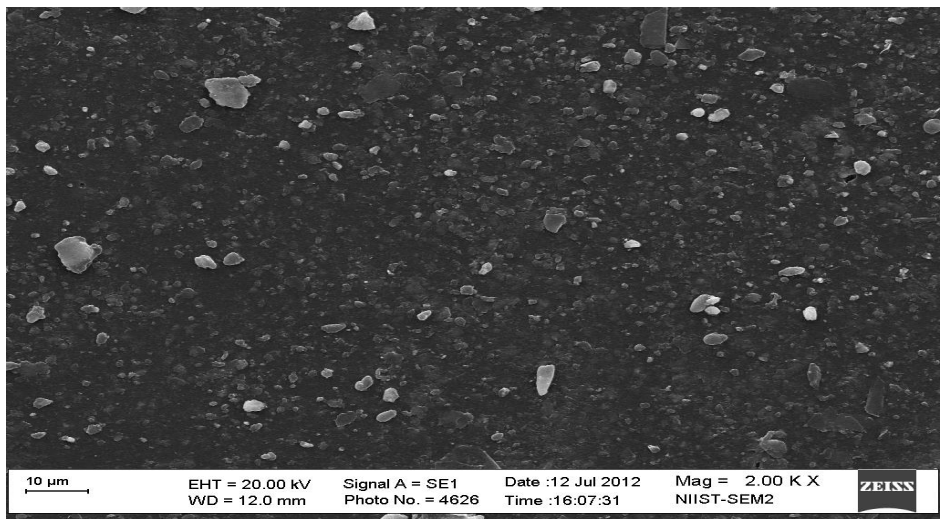


Figure 3: SEM Micrograph for NR/TSO-modified Kaolin (10phr)

### 3.2 Mechanical properties

The result on the mechanical properties of the vulcanizates is given in Table 3. The crack initiation and failure frequencies in the De Mattia flex-crack test are almost similar for all the vulcanizates, except that the vulcanizates containing 2-6 phr of TSO modified kaolin show some improvements over that containing the same dosage of unmodified kaolin. It shows that in all the vulcanizates there is a steady increase in the tensile modulus with the increase in dosage of filler from 2 to 10 phr. However, the values for the vulcanizates containing RSO modified kaolin and TSO modified kaolin are higher than that containing the same dosage of unmodified kaolin. A higher degree of intercalation in the morphological structure resulted in higher tensile

*Corresponding author's e-mail address: mgbemena.ogonna@fupre.edu.ng*

strength and other mechanical properties; this was particularly the case of RSO-modified kaolin/NR composites at 10 phr filler loading where there was an increase in tensile strength which is attributed to the increase in interfacial area of kaolin platelets and good interaction between the kaolin platelets as clearly seen in the SEM and AFM morphologies of RSO-modified Kaolin at 10 phr and a magnification of 10000X. Poor filler dispersion lowers the tensile strength of the material. The surface chemistry of the layered silicates in a polymer matrix plays a crucial role in composites formation. Electrostatic forces present in the silicate layers could complicate the filler dispersion in the polymer matrix. The incompatibility between the hydrophilic silicates and the hydrophobic polymer results in strong inter-particle forces and agglomeration as indicated at 10 phr pristine kaolin filler loading.

Table 3: Mechanical properties of NR vulcanizates containing unmodified and organomodified kaolins

| Sample code | Tensile modulus M-300% (MPa) | Tensile strength (MPa) | Elongation at break (%) | De Mattia flex | | Tear strength (kN/m) |
|---|---|---|---|---|---|---|
| | | | | Crack initiation (cycles) | Failure (cycles) | |
| URK2 | 1.42 | 13.1 | 696 | 71884 | 373451 | 12.78 |
| URK6 | 1.64 | 12 | 628 | 69488 | 206057 | 27.48 |
| URK10 | 2.00 | 12.7 | 712 | 75016 | 298065 | 26.79 |
| MRK2 | 1.9 | 11.7 | 658 | 62116 | 194867 | 16.20 |
| MRK6 | 2.19 | 15.8 | 649 | 52116 | 225380 | 24.73 |
| MRK10 | 2.35 | 15.8 | 625 | 63126 | 290584 | 18.46 |
| MTK2 | 1.17 | 11.1 | 815 | 74629 | 272480 | 22.20 |
| MTK6 | 2.01 | 16.2 | 687 | 73542 | 256491 | 24.79 |
| MTK10 | 2.73 | 20.7 | 648 | 74172 | 288283 | 29.29 |

### 3.3 The Atomic Force Microscopy (AFM)

The results obtained from the tensile tests and SEM revealed that the following selected composites have high tensile strength: NR/Unmodified kaolin composites at 10phr, NR/Rubber Seed Oil modified kaolin composites at10phr and NR/Tea Seed Oil modified kaolin composites at 6phr. These three composite samples were further analyzed by AFM using the tapping mode probe. The AFM 3D images of NR vulcanizates are shown in Figures 4-6 respectively.

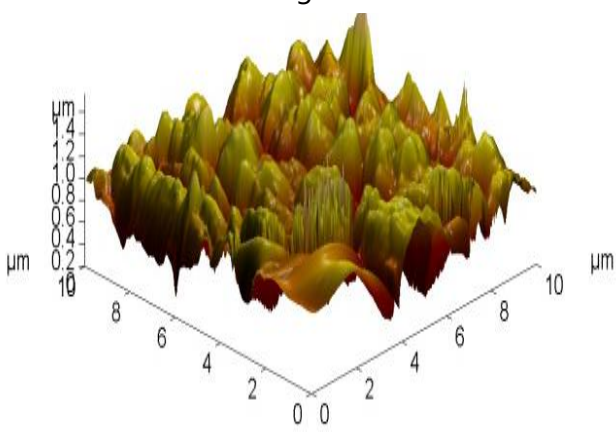


Figure 4: 3D image of NR vulcanizate containing unmodified kaolin (URK10)

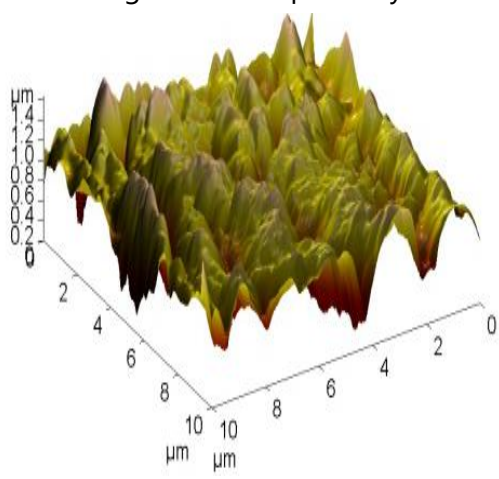


Figure 5: 3D image of NR vulcanizate containing RSO modified kaolin (MRK10)

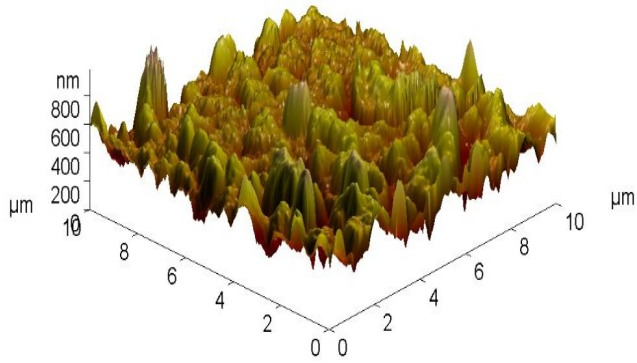


Figure 6: 3D image of NR vulcanizate containing TSO modified kaolin (MTK 6)

The 3D images for the unmodified kaolin filled NR composite as indicated in Figure 4 clearly show filler agglomeration within the NR matrix. In Figure 5 the 3D image in NR/RSO-modified kaolin composites further revealed a good dispersion of the fillers on the rubber matrix as indicated by the white colored peaks while in Figure 6 the level of dispersion of STSO-modified kaolin is an indication that the fillers were well intercalated on the NR matrix.

## 4. Conclusion

The organomodified kaolins were prepared by modification of kaolin with derivatives of rubber seed oil (RSO) and tea seed oil (TSO). Natural rubber (NR) compositions containing 2-10 phr of the modified kaolins showed higher cure rate and state of cure, compared to that containing the same dosage of unmodified kaolin. The vulcanizates containing the organomodified kaolins showed an increase in tensile modulus, tensile strength, tear strength and resistance to fatigue failure. Morphological analysis of the vulcanizates using SEM and AFM showed a more uniform distribution of smaller kaolinite particles in the NR matrix, upon organomodification with RSO and TSO. The results obtained for the optimum cure times, maximum torques and tear strengths of the vulcanizates further revealed that NR/TSO modified vulcanizates at 10phr was found to be the best material for tire sidewalls with the values obtained as 29.29KN/m for the tear strength, 6.80dNm for the maximum torque and 216s for the Optimum cure time, t90 as indicated in Tables 2 and 3. This observation is in tandem with an earlier study on mechanical properties of industrial tire rubber compounds which posited that NR compounds with higher torques and shorter cure times are better sidewall materials (Bijarimi, Zulkafli, and Beg, 2010).

## Acknowledgements

The authors would like to thank DST, New Delhi and CICS, Chennai for the award of RTFDCS fellowship one of the authors under which programme this work was carried out. Our sincere thanks to NIIST, Thiruvananthapuram for providing the necessary facilities and to the Technical Consultancy Division, Rubber Research Institute of India, Kottayam for the measurements of cure characteristics, mechanical properties and resistance to fatigue failure.

## References

Arroyo, M., López-Manchado, MA. and Herrero, B. 2003. Organo-montmorillonite as substitute of carbon black in natural rubber compounds. Polymer, 44: 2447–2453.

Bhowmick, AK., Bhattacharya, M., Mitra, S., Kumar, KD., Maji, PK., Choudhury, A., George, JJ. and Basak, GC. 2010. Morphology–Property Relationship in Rubber-Based Nanocomposites: Some Recent Developments. In: pp.1–83. Available from: http://link.springer.com/10.1007/12_2010_95 [accessed on 11 October 2018].

*Corresponding author's e-mail address: mgbemena.ogonna@fupre.edu.ng*

Bijarimi, M., Zulkafli, H. and Beg, MDH. 2010. Mechanical properties of industrial tyre rubber compounds. Journal of Applied Sciences, 10(13):1345–1348.

Dai, J. 1999. Surface modification of clays and clay–rubber composite. Applied Clay Science [online], 15(1–2):51–65.

Ihueze, CC. and Mgbemena, CO. 2016. Computational modelling of a P195/55 R16 85H radial tire developed from Natural Rubber/ Tea Seed Oil (Camellia sinensis) modified Kaolin vulcanizates. Journal of Presidency University, 3(2):1–10.

Liu, Q., Zhang, Y. and Xu, H. 2008. Properties of vulcanized rubber nanocomposites filled with nanokaolin and precipitated silica. Applied Clay Science, 42(1–2):232–237.

Mgbemena, CO., Ibekwe, NO., Sukumar, R. and Menon, ARR. 2013. Characterization of kaolin intercalates of oleochemicals derived from rubber seed (Hevea brasiliensis) and tea seed (Camelia sinensis) oils. Journal of King Saud University - Science, 25(2):149–155.

Mgbemena, CO., Ihueze, CC. and Menon, ARR. 2016. Performance characteristics and analysis of tailored Natural Rubber/Organo-kaolin Composites. International Journal of Plastics Technology , 20(1):11–27.

Puşcă, A., Bobancu, Ş. and Duţă, A. 2010. Mechanical Properties of Rubber-An Overview. Bulletin of the Transilvania University of Braşov, 3(52):107–114.

Sookyung, U., Thaijaroen, W. and Nakason, C. 2014. Influence of modifying organoclay on the properties of natural rubber/organoclay nanocomposites. Journal of Composite Materials, 48(16):1959–1970.

Sukumar, R. and Menon, ARR. 2008. Organomodified kaolin as a reinforcing filler for natural rubber. Journal of Applied Polymer Science, 107(6): 3476–3483.

Yahaya, LE., Adebowale, KO. and Menon, ARR. 2009. Mechanical properties of organomodified kaolin/natural rubber vulcanizates. Applied Clay Science, 46(3):283–288.

*Corresponding author's e-mail address: mgbemena.ogonna@fupre.edu.ng*