

# NATURAL RUBBER/LAYERED SILCATE NANOCOMPOSITE FOR BUILDING APPLICATIONS

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**Abstract:** Polymeric nanocomposite materials with a nano tag are nowadays moving into the market and are beginning to compete with traditional composite materials in various applications. Nanocomposite materials based on a polymeric matrix and nano-scale particles have offered a great opportunity in sustainable construction/green building applications since its potential capability of addressing key components of the sustainable construction: efficient materials and environmental protection.

Natural rubber (NR)/layered silicate (NRLS) nanocomposites have been prepared by melt mixing of NR with organically modified montmorillonite (OMMT) in the presence of functionalized polar additive and other curing chemicals. The resultant nanorubber vulcanizate structures were characterised with X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD analysis showed that NR molecules diffused into the OMMT gallery in the presence of functionalised polar additive and, as a result, intercalated/exfoliated rubber nanocomposite was formed, the result further confirmed by the analysis of SEM images. The mechanical performances of NRLS nanocomposite material prepared with increasing loading level of OMMT and 90 phr of inert filler (CaCO<sub>3</sub>) were investigated to evaluate the reinforcing effect of OMMT in the presence of inert filler. The mechanical properties of the NRLS vulcanisate were compared with conventional NR vulcanizate containing carbon black (CB) and CaCO<sub>3</sub>.

**Keywords:** Natural rubber, Layered silicate, intercalation, Exfoliation, Polar additive

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## 1 Introduction

In the recent past, polymeric nanocomposites have emerged as one of the most promising alternative to conventional polymeric composites for various applications such as automotive, packaging, building construction, etc. They are bi-phase material in which inorganic phase is dispersed at nano scale within the range of 1-100 nm within the polymeric matrix [1-2]. Polymeric nanocomposites based on different nanoparticles have received a great attention in the construction industry since it has superior mechanical properties and able to impart different functional properties like flame retardancy, thermal and electrical conductivity in comparison to conventional microcomposites [3-4].

Polymeric nanocomposites based on layered silicates (e.g. montmorillonite clay: belongs to 2:1 layered silicates) have probably received the most attention since it offers an enhanced reinforcement and different functional properties at low loading levels. Generally, polymer-layered silicate nanocomposites (PLSN) are divided into three ideal types: phase-separated conventional microcomposites, intercalated nanocomposites (i.e. polymer molecules intercalate into the clay gallery) and exfoliated nanocomposites (clay particles are separated into individual layers and dispersed homogeneously in the polymeric matrix [5]. Nylon 6/layered silicate nanocomposite was the first investigated polymeric nanocomposite by Toyota Research Group, Japan and it was found that mechanical and thermal properties were improved markedly, at low loading levels, in comparison to unmodified polymer and conventional microcomposites [6-7]. Since then different thermoplastics and elastomer nanocomposites based on layered silicates, especially montmorillonite, have been developed, as an alternative for conventional composites, for various applications [8-9].

Thermoplastic and elastomer composites have increasingly become important as engineering materials and they are greatly used in building and construction applications. For example, construction industry is the second largest user for thermoplastics and its composites [10]. Balanced mechanical properties along with a lighter weight, chemical and thermal stability, and flame retardancy and with ease of processing are few of the key properties of polymeric composites that are explored in structural applications [11]. Efficient design and application of these polymeric materials in built environment are important for sustainable construction.

Natural rubber (NR) is one of the interesting engineering materials which are widely used in building applications such as floorings, as shock absorbing material, gaskets, insulator and sealing applications. However, most of the rubber compounds/products used in building applications contain carbon black (most common filler in rubber industry), as a reinforcing material since NR alone does not provide the required properties. The use of rubber products containing fossil based environmental un-friendly carbon black in building environment does not support the rapidly growing concept of green building/sustainable construction. Layered silicates, especially montmorillonite clay, could be a promising alternative to conventional carbon black. Rubber/layered silicate nanocomposites exhibit not only outstanding mechanical properties, but also show functional properties such as barrier and flame retardant properties, at very low loading levels (i.e. < 10 w/w %) of layered silicates [12].

The objective of this study reported here is to prepare green natural rubber nanocomposites by replacing conventional carbon black with organically modified montmorillonite (OMMT) and to characterize the vulcanisation behaviour and nanocomposite structure. Specific focus is given to evaluate the mechanical and other functional properties of the rubber nanocomposites based on OMMT and inert filler (CaCO<sub>3</sub>) in view of building applications.

## **2 Materials and experimental methods**

Ribbed smoked sheet (RSS) grade of NR was selected as the rubber matrix in this study. Montmorillonite clay (Cloisite 20A), modified with dimethyl dihydrogenated tallow quaternary ammonium chloride, has been used to prepare natural rubber/layered silicate nanocomposite and was supplied Suthern Clay Products. Industrial grade vulcanizing chemicals such as sulphur, accelerator, antioxidants are also used in the compound formulations.

### ***2.1 Preparation of natural rubber/layered silicate nanocomposite (NRLS) material***

NRLS nanocomposites were prepared by the melt mixing of NR and OMMT in the presence of functionalized polar additive as an exfoliating promoter and with other vulcanizing chemicals in a laboratory scale Internal Mixer (Haake Rheomix 600), operating at 60 °C (set temperature) and with a rotor speed of 80 rpm. Table 1 presents the exact formulations for each NRLS nanocomposite.

Vulcanization parameters of the nanocompounds were determined using Moving Die Rheometer (MDR: Ektron, EKT-2000S) at 150 °C for 30 min. NRLS nanocomposite vulcanizate sheets of approximately 2 mm thickness were prepared in a hot press at 150 °C for optimum cure time, t<sub>90</sub>, derived from rheographs obtained from the analysis of MDR. These vulcanized sheets of NRLS were used to characterise the nanocomposite structure and mechanical properties.

### ***2.2 Characterization of natural rubber/layered silicate (NRLS) nanocomposite material***

X-ray diffraction (XRD) analysis was performed with a Bruker D8 diffractometer with Cu K $\alpha$  radiation to evaluate the nanocomposite structure in terms of intercalation/exfoliation behaviour of OMMT in the NR. XRD diffractograms of NRLS nanocomposite vulcanizate sheets by scanning over a 2  $\theta$  range from 1 to 10 degrees, at a rate of 0.01/s. The conventional Bragg equation ( $n\lambda = 2d \sin \theta$ ) was used to determine the interlayer spacing of OMMT in the nanocomposite material.

OMMT morphology (dispersion and distribution) within the RLSN material was observed under Scanning Electron Microscope (Hitachi SU 6000), operated at 25 kV.

Table 1: Compositions of NRLS nanocomposite vulcanisates containing different concentration of OMMT

	NR GUM	NRLS4	NRLS8	NRLS10	NRLS4/ 90	NRLS10/ 90	NRLS15/ 90
NR	100	100	100	100	100	100	100
OMMT	-	4	8	10	4	10	15
Polar additive	-	0.46	0.92	1.15	0.46	1.15	1.73
CaCO <sub>3</sub>	-	-	-	-	90	90	90
ZNO	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1
IPPD <sup>a</sup>	1	1	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
MBTS <sup>b</sup>	1	1	1	1	1	1	1

<sup>a</sup> *n*-isopropyl *n*-phenyl *n*-phenylenediammine

<sup>b</sup> Mercaptobenzothiazole disulphide

### 2.3 Mechanical properties of NRLS nanocomposite vulcanisates

Mechanical properties including tensile properties, hardness and rebound resilience of NRLS vulcanisates were analysed to study the effect of OMMT loading levels and CaCO<sub>3</sub> on mechanical property performances.

Tensile properties of NRLS vulcanisate prepared by incorporating OMMT and CaCO<sub>3</sub> were analysed according to ISO standards, ISO 37: 2005 (E), using Instron 3365 Universal Tensometer. The extension of the samples was measured using an optical extensometer.

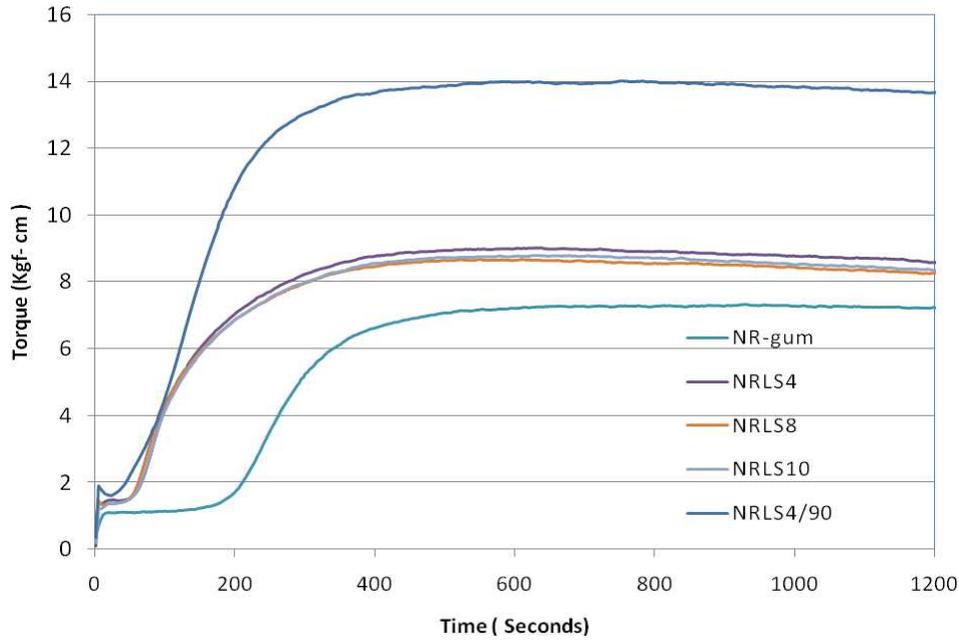
Shore A hardness of the NRLS nanocomposite vulcanisate was measured using ASTM standard, D 2240.

## 3 Results and discussion

Vulcanization curves of NRLS nanocompounds containing different loading levels of OMMT are graphically presented in Figure 1. NRLS nanocompounds (i.e. NRLS4, NRLS8 and NRLS10) have a noticeable higher maximum torque (MH) compared to that of NR-gum compound. These results indicate a higher degree of cross linking and intercalation/exfoliation of OMMT achieved in NRLS nanocompounds. Vulcanisation studies of NRLS nanocompounds further revealed that, as shown in Figure 1, OMMT accelerates the vulcanization process (i.e. increase the cure rate), resulting in reduced the scorch ( $t_{s2}$ ) and optimum cure ( $t_{90}$ ) times. This is attributed to the fact that organic modifier (dimethyl dihydrogenated tallow quaternary ammonium) in the OMMT acts as a catalyst during the vulcanization process. However, NRLS4/90 containing 4 phr of OMMT and 90 phr of CaCO<sub>3</sub> shows the maximum torque but curing rate does not alter significantly due to the incorporation of CaCO<sub>3</sub>.

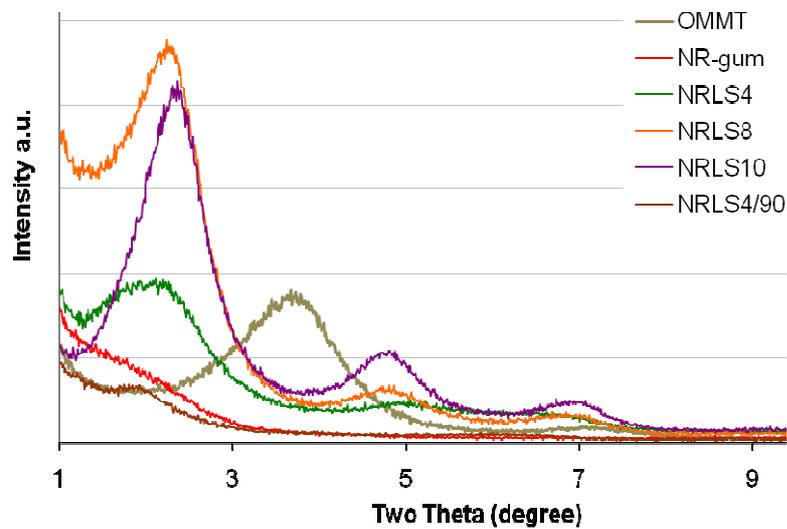
### 3.1 Characterization of NRLS nanocomposite structure

The NRLS nanocomposite vulcanisates prepared by melt mixing of NR with OMMT in the presence of functionalized polar additive followed by vulcanisation were analyzed with X-ray diffraction technique to evaluate the formation of nanocomposite structure. The exact composition of each NRLS nanocomposite material is shown in Table 1. Figure 2 presents the XRD spectra of pure OMMT and NRLS vulcanisates containing different loading levels of OMMT.



**Fig.1:** Vulcanisation curves (rheographs) of NR- gum and NRLS nanocompounds at 150 °C

As shown in Figure 2, the characteristic diffraction peak (001) of OMMT is at  $2.96^\circ$  of two theta and hence interlayer spacing is  $24.5 \text{ \AA}$  (see Table 2). However, when OMMT is melt mixed with NR in the presence of functionalized polar additive, the diffraction peak of OMMT shifted towards a lower Bragg angle. Table 2 presents the two theta positions of the diffraction peaks and the interlayer spacing for each nanocompound comprising different concentration of OMMT. This could be explained by the polar additives intercalating into the OMMT galleries and, as a result, NR molecules were also likely to diffuse into the OMMT galleries. Hence, interlayer spacing of OMMT was increased, resulting in intercalated NR/OMMT nanocomposite structure. For example, interlayer spacing of OMMT in NRLS4 nanocomposite increased from  $23.6 \text{ \AA}$  to  $42.0 \text{ \AA}$  (see table 2).



**Fig.2:** X-ray diffraction spectra of OMMT and NRLS nanocomposites

However, more interestingly, when CaCO<sub>3</sub> is incorporated into the formulation (i.e. NRLS4/90) the diffraction peak of OMMT further shifted towards the lower Bragg angle, indicating further intercalation/exfoliation of OMMT during the melt mixing process.

Table 2: Diffraction peak positions and interlayer distances of OMMT in NRLS nanocomposite vulcanisates

NRLS nanocomposite vulcanisate	Two theta (°)	Interlayer spacing (Å)
OMMT	3.73	23.6
NRLS4	2.1	42.0
NRLS8	2.29	38.5
NRLS10	2.37	37.2
NRLS4/90	1.85	47.7

Since XRD data confirms the intercalation of NR molecules into the OMMT galleries, SEM micrographs of NRLS nanocomposite materials were analysed to evaluate the OMMT dispersion within the nanocomposite material. Figure 3 shows the NRLS nanocomposite material containing 4 phr. of OMMT (NRLS4) at a lower magnification (3-a) and a higher magnification (3-b and c). As shown in Figure 3 (a), particulate materials are dispersed uniformly throughout the NR matrix, indicating better compatibility is achieved between OMMT and NR through the functionalised polar additive. On the other hand, high magnification images show the nm size thickness of the OMMT clay stack in the nanocomposite material. It can be clearly seen that these stacks are contained only few individual clay platelets, implying that larger OMMT clay stacks exfoliate/delaminate into smaller stacks during the compounding process.

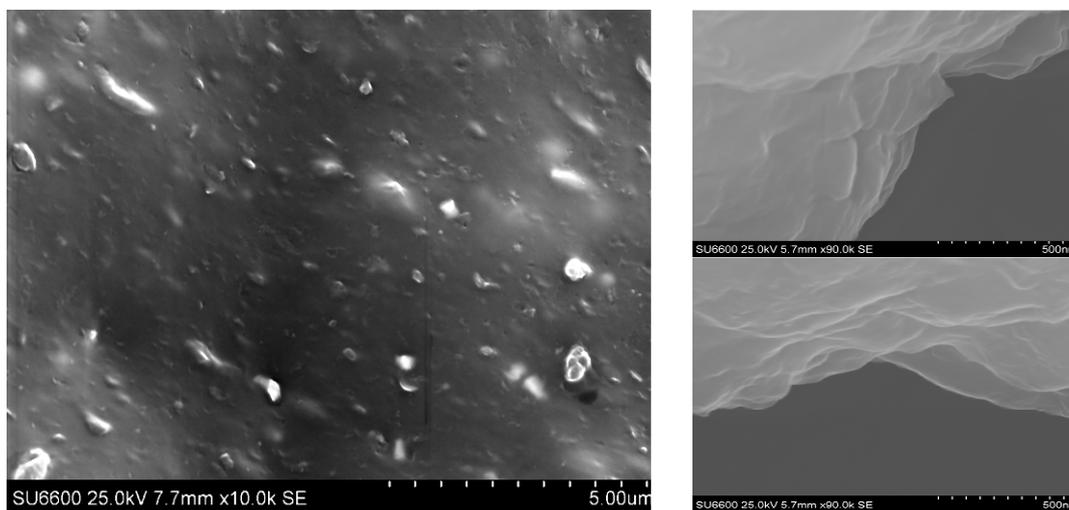


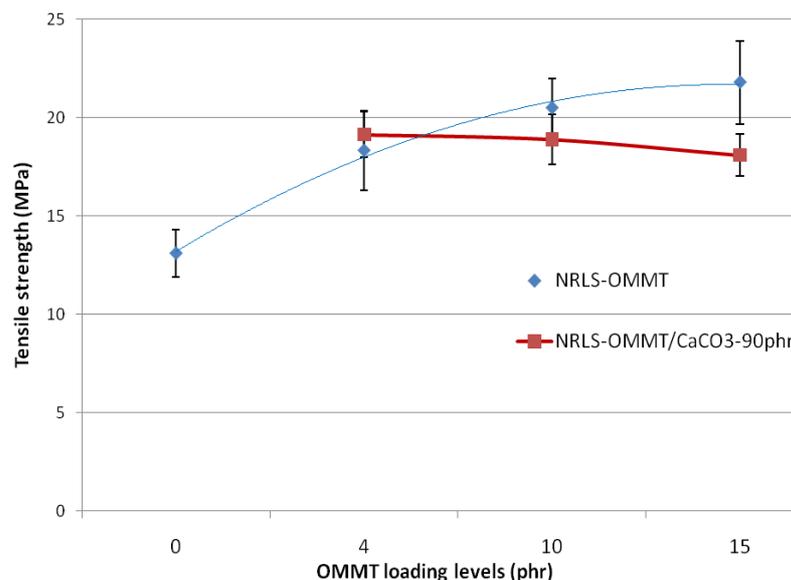
Fig.3: SEM micrographs of NRLS4; (a) dispersability of OMMT in NRLS material at low magnification, 10,000. (b) & (c) thickness of the OMMT stack at a higher magnification

From these X-ray diffraction data and SEM images prove the formation of intercalated/exfoliated OMMT structure with in the NR matrix.

### 3.2 Mechanical properties of NRLS nanocomposite vulcanisates

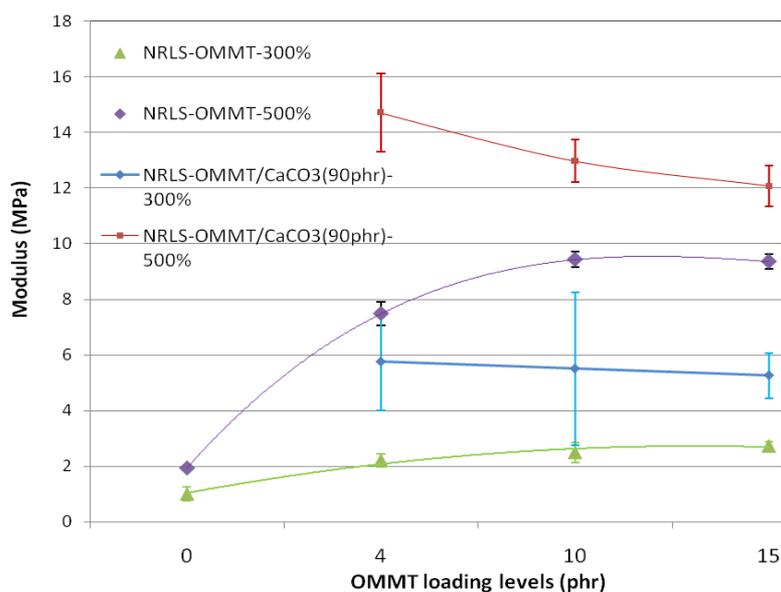
The reinforcing effect of OMMT and the suitability of this new green material (NRLS nanocomposites), which does not contain carbon black, for building applications were evaluated by analysing the mechanical properties of NRLS nanocomposite vulcanisates.

Figure 4 and 5 show the tensile properties (tensile strength and tensile modulus) of NRLS nanocomposite vulcanisates containing OMMT as the only reinforcing material and NRLS/CaCO<sub>3</sub> nanocomposite vulcanisates containing 90 phr of CaCO<sub>3</sub> as inert filler in addition to OMMT. All NRLS nanocomposites (e.g. NRLS4, NRLS8) containing only OMMT showed a higher tensile strength and modulus with compared to that of NR-gum compound. The improvement of tensile properties of NRLS nanocomposites depends on OMMT aspect ratio, OMMT mechanical properties and the interaction between the NR matrix and the OMMT. As explained in the characterisation of NRLS nanocomposite structure, NR molecules intercalate into the OMMT gallery in the presence of polar additive and, as a result, significantly improve the OMMT exfoliation and subsequent dispersion. Exfoliation of OMMT particles into the nano-meter range, resulting in higher aspect ratio, is the key to improve the tensile properties of NRLS nanocomposite material. However, the tensile NRLS vulcanisates increased rapidly with increasing OMMT content up to 10 phr and, when OMMT content increased beyond 10 phr, the improvement in tensile properties is gradually less. Reduced improvement of tensile properties beyond 10 phr of OMMT could be attributed to that of lower degree of exfoliation at high concentration of OMMT. The lower degree of exfoliation results in a higher number of individual OMMT layers (OMMT platelets) per clay stack and hence decreases the effective length to diameter ratio (aspect ratio).



**Fig.4:** Comparison of tensile strength of nanocomposite vulcanisates of NRLS-OMMT and NRLS-OMMT/CacCO<sub>3</sub>-90phr).

Generally, incorporation of inert fillers such as CaCO<sub>3</sub> deteriorates the reinforcement of rubber compound vulcanisates. However, although the strength characteristics (tensile strength) were slightly reduced by mixing 90 phr of CaCO<sub>3</sub> into the NRLS nanocomposites, NRLS/CaCO<sub>3</sub> nanocomposites vulcanisates maintained better tensile properties compared to that of NR-gum compound. This would explain that improved reinforcement obtained due to the exfoliation of OMMT does not significantly deteriorate by incorporating CaCO<sub>3</sub>.



**Fig.5:** Comparison of tensile modulus nanocomposite vulcanisates of NRLS-OMMT and NRLS-OMMT/CacCO<sub>3</sub>(90phr).

Table 3 shows the comparison of mechanical properties between the new NR nanocomposite vulcanisate material containing both OMMT and CaCO<sub>3</sub> and conventional NR vulcanisate containing carbon black and CaCO<sub>3</sub>. As shown in Table 3, in comparison to conventional carbon black rubber compound (NRCB30/90), similar mechanical performances (i.e. tensile properties, tear strength and hardness) are achieved in NRLS/CaCO<sub>3</sub> nanocomposite vulcanisate containing no carbon black. Characterisation of mechanical properties clearly showed that environmental unfriendly carbon black can be replaced with a lower loading level of OMMT as a reinforcing material and this new elastomeric nanocomposite material would be a potential material for applications in sustainable buildings.

*Table 3: Mechanical properties of NRLS/CaCO<sub>3</sub> nanocomposite vulcanisate and conventional NR vulcanisate (NRCB30/90)*

Compound	Hardness (Shore A)	Tensile strength (MPa)	Modulus-300% (MPa)	Tear strength (KN/m)	Elongation (%)
NR-gum	31.75	13.15	0.99	29.15	726
NRLS4/90	55.92	19.14	5.75	42.01	557
NRLS10/90	57.15	18.90	5.50	37.10	615
NRLS15/90	56.40	18.10	5.26	35.96	618
NRCB30/90 <sup>a</sup>	59.50	15.56	5.95	33.35	521

<sup>a</sup> Conventional NR vulcanisate containing 30 phr of carbon black and 90 phr of CaCO<sub>3</sub>

#### 4 Conclusion

A modified method of preparing natural rubber/layered silicates nanocomposites in the presence of functionalised polar additives and its performances characteristics were presented, in view of replacing conventional NR compound containing carbon black. XRD results revealed that polar additives promote the intercalation on NR molecules into the OMMT galleries whilst SEM images showed the exfoliation of OMMT particles into nano meter scale and subsequent uniform dispersion

throughout the NR matrix. Vulcanisation process of NRLS is accelerated by the OMMT due to the presence of amine type organic modifier.

NRLS nanocomposite prepared by incorporating both OMMT and the inert filler (CaCO<sub>3</sub>) shows good reinforcement and its mechanical performances are as good as with the conventional NR compound. Hence, this new natural rubber nanocomposite material is a potential candidate for green building applications.

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## Acknowledgements

Authors would like to acknowledge the technical support and the materials (NR and vulcanising chemicals) given by the Research and Development Division of Loadstar (Private) Limited.

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