

## **Reinforcement and curing characteristics of organoclay filled natural rubber nanocomposites**

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### **Abstract**

*Natural rubber (NR) - organoclay nanocomposites (NROCN) and NR-clay (unmodified montmorillonite clay) composites (NRCC) were prepared using different loading of OC/unmodified clay by melt compounding process using a laboratory scale internal mixer in view of investigating the organoclay (OC) effect on curing characteristics and reinforcing behaviour in NR compound formulations.*

*X-ray diffraction analysis of NROCN's revealed predominantly exfoliated OC structures within the NR nanocomposite materials, especially with a lower loading of OC where as NRCC's showed MMT clay aggregates with larger clay stacks leading to conventional NR composite materials.*

*Vulcanization characteristics of the clay filled NR compounds, especially processing safety, curing time and delta torque, have been interpreted with respect to the organic modifier in the OC and OC clay loading.*

*NROCN vulcanizates have shown a significant enhancement in solid-state mechanical properties compared to those of NR gum and NRCC vulcanizates. Mechanical property data have been explained in terms of compatibility, degree of exfoliation and clay loading.*

**Key words:** exfoliation, nanocomposite, natural rubber, montmorillonite, organoclay, reinforcement, vulcanization

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### **Introduction**

Natural rubber can be converted into useful elastomeric engineering materials for many applications when it is reinforced with filler material. In general, filler can be defined as fine

particulate materials that are often used to enhance the performances and various functional properties of the elastomeric matrix, depending on the applications. The main aim of filler addition is to improve physio-

mechanical properties and to reduce the cost of the compound. Typical reinforcing filler used in rubber compounding is carbon black and silica and, use of carbon black with rubber causes environmental pollution and gives a rubber a black colour (Galimberti, 2011). However, for lighter coloured rubber products, silica filler is commonly used (Chonkaew *et al.*, 2011; Murakami *et al.*, 2001; Poh and Ng, 1998).

In recent past, polymer nanocomposites have attracted a great interest in both academia and industry as an alternative for conventional polymer composites because of the unique properties achieved with the nanocomposites (Ratnayake and Haworth, 2006; Ratnayake *et al.*, 2008). Furthermore, in recent years rubber-clay (layered silicate) nanocomposites have shown a great potential over conventional carbon black filled rubber compounds, because they often exhibit remarkable improvement in material properties when compared with neat rubber or conventional rubber compounds (Zhang *et al.*, 2008). Among natural clays, montmorillonite (MMT) clay is the most commonly used reinforcing material in nanocomposite preparation due to its high cation exchange capacities, large surface area, good surface reactivity and surface adsorptive properties. In general, clay minerals are composed of silicate layers/platelets of 1 nm thick and 200–300 nm in the lateral dimensions. Depending on the strength of interfacial interactions

between the polymer matrix and the silicate layers, conventional, intercalated and exfoliated nano composites are thermodynamically achievable (Qureshi *et al.*, 2010; Zhang *et al.*, 2005). One of the drawbacks of using the MMT clay mineral as reinforcing filler for rubber is the incompatibility between hydrophilic clay and hydrophobic polymer, which often causes agglomeration of the clay within the polymer matrix. Therefore, surface modification of the clay is an important step to achieve rubber nanocomposites. The cations, which are placed within the clay gallery, can be exchanged with other inorganic or organic ions, for example quaternary alkyl ammonium ions (Yahaya *et al.*, 2010). Organophilic modification makes the clay silicate layers compatible with the polymer. Such modified clays are commonly called as organoclay (OCs) (Zang *et al.*, 2005).

In Rubber-clay nanocomposites, incorporation of a few weight percent of OC minerals that are properly dispersed throughout the polymer matrix, thus create much higher surface area for polymer/OC interaction as compared to conventional composites resulting in better reinforcement (Bhowmick *et al.*, 2010). Reinforcement of rubber is associated with the enhancement of the modulus, failure properties (tensile and tear strength) *etc.*, of the vulcanizates. However, to achieve nano-reinforcement, clay particles should be separated/delaminated into individual clay platelets which are 1 nm in

thickness (Hakim and Ismail, 2009). Generally, reinforcement of the rubber-clay nanocomposite predominantly depend on the cross linking chemistry of the rubbers, nature of the fillers, the physical and chemical interaction of the clay layers with the rubber matrix and, especially, on the degree of clay exfoliation/dispersion within the rubber matrix (Amarasiri *et al.*, 2013). Hence, optimizing curing characteristics, especially processing safety and curing efficiency, degree of filler dispersion and filler-matrix interaction is vital to achieve the desired processability and physio-mechanical properties of any filled rubber compounds.

The objective of this research study was to investigate the effect of organoclay, especially organic modifier on curing characteristics and reinforcement of the NR compounds. Curing properties and reinforcement of organoclay filled NR compounds are also compared against the pristine MMT clay.

## **Materials and Methods**

### **Materials**

NR in the form of ribbed smoked sheet (RSS) with a Mooney viscosity of 95 (ML (1+4) 100°C) was purchased from Shums Rubber and Company Ltd. Sodium montmorillonite clay (Na<sup>+</sup>-MMT) with a cation exchange capacity of 95 meq of clay and organically modified montmorillonite clay (Closite

20A) supplied by Southern Clay Products, Inc. Co. Ltd. were used as clay mineral. Closite 20A is a surface-modified with dimethyl dihydrogenated tallow, quaternary ammonium modifier. The mean dry particle size of the organoclay is 6-13 µm. All other rubber compounding ingredients used were of commercial grade.

### **Preparation of natural rubber/clay nanocomposites**

Natural rubber/organoclay nanocomposites (NROCN) were prepared by melt compounding of NR with organoclay in the presence of other compounding chemicals in a laboratory scale internal mixer, model Haake PolyLab OS – Rheomix 600, operating at on-set temperature of 60 °C and with a rotor speed of 80 rpm for 12 minutes. In addition, NR/clay composites (NRCC) were also prepared with equivalent unmodified montmorillonite clay loading similar to organoclay using the same internal mixer at similar processing parameters to evaluate the reinforcing and curing effect of organoclay in comparison to unmodified clay. The organoclay/unmodified clay filled NR compounds were conditioned at 23 ± 2 °C for 24 h prior to cure assessment. Table 1 presents the exact compound formulation for each NROCN and NRCC.

**Table 1.** Compound formulations for NROCN and NRCC

Ingredients	NRCC (phr)	NROCN (phr)
Natural rubber	100	100
MMT	2-10	-
OMMT	-	2-10
Zinc oxide	5	5
Stearic acid	2	2
IPPD <sup>a</sup>	1	1
Sulphur	2.5	2.5
TBBS <sup>b</sup>	1.2	1.2
CTP <sup>c</sup>	0.4	0.4

<sup>a</sup>N-Isopropyl- N'-phenyl-P-phenylenediamine, <sup>b</sup>N-t-butylbenzothiozole-2-sulphanamide, <sup>c</sup>N-(cyclohexylthio) phthalimide

#### Analysis of cure characteristics

The cure characteristics of organoclay/unmodified clay filled NR compounds were studied using a Moving Die Rheometer (EKTRON-2000 S) at 150 °C. Cure characteristics of each compound such as cure time ( $T_{90}$ ), scorch time ( $T_{S2}$ ), cure rate index (CRI) and maximum torque were derived from the rheographs. Compounds were then compression moulded at 150 °C for the respective cure times derived from rheographs.

#### Characterization NR nanocomposite structures

Both NROCN and NRCC vulcanizate sheets prepared with compression moulding were analysed with X-ray diffraction technique to evaluate the intercalation and exfoliation behaviour of clay and to determine the interlayer spacing of clay within the nanocomposite materials. X-ray diffraction (XRD) analysis of the

nanocomposites was performed with a Bruker D8 diffractometer at a wave length of 1.54 Å of Cu K $\alpha$  radiations, by scanning over Bragg angle ( $2\theta$ ) range from 1-10° at a scanning rate of 1°/min. The conventional Bragg equation ( $n\lambda = 2d \sin \theta$ ) was used to calculate the interlayer spacing of the clay in the nanocomposite materials.  $\lambda$  is the wave length of X-rays,  $d$  is the crystal lattice spacing,  $\theta$  is the angle between incident radiation and the scattering plane, and  $n$  is the order of reflection.

#### Reinforcing effect of organoclay

Solid state mechanical properties of NROCN vulcanisates were analysed in comparison to NRCC vulcanisates and NR-gum vulcanisates containing no clay to study the reinforcing effect of organoclay. Tensile and tear properties of the NR vulcanisates were performed at a cross-head speed of 500 mmmin<sup>-1</sup> using INSTRON, model 3365 Universal Testing Machine according to ISO 37

(2005) and ISO 34 (2010) standard methods respectively. Hardness (IRHD) and compression set were measured according to ISO 7619 (2010) and ISO 815-1(2008) respectively.

#### **Analysis of tensile fracture surface**

Tensile fracture surfaces of organoclay filled NR nanocomposites and unmodified clay filled NR composites were observed under scanning electron microscope (SEM) to understand the tensile fracture behaviour of NROCN. SEM analysis of the clay filled NR vulcanizates was carried out with an electron microscope, model HITACHI - SU6600 (SEM) at high vacuum mode operated at 30 kV. The fracture surfaces of the specimens were mounted on aluminium stubs and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

### **Results and Discussion**

#### **Vulcanization characteristics of organoclay/clay filled rubber compounds**

Curing characteristics of the clay filled NR compounds measured with the moving die rheometer are presented in Table 2 whilst Figures 1 and 2 show the effect of organoclay/clay on scorch time,  $TS_2$  and cure time,  $T_{90}$  for both NROCN and NRCC compounds respectively.

As shown in Figures 1 and 2, NR-gum compound (containing no clay) cured

with a conventional vulcanization system exhibited a good processing safety; a scorch time of 473 s and optimum cure of 1008 s. However, addition of organoclay into the NR showed a significant reduction in on-set vulcanization time (scorch time) and, as a result reduced processing safety and curing time of the compound. For example, scorch time of NROCN compound containing 2 phr of OC is reduced from 473 s to 135 s whilst optimum cure time is compressed from 1008 s to 426 s. These curing data indicates that organoclay behaves as an effective accelerating agent for NR vulcanization reaction. This could be attributed to the fact that organic modifier, dimethyl dihydrogenated tallow quaternary ammonium, in the organoclay acts as an accelerating agent by reducing the activation energy of the sulphur vulcanization reaction, resulting in reduced on-set vulcanization time. It has been reported (Galimberti, 2011; Jacob *et al.*, 2007; Ishiaku *et al.*, 1998; Akiba and Hashim, 1997) that amine groups facilitate the curing reaction of NR compounds.

In contrast to NROCN compounds, NRCC compounds do not show a significant variation of scorch time and optimum cure time in comparison to NR-gum compound, further confirming the effect of organic modifier on vulcanization reaction.

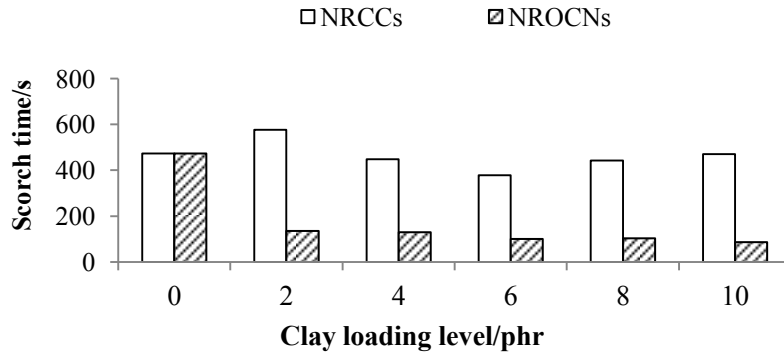


Fig. 1. The effect of clay loading on scorch time of NRCCs and NROCNs

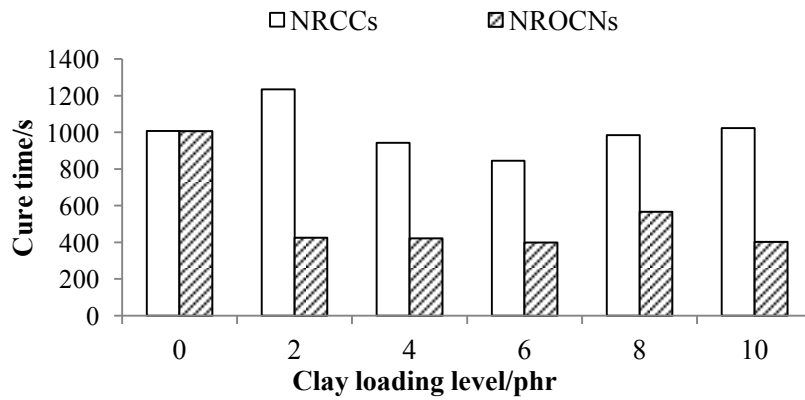


Fig. 2. The effect of clay loading on cure time of NRCCs and NROCNs

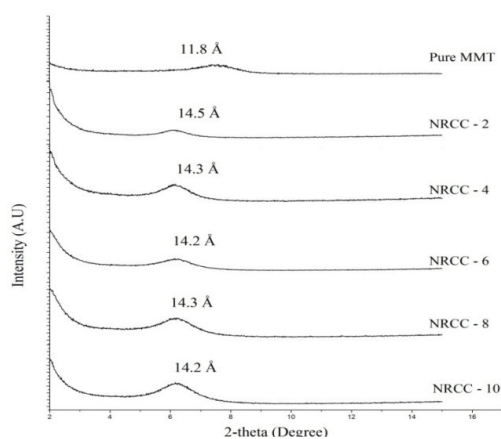
Table 2. Curing characteristics of NRCCs and NROCNs

Clay loading (phr)	CRI/s <sup>-1</sup>		MH/ dNm		ΔM /dNm	
	NRCC	NROCN	NRCC	NROCN	NRCC	NROCN
0	0.19	0.19	13.93	13.93	12.47	12.47
2	0.15	0.34	14.81	17.45	13.58	15.68
4	0.20	0.34	14.36	18.15	12.93	16.43
6	0.21	0.33	14.55	19.05	12.89	17.57
8	0.18	0.22	14.29	18.40	12.47	17.08
10	0.18	0.32	14.49	18.57	12.94	16.88

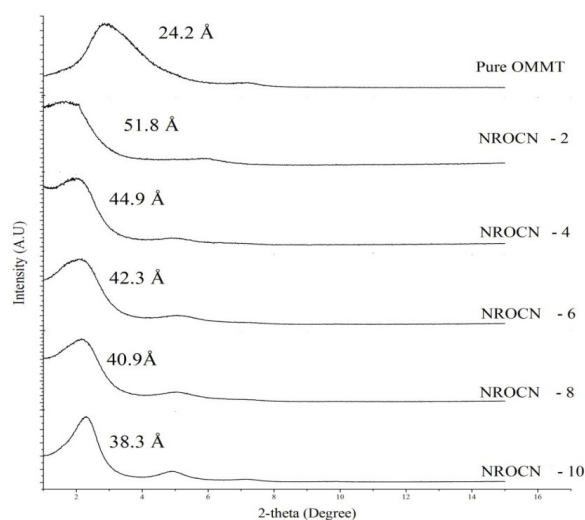
Table 2 shows the cure rate index, maximum torque, MH, and delta torque ( $\Delta M$ , torque difference between maximum torque and minimum torque) for both NRCCs and NROCNC compounds. It can be seen that with an increase of organoclay loading  $\Delta M$  increased gradually to a maximum level at 6 phr beyond that no significant change whereas there is no significant change in  $\Delta M$  of NRCC compounds. In general,  $\Delta M$  of a NR compound is an indication of the crosslink density of the compound and the reinforcement achieved with filler. These results clearly suggest that NROCN compounds have higher crosslink density than that of NRCC compounds, and as a result likely to have a higher reinforcing effect of organoclay.

### Characterization of NR-clay nanocomposite materials

Figures 3 and 4 represent the X-ray diffractograms for unmodified clay (MMT) filled and organoclay (OC) filled vulcanizates, respectively. The characteristic diffraction peak ( $d_{001}$ ) of pure MMT clay is appeared at Bragg angle of  $7.33^\circ$  (Fig. 3), resulting in interlayer spacing of 11.8 Å. As shown in Figure 3, when NRCC is prepared by incorporating MMT clay, diffraction peaks ( $d_{001}$ ) of NRCC's are slightly shifted towards lower Bragg angles. This could be due to the diffusion of low molecular weight substances used in compounding process into the clay inter gallery space. Based on the X-ray diffraction data of NRCC, it is clear evident that NR molecules do not intercalate into the MMT clay gallery and as a result phase separated conventional microcomposites are formed.



**Fig. 3.** X-ray diffractograms for NRCCs prepared with different loading of unmodified (MMT) clay



**Fig. 4.** X-ray diffraction spectra for NROCNS prepared with different loading of organoclay

As shown in Figure 4, pure OMMT clay shows the diffraction peak ( $d_{001}$ ) at Bragg angle of  $2.84^\circ$  which is assigned to the interlayer spacing of 24.2 Å. When NROCNS were prepared with OC, as presented in Figure 4, the  $d_{001}$  X-ray diffraction peak of OC in all nanocomposites shows a much more significant shifting towards a lower Bragg angle, resulting in significant increase in the interlayer spacing than pure OC. The significant increase in OC clay gallery space in the NROCNS can be explained referring to the hypothesis that NR molecules along with low molecular weight substances intercalate into the clay gallery during the compounding process resulting in an expansion in the gallery region due to the compatibility between the two entities. For example, as result of this intercalation of NR molecules, the

diffraction peak of 2 phr OC filled NROCNS shifted from 24.2 Å (pure OC, as supplied) to 51.8 Å, with an increase of 27.6 Å. Higher interlayer spacing caused to weaken the Vander-Wall attractive forces between clay platelets and as a result, exfoliation of OC in the NROCNS is facilitated during the high shear melt mixing process in the internal mixer. Hence, OC in the NROCNS exfoliates into either single platelets or smaller stacks with a few clay platelets, resulting in intercalated/exfoliated nanocomposite structure. However, as shown in Figure 4, with the increase of OC loading from 2 to 10 phr, X-ray diffraction peak becomes gradually narrow and shifted slightly towards a higher diffraction angle. This implies that higher clay loading affects to the degree of exfoliation and resulting thicker clay

stacks containing comparatively higher number of clay platelets.

### Mechanical properties of NROCN vulcanizate materials

The effect of organoclay on reinforcement of NROCN vulcanizate materials were evaluated in comparison to NR-gum vulcanizate and NRCC vulcanizates containing equivalent clay loading similar to NROCNs vulcanizates.

Figure 5 shows the tensile stress-strain curves for NROCNs vulcanizates with increasing loading levels of organoclay while Figures 6 and 7 show the tensile strength and tear strength of both NROCN and NRCC vulcanizates. Stress-strain properties such as tensile strength and tear strength have clearly shown that modified clay significantly enhanced the reinforcement of NROCN vulcanizates compared to that of NR-

gum and NRCC vulcanizates. This can be explained referring to the argument that the organoclay is more compatible with NR matrix than unmodified MMT and as a result NR molecules diffuse into the organoclay gallery, leading to a better exfoliation/dispersion of organoclay in the NR matrix. As a result, organoclay particles are separated into either individual clay platelets with 1 nm thickness or smaller stacks with a few clay platelets as confirmed by X-ray diffraction results (Fig. 4). Improved dispersion/exfoliation of organoclay within the rubber matrix would lead to increase the aspect ratio as well as the specific surface area of organoclay. Higher surface area is caused to improve interfacial interaction between organoclay and NR molecules resulting in good strength characteristics of NROCNs vulcanizates.

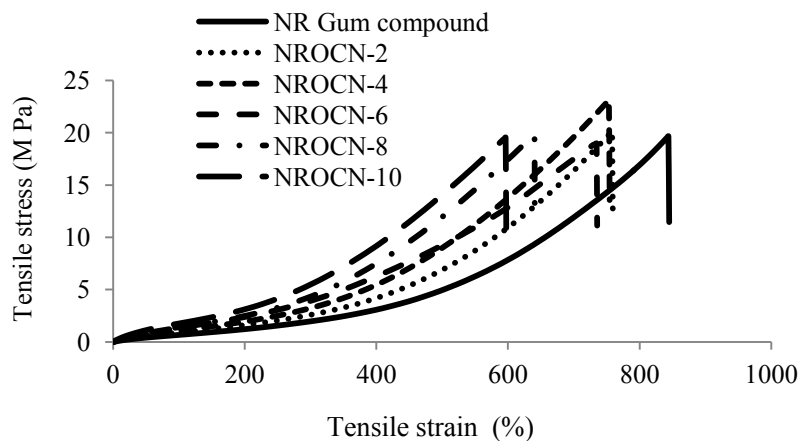
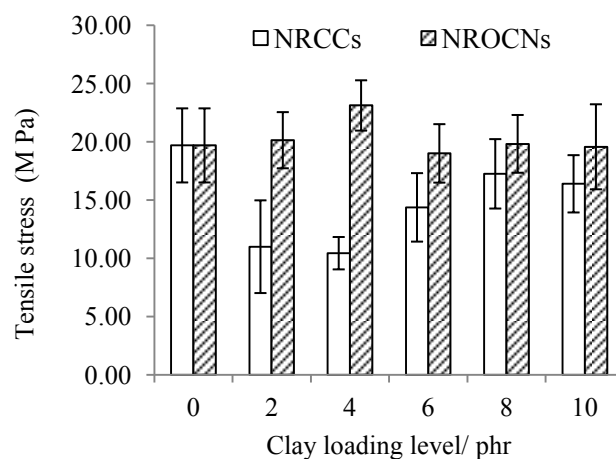


Fig. 5. Stress-strain curves of NROCNs vulcanizates



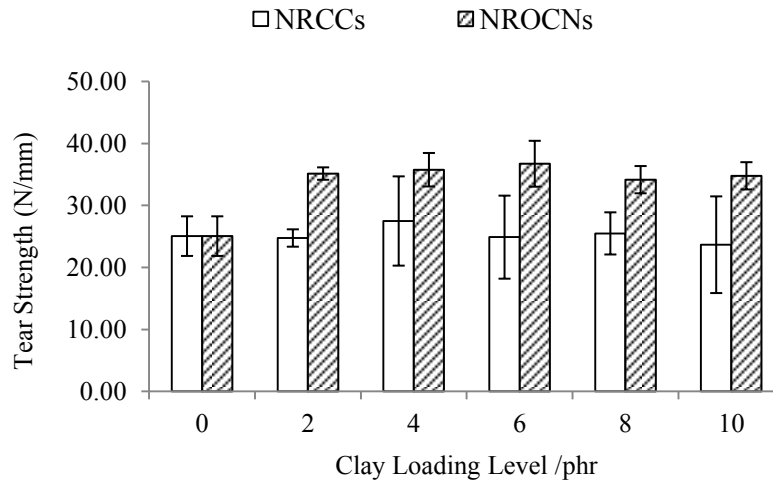
**Fig. 6.** Effect of clay loading on tensile strength of NRCCs and NROCNs

On the other hand, addition of unmodified MMT clay into NR reduce both tensile strength and tear strength, suggesting that MMT clay does not exfoliate during the compounding process due to the incompatibility with NR and resulting in agglomerated larger clay stacks in the NRCC vulcanizates. Those larger clay particles act as non-reinforcing filler and therefore reduce the strength characteristics.

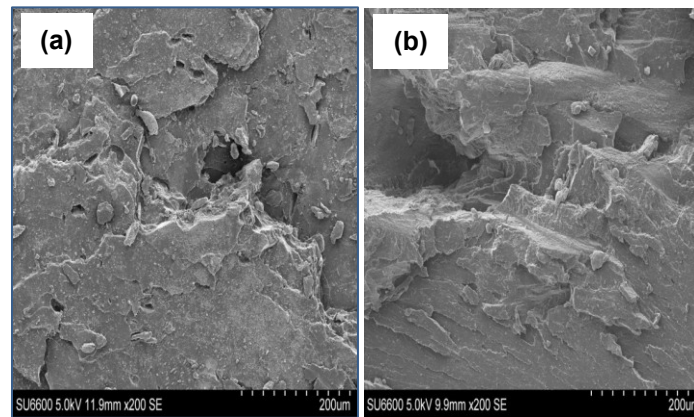
A significant improvement (about 40%) of tear strength was observed in NROCN in comparison to NR-gum and NRCC (Fig. 7). In NROCN, higher degree of exfoliation and enhanced compatibility, as a result of organic modification, with the NR matrix would result more interaction with the matrix. The stress generated at the interface between NR and organoclay is effectively transferred to the bulk NR

and hence resistance to crack initiation is improved in NROCN in comparison to NRCC. But in the case of NRCC, unmodified MMT clay dispersed in the matrix as stacks with micrometer thickness. These larger clay stacks have poor interaction with the NR matrix, leading to create stress concentrating points and as a result crack initiation start at a lower force, leading to poor tear strength in NRCC.

According to Figures 6 and 7, tensile and tear strength show a maximum value at 6 phr of organoclay loading, beyond above it reduces. At higher OC loading, degree of exfoliation is reduced, as shown in X-ray diffraction spectra in Figure 4, and therefore more intercalated clay morphology (*i.e.* larger clay stacks) within the nanocomposite material, resulting in overall reduced strength characteristics.



**Fig. 7.** Effect of clay loading on tear strength of NRCCs and NROCN



**Fig. 8.** SEM micrographs showing tensile fracture surface of (a). NRCC-6 (b). NROCN-6

Figure 8 (a) and (b) shows the SEM micrograph of tensile fracture surfaces of NRCCs and NROCN with 6 phr filler loading respectively. A significant decrease in voids and cavities in NROCN was observed compared to that of NRCC. Based on these results, it can be suggested that the rougher the

fracture surface with many curved tearing with minimal voids or cavities, the better the failure properties of the nanocomposites. Arroy *et al.* reported that smooth fracture surface usually indicates low compatibility accompanied with premature and rather brittle-type fracture (Arroy *et al.*, 2005).

Modulus at 300 % elongation at break, hardness and compression set of the studied rubber compounds are compiled in Table 3. Low reinforcing effect of un-modified MMT clay was evident with the mechanical properties of NRCC vulcanizates as shown in Table 3. A poor exfoliation and dispersion of un-modified MMT clay within NR matrix, because of limited compatibility, was expected and, but, a marked increase in mechanical properties was observed with the organoclay, as filler.

As shown in Table 3, improvement in hardness of NROCN vulcanizates further confirmed the significant reinforcing ability of OC in NR compounds. Addition of 6 phr

organoclay into NR (NROCN-6) increased by about 43% in comparison to NR-gum vulcanizate whereas no significant change in hardness with the addition of un-modified MMT clay. Improved hardness is achieved with a lower loading of OC because of the exfoliation of clay particles and subsequent uniform dispersion of clay platelets/smaller stacks within the NR matrix. In addition, higher crosslink density achieved due to OC is further contributed to improve the hardness. In contrast, lower hardness value for NRCCs vulcanizates clearly confirm the formation of conventional phase separated microscale composite, with a poor rubber–filler interactions.

**Table 3.** Mechanical properties of NROCN and NRCC vulcanizate

Composite code	Clay content (phr)	300% Modulus (MPa)	Elongation at break (%)	Hardness (IRHD)	Compression set (%)
NRCC	0	1.97	844	33.7	6.49
	2	1.45	791	29.7	5.91
	4	1.49	780	30.5	6.85
	6	2.08	755	30.9	5.45
	8	2.51	745	31.5	5.78
	10	2.45	745	30.8	6.37
NROCN	0	1.97	844	33.7	6.49
	2	2.59	758	44.9	6.77
	4	3.24	754	45.1	8.77
	6	3.93	735	48.2	12.21
	8	4.34	641	48.0	12.61
	10	5.50	596	49.2	13.66

More importantly, elasticity as measured with elongation at break, of NROCNs, especially with an OC loading less than 6 phr, was not sacrificed while improving the stiffness and strength of the NROCNs. As clearly illustrated in Table 3, elongation at break of 6 phr of OC filled NROCN is reduced from 844 % (EB of NR-gum vulcanizate) to 735 %, demonstrating a marginal reduction of elasticity of NROCNs with respect to NR-gum vulcanizate. However, on the other hand, without reinforcing, equivalent reduction of elasticity in NRCC prepared with unmodified MMT clay was observed, further indicating the significant advantage of using OC as a reinforcing material for NR compounds. It is important to note that the elastic characteristic, as deduced from the compression set measurements, of NR matrix hardly varies with the addition of the organoclay (Table 3), especially up to the addition of 6 phr of organoclay. These results clearly indicate that elasticity of NROCN vulcanizates was marginally affected with the addition of OC, especially with lower loadings.

### **Conclusion**

The effect of organoclay on curing characteristics and reinforcing effect of NR compounds were studied in comparison to equivalent un-modified MMT clay filled NR compounds.

Rheological studies in terms of vulcanization kinetics have shown that organoclay reduces the activation energy of the sulphur vulcanization

reaction and as a result significant reduction of processing safety as measured by on-set vulcanization time of the NROCN compounds. Enhanced crosslink density of the NROCN's indicated the improved compatibility between OC and the NR matrix.

X-ray diffraction data revealed that intercalated/exfoliated nanoclay structure is formed when OC is melt compounded with NR, especially with lower OC loading. However, with the increase of OC loading, intercalated OC structure with a higher number of clay platelets becomes dominant, leading to reduced degree of exfoliation. On the other hand, un-modified MMT clay has not shown any intercalation/exfoliation process during melt compounding process, resulting in phase separated conventional micro-composite.

A significant increase in tensile properties and hardness of the NROCN's vulcanizates relative to NR-gum and NRCC vulcanizates confirms the significant reinforcement effect of OC against un-modified MMT clay in NR compound formulations. In addition, stiffness and strength of the NROCN's vulcanizates were improved while maintaining a good elasticity, as measured by elongation at break and compression set, similar to the NR-gum vulcanizate.

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