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Morphology, Physical and Flame Retardant Properties of Epoxidised Natural Rubber (ENR) Organoclay Compound

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Epoxidised natural rubber (ENR) has good oil resistance and gas barrier properties. Despite a number of superior qualities, one of the drawbacks that limits usage of ENR is its inherent high flammability. Currently, much attention is focused on the use of layered silicates (clay), to produce materials with enhanced flame retardance and superior physical properties.Therefore, in this study, we investigate the effect of nanoclay on the flame behaviour and physical properties of ENR 50. Several tests including limiting oxygen index (LOI), underwriters laboratory (UL-94), tensile strength and morphology characterisation were performed on ENR samples containing three different types of clay. It was found that flame from ENR 50 filled with 10 p.p.h.r. for all types of clay tested could not self extinguish. According to the vertical burning test, UL-94, there is no classification or rating given to such materials. Similarly, the incorporation of clay in ENR did not enhance the LOI value. The improvement in physical and barrier properties of ENR containing C15A indicated that an exfoliated structure was formed in the rubber matrix as supported by the X-ray diffraction (XRD) and transmission electron microscopy (TEM) results.

Keywords: Flame retardant; ENR 50; organoclay; exfoliated

Legislation on fire safety requirements especially in USA and UK has been the driving force behind the use of halogen free flame retardants in recent years. Halogenated flame retardants such as bromine and chlorine containing polymers are believed to contribute to highly toxic dioxin emissions during incineration processes[1,2]. Therefore, efforts must be continued to search for alternative materials to replace halogenated flame retardants that are still widely used in various flame retardant applications.

The recent emergence of polymer nanocomposites offer promising developments in the area of flame retardance over conventional formulations. Polymer clay nanocomposites are hybrids composed of

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layered silicates (clay) dispersed in a polymer matrix in the form of reticular layers of crystals about 1 nm thick, with a lamellar aspect ratio between 100 and 1000. Due to its high aspect ratio and surface area, the inclusion of organically modified clay in a polymer matrix leads to enhancement in various properties, including stiffness, dimensional stability, barrier properties, thermal stability and flame retardancy[3]. Another advantage is the lower loading levels used (less than 10 wt%) to design flame retardant nanocomposites, reducing the use of highly toxic additives in traditional flame retardant formulations[1,3].

Incorporating nanoclay in an ENR compound is expected to exhibit an improvement in flame retardance and mechanical properties. Several authors[4-7] have studied mechanical properties of ENR related to nanoclay as reinforcement however the flame retardance properties were not fully investigated. Hence, the objective of this study is to assess nanoclay as a single FR additive in ENR compounds. Flame retardance of the nanocomposites was evaluated using LOI and UL-94 tests. In addition, the effect of different types of nanoclay on physical and barrier properties of ENR compounds was also evaluated. The structure of the nanocomposites was characterised by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

EXPERIMENTAL

Materials

The Malaysian Rubber Board supplied ENR under the trade name, ENR 50 with a 50% epoxidisation. The pristine clay used in this work is sodium montmorillonite (Na+MMT), while the commercial organoclays used were supplied under the trade name of Cloisite 15A (C15A) and Cloisite 30B (C30B). Other compounding ingredients such as sulphur and stearic acid were obtained from Centre West Chemicals Sdn. Bhd., N-t-butyl-2-benzothiazole sulphenamide (TBBS) and 2,2,4 – trimethyl-1,2-dihydroquinoline (TMQ) from Luxchem Trading Sdn. Bhd., calcium stearate was obtained from Galin Enterprise while zinc oxide was obtained from Prima Interchem Sdn. Bhd. All materials were used in the original supplied form.

Sample Preparation

ENR 50 nanocomposites were prepared by melt mixing in a Banbury internal mixer, BR 1600 (1.6L). The curatives were then added to the masterbatches using a two-roll mill at a roll temperature of 50°C.

Measurement of Cure Characteristics and Physical Testing

Cure characteristics of the rubber compounds were studied using a Monsanto moving die rheometer (MDR 2000) according to *ISO 6502* at 150°C. The respective cure times measured as t_{90}, scorch times t_2, maximum torque (MH), minimum torque (ML), *etc.* were determined from the rheograph. The compounds were then compression moulded at 150°C based on the respective cure times, t_{90}. Mooney viscosity of the compounds were determined at 100°C using a Monsanto Mooney viscometer (MV 2000) according to *ISO 289*.

Dumbbell shaped samples with a length of 95 mm were cut from a 2 mm thick moulded sheet. The tensile testing procedure was carried out according to *ISO 37*. An Instron universal testing machine (Model 4206) operating at 500 mm/min was used to determine tensile properties such as ultimate tensile strength and elongation at break. It should be noted that most tests were performed on ENR samples containing 5 p.p.h.r. of all types of clay tested, however specific tests such as flame retardance and air permeability were determined from ENR samples with 5 and 10 p.p.h.r. filler loading.

Air Permeability Test

Determination of air permeability to obtain permeability coefficient, Q was carried out at a constant volume according to the procedures specified in *ISO 2782*.

Characterisation

X-ray diffraction (XRD) experiments were performed directly on the samples using a Shimadzu X-ray Diffractometer XRD – 6100 (40kV - 40 mA) employing CuKα radiation (λ = 0.1542 nm) to evaluate the dispersion state oforganoclay in the ENR matrix. The samples were scanned at a low angle (from 2° to 10°) and scanning rate of 2° min^{-1}.

Ultrathin sections were prepared using acryo-ultramicrotome at -100°C and stained with osmium tetroxide vapour for one hour. The ultrastructure and distribution of the nanocomposites was then examined using a Philips CM12 transmission electron microscope (TEM).

Flame Retardance Test

LOI was measured using a fire testing technology instrument on moulded sheets ($100 \times 6.5 \times 3$ mm^3) according to the standard "oxygen index" test (*ISO 4589*). It measures the minimum concentration of oxygen in a nitrogen/oxygen mixture required to support combustion of a test sample under specified test conditions in a vertical position where the top of the test sample is ignited with a burner.

UL-94 classification was obtained on sheets ($127 \times 12.7 \times 3.0$ mm^3) according to the conditions of the standard test (*ASTM D 3801*) in a vertical position where the bottom of the sample is ignited with a burner. This test provides a qualitative classification of the flame resistant samples labeled as V0, V1 and V2.

RESULTS AND DISCUSSION

Cure Characteristics

Cure characteristics of ENR filled with different types of clay at 5 p.p.h.r. loadings are summarised in *Table 1*. From the results, it can be seen that ENR filled with modified clays (C30B and C15A) exhibited shorter cure and scorch times compared to the control compound. Similar results have been reported by other authors with different host matrices[4,5,7–9]. The trend observed was probably attributed to the ammonium group of the organic cations from the organoclay.

TABLE 1. CURE CHARACTERISTICS OF ENR FILLED WITH DIFFERENT TYPES OF NANOCLAY

Formulations	t_2 (min)	t_{90} (min)	ML (dNM)	MH (dNM)	△torque, (MH-ML), dNM	Viscosity, ML(1+4) at 100°C
ENR	2.7	5.2	0.7	6.0	5.3	57
ENR/Na+MMT-5	2.8	5.6	0.8	6.6	5.8	57
ENR/C30B-5	2.0	5.0	0.8	6.6	5.8	60
ENR/C15A-5	1.5	4.9	0.8	7.2	6.4	53

The viscosity of ENR filled with 5 p.p.h.r. C15A decreases slightly in comparison to other types of nanoclay. This is probably due to better orientation and dispersion of the exfoliated clay layers which will be discussed further in this paper.

Effect of Different Types of Clay on Flame Behaviour of ENR Compounds

The effect of different types of nanoclay on flame retardance of ENR was characterised by the LOI and UL-94 vertical test. Although the LOI test cannot reflect the actual combustion situation of a material in fire, it is a reproducible test to give a primary and relative comparison of the flammability of materials. Hence, it is used to evaluate flame retardance of rubber based nanocomposites in this work. There was no enhancement in the LOI values (<19%) with the incorporation of nanoclay compared with the control at different loadings (5 and 10 p.p.h.r.). Furthermore, the flame from ENR 50 filled with 10 p.h.r. of all types of clay tested did not extinguish until the entire polymer component was burnt. According to the vertical burning test, UL-94, there was no classification or rating given to all the compounds tested.

It has been reported[10] that during the burning process, incorporation of organoclay in polymer matrix promotes formation of a structured char that insulates the surrounding polymer from decomposition. In this work, it is revealed that nanoclay alone is not sufficient to improve flame retardancy of the ENR compound. At some stage of the LOI test, when the sample absorbs more heat, the char layer was physically broken and burning continues. This implies that a strong coherent char layer was not formed in ENR nanocomposites.

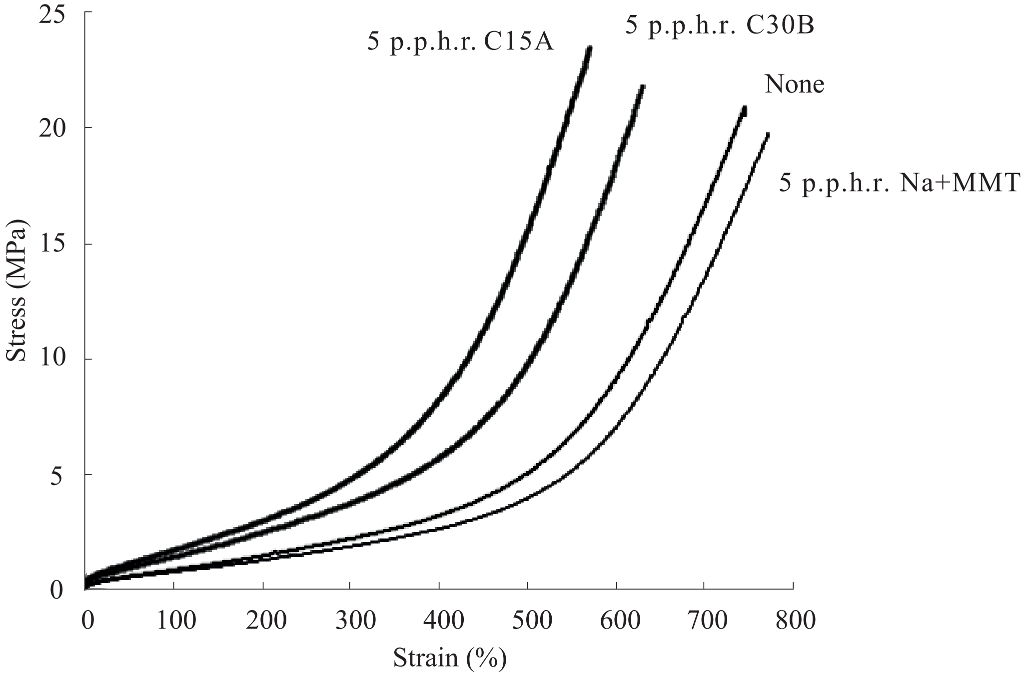


Figure 1. Stress-strain curves for ENR with different types of nanoclay

Physical Properties

Figure 1 shows the stress-strain curves for ENR with various types of nanoclays at a 5 p.p.h.r. loading. The ENR filled with 5 p.h.r. of C15A shows an enhancement in the tensile strength and inverse trend for the elongation at break compared with corresponding pure ENR. This can probably be attributed to its exfoliated structure as observed in the TEM micrograph (*Figure 5*).

The hardness values of all compounds are shown in *Figure 2*. The hardness of rubber compounds generally increases with the addition of reinforcing fillers (carbon black and silica)[9]. In this work, the addition of organo-modified clay slightly increases the hardness of the ENR nanocomposites with ENR containing 5 p.p.h.r. of C15A having the highest value. The increase in hardness is likely due to higher crosslink density in the matrix. This is in agreement with the earlier results for delta torque, (MH-ML) as a higher delta torque normally indicates higher crosslink density.

X-ray Characterisation and TEM Analysis of the Clay-rubber Composites

The most important phase in the preparation of a nanocomposite is the delamination of the layered silicates, which is commonly referred to as exfoliation. A number of studies[8,10-13] have shown that an outstanding performance of the polymeric nanocomposites can be achieved when the clay nanolayers are uniformly dispersed or exfoliated in the polymer matrix, as opposed to being aggregated or phase separated as tactoids or simply intercalated.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques were performed on ENR composites to study the degree of filler dispersion. The XRD

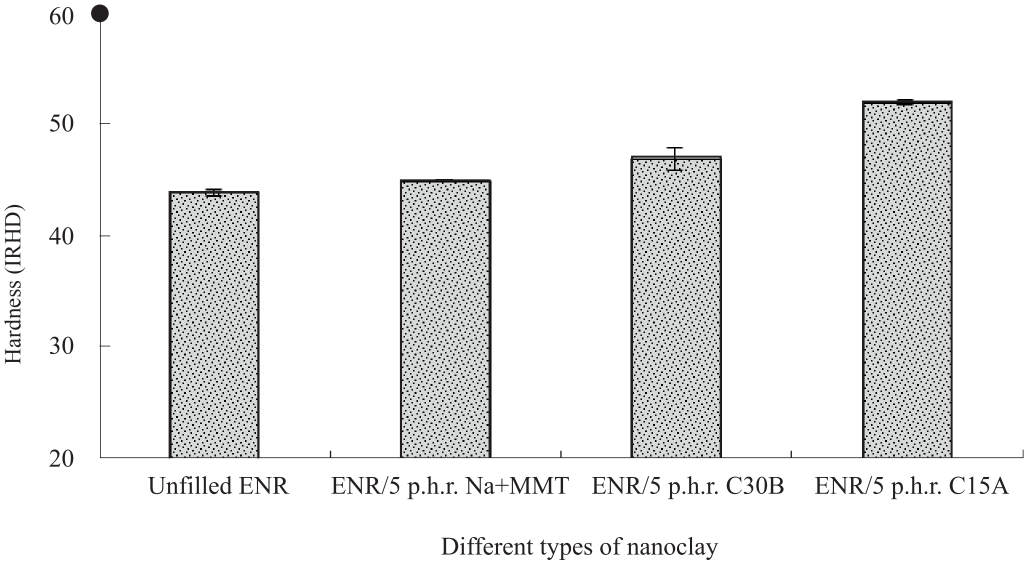


Figure 2. Effect of different types of nanoclay on hardness of ENR

spectra of ENR composites filled with C15A, C30B and Na+MMT and corresponding neat clays are shown in *Figures 3* and *4*. The interlayer spacing, known as d-spacing of the organoclay, is derived from the peak position (d_{001}-reflection) in the XRD diffractograms.

Figure 3 shows that the main peak of C15A at 2θ = 2.58° has disappeared in the ENR/C15A compound, indicating that the exfoliated structure is obtained in the ENR matrix. In contrast, the d001 peak of C30B (2θ = 4.7°, d =1.88 nm) in the ENR/C30B compound has shifted towards higher angles 2θ = 5.2°, corresponding to an interlayer spacing of 1.76 nm. A similar diffraction pattern is also found for the ENR/Na+MMT compound as presented in *Figure 4*. The main peak of NA+MMT (2θ = 5.74, 1.54 nm) in the ENR/Na+MMT has shifted towards higher angles at 2θ = 6.24°, corresponding to an interlayer spacing of 1.42 nm. Thus, a reduction of the interlayer spacing from 1.88 nm to 1.76 nm and 1.54 nm to 1.42 nm, respectively, for ENR/C30B and ENR/Na+MMT was observed from their XRD spectra. These results suggest that both C30B and Na+MMT clays tend to reagglomerate in the ENR compound.

TEM analysis indicated a homogenous morphology yielding a finer dispersed phase and uniform distribution of clay in the ENR matrix containing 5 p.h.r. of C15A as shown in *Figure 5(a)*. Furthermore, exfoliated clay can be seen clearly as thin dark lines, which indicate a single clay layer. On the other hand, TEM images demonstrated thick dark lines or multilayer bundles (silicate layers) both in ENR/C30B an ENR/Na+MMT compounds, which suggest an actoid structure or commonly known as agglomerated structure (*Figures 5 (b) and (c)*). All TEM observations are in good agreement with the XRD analysis.

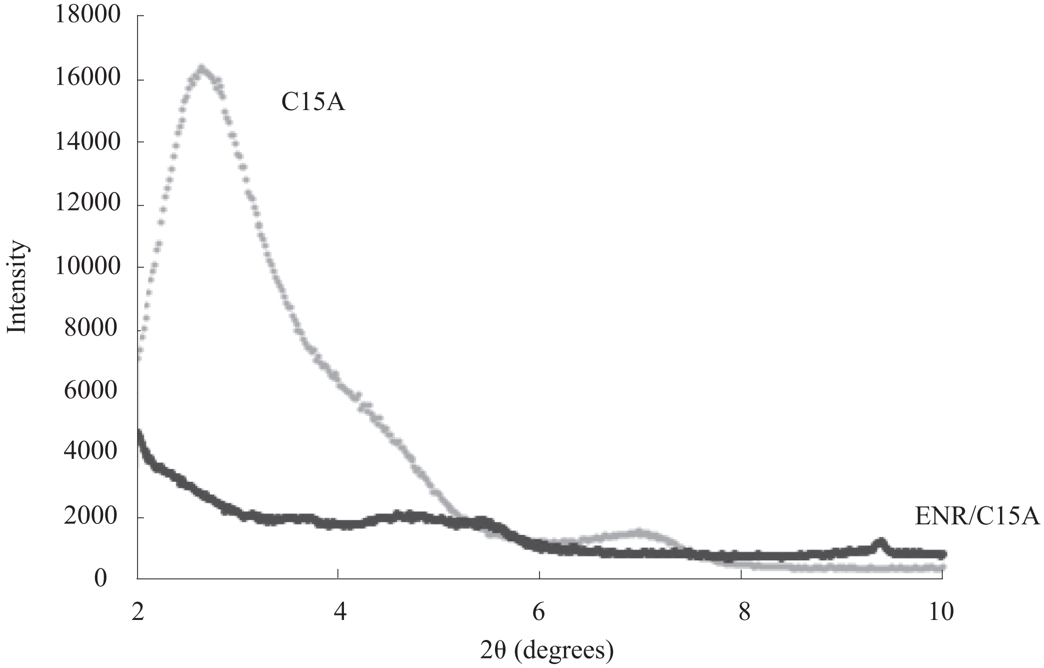


Figure 3. XRD patterns for organoclay filled (5 p.p.h.r. C15A) ENR nanocomposites.

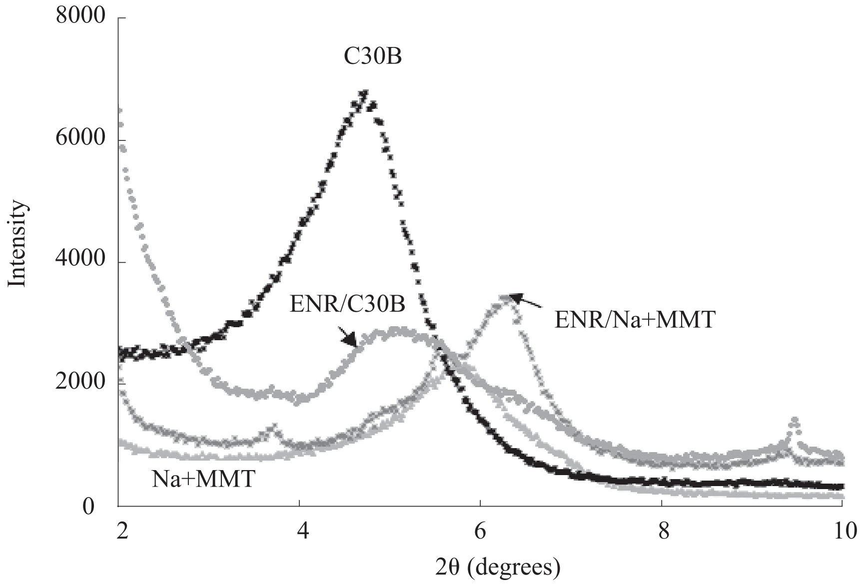
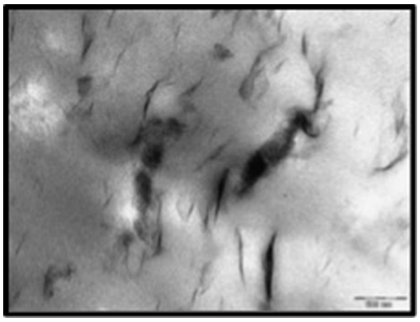
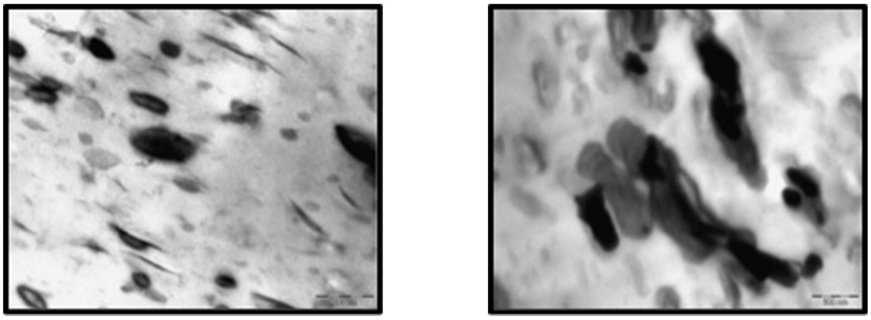


Figure 4. XRD patterns for organoclay filled (5 p.p.h.r. Na+MMT and 5 p.p.h.r. C30B) ENR nanocomposites.



a) 5 p.p.h.r. of C15A



(b) 5 p.p.h.r. of C30B

(c) 5 p.p.h.r. of Na+MMT

Figure 5. TEM micrographs of ENR/organoclay nanocomposites

Effect of Different Types of Clay on Barrier Properties of ENR

Several factors contributed to the improvement in barrier properties of nano-composites such as filler orientation, interfacial interactions between filler and the host matrix as well as distribution of the silicate layers in the polymer matrices. However, the main factor behind the improvement of barrier properties is not fully understood yet[14].

The air permeability of ENR compounds with different types of nanoclay is given in *Figure 6*. A decrease of 19%, 32%, 47% was observed at 5 p.p.h.r. loading of the Na+MMT clay, C30B and C15A organoclay respectively, whereas a much higher decrease in air permeation was observed at 10 p.p.h.r. of all types of clay tested. It is assumed that lower interlayer spacing in C30B and Na+MMT as compared to C15A is the main reason for the differences in their barrier performances, which is confirmed by the XRD analysis. Hence, in ENR/C15A, ENR molecules can easily enter into the gallery space to break the layer structure, resulting in exfoliated orientation within the matrix as shown by the TEM observation (*Figure 5(a)*).

CONCLUSION

Results of the UL-94 and LOI tests indicated that the incorporation of clay (Na+MMT, C30B and C15A) at 5 and 10 p.p.h.r. loadings as single additives did not portray any significant improvement of flame retardance behavior in ENR compounds. In view of the disadvantages, it is evident that clay fillers should be combined with conventional flame retardants, in order to develop synergistic systems.

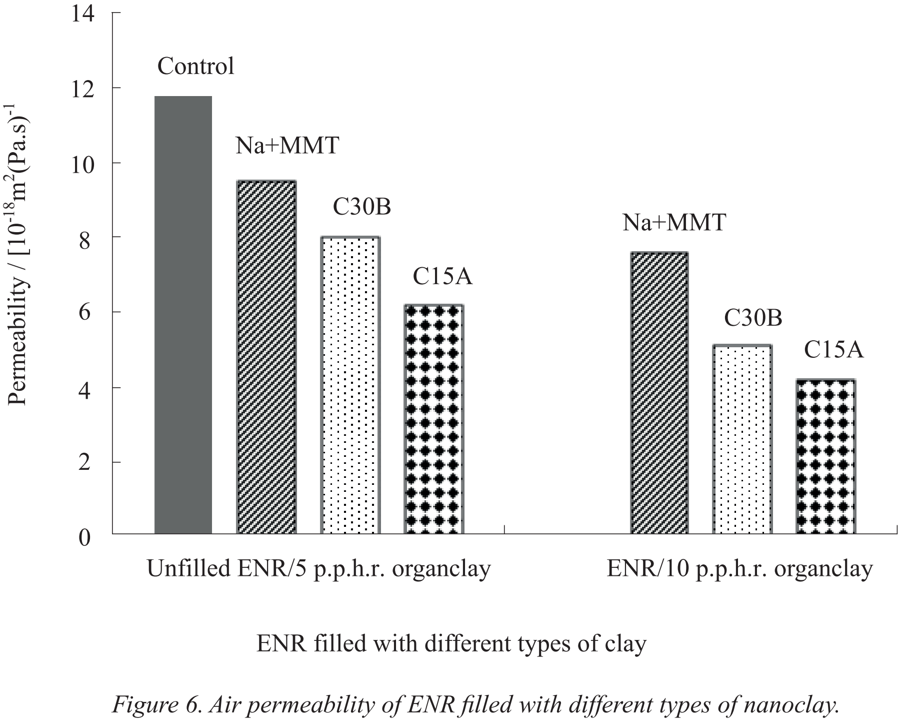


Figure 6. Air permeability of ENR filled with different types of nanoclay.

Improvement in barrier properties is observed with the addition of clay in ENR compounds. A sufficient nanoscopic dispersion of clay was achieved in particular for C15A resulting in 47% reduction of the air permeability compared to the control compound. The enhancement in physical and barrier properties were evidently influenced by the dispersion of silicate layers in ENR compounds as determined by XRD measurements and TEM micrographs.

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