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Value-added Natural Rubber Skim Latex Concentrate/Montmorillonite as Environmentally-friendly Nanocomposite Materials

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Skim latex concentrate (SLC) is being evaluated as a new value-added raw material to produce wet masterbatch with nano dispersed layered clay or montmorillonite (MMT). Raw skim latex (SL) is a by product obtained during the centrifugation process to concentrate field latex into latex concentrate (LC). Skim latex is subsequently concentrated to SLC by the environmentally-friendly ultrafiltration membrane separation method. The aim of this study is to utilise the uniqueness of SLC based on its uniform and narrow particle size distribution and higher protein content compared to the centrifuged latex concentrate. Increase of vulcanisation rates of the nanocomposite was observed when control material, namely centrifuged LC, was replaced with skim latex concentrate. In addition, both the maximum torque and delta torque were raised with increasing filler contents up to 10 p.h.r. The vulcanised properties such as tensile strength, modulus, tear strength, hardness and compression set were also found to have improved. Furthermore, there was a reduction of 18% to 29% in air permeability for rubber clay nanocomposites prepared from SLC compared to the neat NR skim rubber. It is believed that the improvement in mechanical and barrier properties observed is partly related to the homogeneous dispersion of the layered clay within the smaller and more uniform latex particles in the NRSLC as examined by microscopy techniques.

Keywords: NR/clay; wet masterbatch; nanocomposite; NR skim latex concentrate; centrifuged latex concentrate

The development of polymer/clay nanocomposites has gained a lot of interest in the last 20 years. Nevertheless, in recent years, studies on NR/clay nanocomposites have been widely researched by polymer scientists. The main reasons for adding clay fillers to rubber are to enhance mechanical properties and also to make the final product less expensive. In this study, the term clay is a general name for layered silicate minerals which specifically refers to montmorillonite (MMT).

Layered silicates or MMT are comprised of silicate layers having a planar structure of 1 nm thickness and up to 500 nm length. The ability of layered silicates to separate into individual layers with a very high aspect ratio and to undergo ion exchange reactions with

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inorganic or organic cations are of general concerns in making rubber-organoclay nanocomposites. However, the most important phase in the preparation of a nanocomposite is the delamination of the layered silicates, which is commonly termed as exfoliation. A number of studies[1–6] has shown that an outstanding performance of the polymeric nanocomposites can be achieved when the exfoliated structure dispersed in the polymer matrix. This is because exfoliated clay at the nano level possesses a large aspect ratio that could increase the interaction with the host polymer and consequently, enhance the mechanical properties of the polymer composites[1–6].

Generally, the methods for preparing rubber/clay nanocomposites are co-coagulation[1,2], melt intercalation[3,4], *in-situ* polymerisation[5] and also latex compounding[6]. *In-situ* polymerisation and melt intercalation are processes in which organoclay must be employed while the others require only pristine clay. Here, the focus was given to the rubber/clay nanocomposites prepared from wet masterbatch method in order to improve the degree of clay dispersion within the rubber matrix. NR latex is a macroscopic dispersion of rubber particles in an aqueous medium. On top of that, some layered silicates are suitable additives for latex, provided that in aqueous dispersions, the clay tends to 'swell' (*i.e.* its layers are separated by hydration), thus making a good dispersion in the rubber possible.

In this study, an attempt was made to produce rubber/clay nanocomposites *via* wet masterbatch method using NR skim latex concentrate (NRSLC) as a raw material. NR skim latex (NRSL) is a by-product obtained during the centrifugation process to concentrate field latex into latex concentrate. The skim latex is subsequently concentrated to NRSLC by ultrafiltration membrane separation process (*Figure 1*)[7]. The mixture between clay slurry and NRSLC is called MBSLC/MMT masterbatch. In this process, the masterbatch was treated as solid rubber to produce vulcanised NR/MMT nanocomposites. The vulcanised properties of MBSLC/MMT nanocomposites were compared with the nanocomposites prepared from centrifuged latex LC as a control. The aim of this investigation is to utilise the uniqueness of skim latex concentrate (SLC) of its uniform and narrow particle size distribution and higher protein content to enhance the physical properties of its masterbatch compared to that of LC masterbatch. The smaller, uniform particle sizes[8] and the presence of protein are known to play a crucial role in inducing strength to the rubber-based nanocomposites[9].

MATERIALS AND METHODS

Materials

The materials used to prepare natural rubber latex masterbatch are presented in *Table 1*. Raw skim latex is produced as a by product during the centrifugation process to concentrate field latex into LC, which is an industrial raw material for manufacturing latex dipped goods. During centrifugation, smaller latex particles (large molecular mass coiled into smaller particles) together with non-rubbers (protein, sugar and minerals) which form the denser portion, are separated from larger rubber particles but have lower density. Ultrafiltration (UF) membrane separation process can be used to separate latex free serum from raw skim latex while increasing the dry rubber content (DRC) from *ca*. 5% to *ca*. 30% (*Figure 1*). This is a cleaner processing option for raw skim latex compared to the acid coagulation method and could yield two new raw materials. The two new raw materials are skim serum and skim latex concentrate. Sugar and protein could be extracted from the skim serum while discharging clean water as the final product[8]. Analysis has been carried out

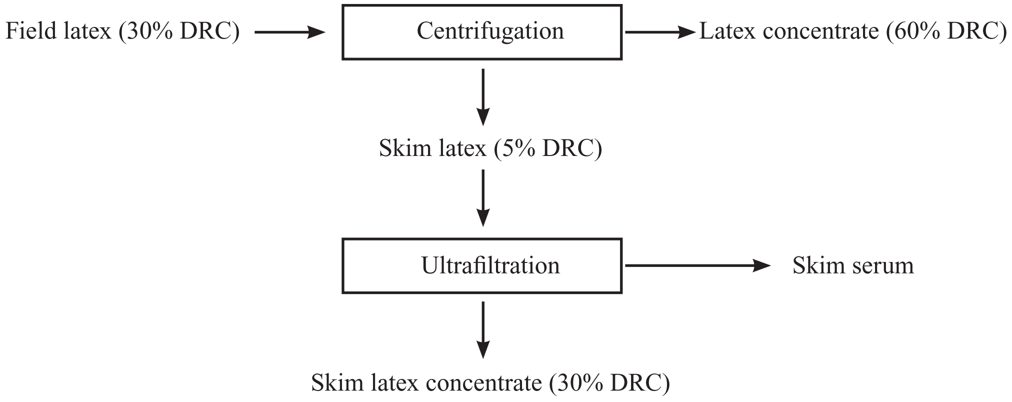


Figure 1. The process of producing NR skim latex concentrate.

TABLE 1. MATERIALS FOR NATURAL RUBBER LATEX MASTERBATCH

Materials	Concentration %	Supplier
Centrifuged LC	DRC 30% (diluted from 60%)	Malaysian Rubber Board
Skim latex	DRC 30%	Malaysian Rubber Board
Clay (Montmorillonite)	(cation exchange capacity = 92 mquiv/100g of clay).	Linfangzi Clay Factory, Jilin, China
Formic Acid	10%	System

using Zeta Plus particle sizing to determine latex particle size. Particle size of latex is presented in *Table 2*.

Preparation of NR/Clay Masterbatch

Clay was dispersed in water by vigorous stirring (500 r.p.m.). The slurry was left to mature for 48 h and particle size analysis was carried out using particle size analyser (Shimadzu). The clay particle size distribution is demonstrated in *Table 3*. The swollen clay was then mixed with latex and the mixture was stirred for 2 h, followed by an addition of formic acid as the coagulant. The coagulum formed was washed well with water. The composition of the wet masterbatch is described in *Table 4*. Finally, the dried mixture obtained which was termed as NR/Clay masterbatch, was dried in an oven at 70ºC for 24 h. The NR/Clay masterbatch was then treated as solid rubber, subsequently compounded and vulcanised with a standard cure system.

Compounding

The NR/Clay nanocomposites of compositions shown in *Table 5* were compounded on a two-roll mill with roll temperature of about 50°C. In this study, the semi-EV cure system was used to carry out the comparative study.

Determination of Cure Characteristics

Compound cure characteristics were analysed using a MDR 2000 at a temperature

TABLE 2. RUBBER LATEX PARTICLE SIZE ANALYSIS

Types of latex	Effective diameter (nm)	Mean diameter (nm)
Latex centrifuge 30% DRC	444	743
Raw skim latex 5% DRC	200	240
Skim latex concentrate 30% DRC	193	208

TABLE 3. PARTICLE SIZE DISTRIBURTION AFTER 48 HOURS

Time (h)	Particle size (µm)			
	Mean	25%	50%	75%
18	4.659	2.039	4.360	9.508
24	5.318	2.156	4.794	11.361
42	4.163	2.069	4.219	8.533
48	3.792	1.970	3.919	7.665

TABLE 4. THE COMPOSITION OF NATURAL LATEX MASTERBATCH

Ingredients	Dry (parts by weight(g))	Wet (parts by weight (g))
5% Clay slurry (weight based on parts per hundred rubber)	25, 50	500, 1000
Latex (30% DRC)	500	1670
SDS 10%	10	100

TABLE 5. RUBBER COMPOUND FORMULATIONS

Formulation	p.h.r.			
MBLC-MMT	105	110	0	0
MBSL-MMT	0	0	105	110
ZnO	5	5	5	5
Stearic Acid	2	2	2	2
Permanax TMQ	2	2	2	2
Sulphur	1.5	1.5	1.5	1.5
TBBS	1.5	1.5	1.5	1.5

of 150ºC for 40 min and a frequency of 1.66 Hz. The characteristics of cure consist of time to optimum cure (T_{95}) and state of cure (M_H-M_L). The scorch time, t_2 of the mixes were also examined. The compounds were pressed using hot press and cut into standard shapes.

Mechanical Properties and Crosslink Density

Tensile properties were measured according to *ISO 37* specifications on an INSTRON at a crosshead speed of 500 mm/min. Tear strength was determined according to *ISO 34* with a crosshead speed of 100 mm/min. Measurements of hardness were carried out according to *ISO 48* while the compression set was measured following the recommendation of *ISO 815* for 24/70ºC. Measurements of air permeability to determine permeability coefficient Q, were carried out at constant volume according to the procedures specified in *ISO 2782*. The crosslink density results were determined on the basis of solvent-swelling measurements at room temperature by application of the Flory-Rehner equation[9].

$$(2M_c)^{-1} = \frac{\ln(1\text{-}v) - v - xv^2}{2_p V_0 \; v^{1/3}} \qquad \ldots 1$$

$(2M_c)^{-1}$ = degree of crosslinkings
x = rubber – solvent interaction parameter
(0.39 @ 25°C)
V_0 = molar volume of the solvent (105.75)
V = volume fraction

The volume fraction of polymer V, was calculated by the next *Equation 2*[10]: where W_1 and W_2 are the weights of the vulcanisate after deswelling and weight of the vulcanisates in the swollen state respectively, and *p* and p_S are the densities of the solvent (0.87 g/cm^{-3}) and the rubber (0.92 g/cm^{-3}), respectively.

$$V = \frac{W_2}{W_2 + p/p_S\,(W_1 - W_2)} \qquad \ldots 2$$

Microscopy Analyses

Cryogenic fracture surfaces were prepared for observing filler dispersion. The specimens were sputter coated with Au (gold) and investigated under a JEOL, field emission electron microscopy (FESEM) at low accelerating voltage 2 KV. The detailed investigation of clay dispersion state was observed by a transmission electron microscopy (TEM). Ultra-thin sections were prepared by cryo-ultramicrotomy at –110ºC using glass knives. Sections were collected on a copper grid and examined with a Philips TEM at low and high magnifications.

RESULTS AND DISCUSSIONS

Cure Characteristics and Crosslink Density

The vulcanisation curves of the nanocomposites studied are graphically represented in *Figure 2*, as obtained from the MDR 2000 measurements. The curing characteristics, expressed in terms of the vulcanisation times, scorch time (t_{S2}) and optimum cure time (t_{95}), as well as the maximum and minimum values of torque, M_H and M_L, respectively, and delta torque (M_H-M_L) deduced from the curves are compiled in *Table 6*. It can be seen that the torque maximum was found to increase with increasing proportion of filler content but no significant effect was observed on the minimum. The torque maximum is correlated with durometer modulus and hardness. Thus, this result proposes that the incorporation of clay will increase the stiffness of the nanocomposites. A similar trend was observed for a torque difference (M_H-M_L). The torque difference increased proportionally with clay content, which indicates the extent of crosslinking and rubber-filler interaction of the nanocomposite. This observation is supported by a chemical crosslink density measurement as shown in *Figure 3*. It was found that MBSLC/MMT containing 10 p.h.r. clay exhibited higher crosslink density than MBSLC/MMT filled with 5 p.h.r. clay.

Relatively, the nanocomposites prepared from MBSLC exhibited different cure characteristics as compared to that of MBLC/MMT nanocomposites even at equal amounts of filler loadings. MBSLC/MMT nanocomposites present shorter cure time and scorch time than MBLC/MMT nanocomposites. It is deduced

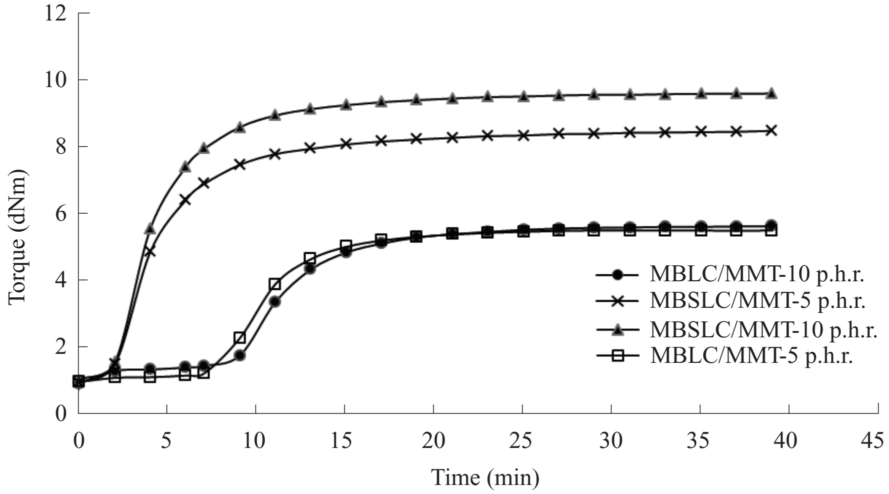


Figure 2. Rheometer curves of the NR/MMT nanocomposites.

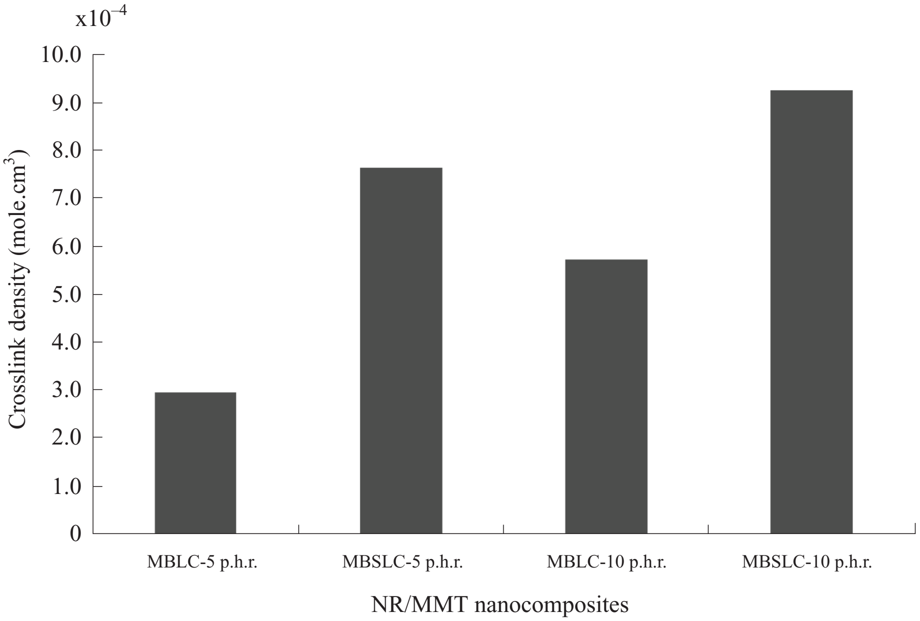


Figure 3. Crosslink density of NR/MMT nanocomposites.

that the lower cure time which relates to the increase of vulcanisation rate in the MBSLC/MMT could be due to the presence of high content of non-rubbers such as proteins and sugars in SLC which is known to improve cure characteristics. It has been reported that with the addition of NR serum paste (NRSP), which had high protein content and the presence of other non-rubbers such as sugars, when added in various proportions into the formulation significantly improved cure rate of the compounded natural rubber[11]. Furthermore, from a rubber processing point of view, the reduction in scorch time suggesting that a tendency of MBSLC/MMT to get scorched is higher as compared to the MBLC/MMT compound. However, this potential drawback can be counteracted by including a pre-vulcanisation inhibitor (PVI). On the other hand, both the maximum torque and delta torque of MBSLC/MMT nanocomposites are higher than those prepared from MBLC, which suggests a higher compatibility at the filler/elastomer interface. It is interesting to note, that these trends observed were partly attributed to that of homogenous dispersion during mixing of clay into the NRSLC. This could be due to NRSLC having smaller and more uniform particle sizes as compared to the centrifuged latex LC.

Mechanical Properties

The use of layered silicates in rubber has shown greater improvement in mechanical properties[1–6]. There are several factors that influence the mechanical properties of polymer/nanocomposites such as interaction between the clay and polymer matrix as well as the degree of clay dispersion in the matrix. According to Zhang *et al.*[13], for latex compounding method, the factors affecting the final dispersion level of clay in rubber nanocomposites mainly include size of rubber latex particles, amount of latex and speed of co-coagulating rubber latex and clay layers. All the factors mentioned above will provide nanocomposites with fewer non-exfoliated layer aggregates and even a complete exfoliated structure of layered silicates[13].

Mechanical properties of NR/MMT nanocomposites are listed in *Table 7*. It is observed that the nanocomposites prepared from MBSLC exhibited higher tensile strength as compared to those prepared from MBLC, irrespective of the filler loadings. A similar trend can also be seen for tear strength. The improvement of the tensile and tear strength is probably due to high gum strength of rubber hydrocarbons recovered from NRSLC. This is due to the nature of the skim rubber that possesses high molecular weight. It has also been suggested in previous reports[14] that higher molecular weights were associated with smaller rubber particles. This is in line with the observation made by another researcher[15] whereby the skim latex has smaller and narrow particle size distribution when compared with centrifuged latex concentrate. Furthermore, as mentioned earlier, the narrow particle size distribution of NRSLC is suggested to be one of the factors that influence the final dispersion of the clay[13] leading to a homogenous dispersion of MMT in rubber matrix that consequently enhanced the strength of the composites. However, a decrease in elongation at break is observed for nanocomposites prepared from MBSLC as compared to those prepared from MBLC. This fact can be attributed by the increase of crosslink density in the nanocomposites.

Tensile modulus is a measure of stiffness for rubber vulcanisates. From the results obtained, the M100 and M300 of MBSLC/MMT nanocomposites at both filler loadings show noticeable increases compared to the control. It can be suggested that more reinforcing effect of clay layers in NR can be seen in MBSLC/MMT nanocomposites. It is believed that the nature of NRSLC has enhanced the interaction between the clay

TABLE 6. CURE CHARACTERISTICS OF THE NR/MMT NANOCOMPOSITES

Cure characteristics	Types of Natural Rubber Masterbatch			
	MBLC-5 p.h.r.	MBSLC-5 p.h.r.	MBLC-10 p.h.r.	MBSLC-10 p.h.r.
Maximum torque (M_H) dNm	5.49	8.48	5.62	9.61
Minimum torque (M_L) dNm	0.95	0.93	0.91	1.03
Delta torque (M_H-M_L) dNm	4.54	7.55	4.71	8.58
Cure time (t_{95}) (Min)	18.2	15.69	21.1	13.87
Scorch Time (t_{S2}) (Min)	9.7	2.67	10.5	2.58

TABLE 7. MECHANICAL PROPERTIES OF NR/MMT NANOCOMPOSITES

Properties	Compound			
	MBLC-5 p.h.r.	MBSLC-5 p.h.r.	MBLC-10 p.h.r.	MBSLC-10 p.h.r.
Tensile strength (MPa)	21.0	25.3	22.0	24.4
M100 (MPa)	0.84	1.92	0.80	2.12
M300 (MPa)	1.58	4.55	2.61	5.53
Elongation at break (%)	720	601	707	583
Tear strength (N/mm)	25	35	15	36
Hardness (IRHD)	40	61	41	64
Compression set % (22h/70ºC)	23	38	27	39

layers and the NR macromolecular chains during the masterbatch preparation stage. In addition, the increase of tensile modulus is proportional with the clay content in MBSLC/MMT nanocomposites. The improvement of the modulus at higher filler loadings is probably due to the extent of crosslink density and rubber-filler interaction as discussed in the previous section. Moreover, hardness and compression set measurements are in agreement with the tensile and tear strength. The increase in hardness is related to a higher strength of the composite. On the other hand, the increment in hardness of MBSLC/MMT nanocomposites can also be attributed to a reduction of elastic behaviour as suggested by the higher compression set values obtained.

Air Permeability

Reducing gas permeation rates are important features of polymer/clay nanocomposites. Based on the results described in *Figure 4*, the nanocomposites prepared from MBSLC containing 5 and 10 p.h.r. clay had clear decreases of air permeability. The values of permeability reduction were found to be as much as 18% and 29% respectively compared to the neat NRSLC compound. However, the nanocomposites prepared from MBLC filled with 5 and 10 p.h.r. clay presented only 0.03% and 1.3% reduction of air permeability respectively compared to the pure NRLC. The improvement of air barrier properties of the MBSLC /MMT nanocomposite could be due to a homogenous dispersion of layered silicates within smaller particle sizes in NRSLC that probably form a tighter structure in the composite. The barrier mechanism of clay layers has been discussed in detail in the previous report by Peiyao Li *et al*.[16]. It was assumed that the practical movement of the molecules to enter or pass through the material was prolonged due to the existence of nanodispersed clay layers, which would have reduced the number of molecules that passed through. This is because the nanodispersed layers has formed a "barrier" to improve the barrier properties of the materials.

Scanning Electron Microscopy (SEM)

Figures 5(a) to *(d)* show the SEM micrographs of MBLC/MMT and MBSLC/MMT nanocomposites at low magnification (2,500 X). As seen from the fracture surface images, MBSLC/MMT nanocomposites exhibit relatively homogenous morphology with finer and uniform dispersion of clay as compared to the MBLC/MMT nanocomposites at both filler loadings studied. In addition, measurement of particle size from SEM images at high magnification (10 000X) in *Figures 6(a)* and *(b)* show that the average size of clay particles dispersed in MBSLC/MMT and MBLC/MMT nanocomposites were around 0.337µm and 0.402µm respectively. Furthermore, no significant agglomerates were observed on the examined surfaces. These results suggest that more homogeneous clay dispersion with smaller particle size is obtained in MBSLC/MMT nanocomposites as compared to MBLC/MMT. This explains why nanocomposites prepared from NRSLC exhibit better mechanical and barrier properties than the control.

Transmission Electron Microscopy (TEM)

To observe the dispersion of nanoscale clay in the NR matrix, the TEM observation of MBSLC/MMT containing 5 p.h.r. clay in

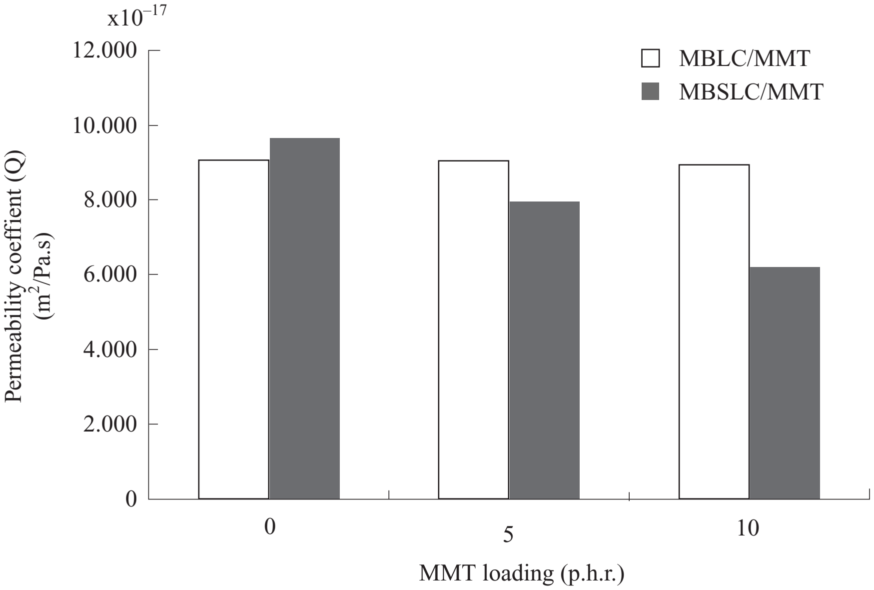
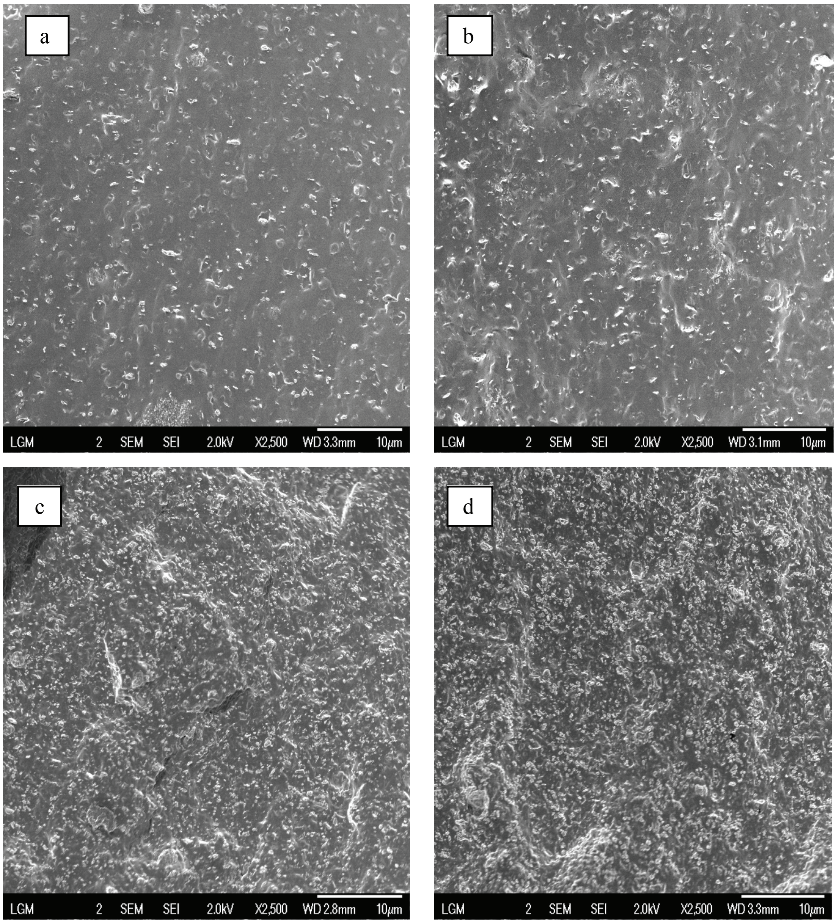


Figure 4. Air permeability of NR/MMT nanocomposites.



Figures 5(a) to (d): Fracture surface of NR/Clay nanocomposites at low magnification (2500X) (a) MBLC/MMT–5 p.h.r., (b) MBLC/MMT-10 p.h.r., (c) MBSLC/MMT-5p.h.r. and (d) MBSLC/MMT 10 p.h.r.

Figures 7(a) and *(b)* had been screened at high and low magnifications respectively. In the images, the light colored area was NR matrix and the dark lines were the single layers. The detailed structure of MBSLC/MMT nanocomposites as presented in *Figure 7(a)* was observed under high magnification with a 200 nm scale bar. The TEM micrograph clearly shows the single layers tended to split apart to form an exfoliated structure in the matrix. However, to study the clay dispersion in a large range, the TEM micrograph was taken at a low magnification with a 500 nm scale bar. From the observation of the TEM image in *Figure 7b*, the degree of exfoliation seems to be quite small, though several small individual linear streaks of exfoliated clay can be observed. Furthermore, some of the clay showed a partly exfoliated and aggregated structure. In addition, clay particles are very beam sensitive in the heat of the electron beam. Thus, this produces the white streaks between some of the clay layers which can be noticed in the images. This result suggests that the NR/Clay

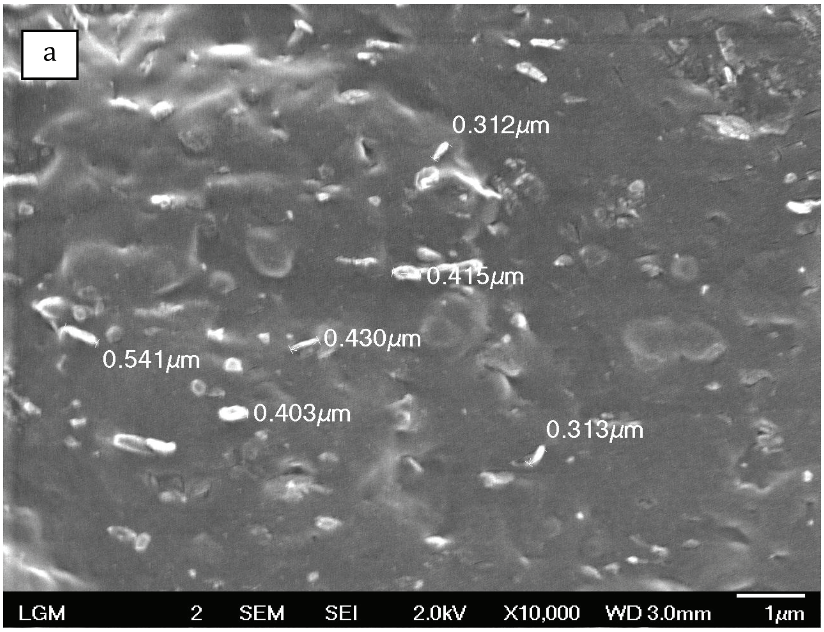


Figure 6(a). Fracture surface of MBLC/MMT (5 p.h.r.) nanocomposite at high magnification (10, 000X).

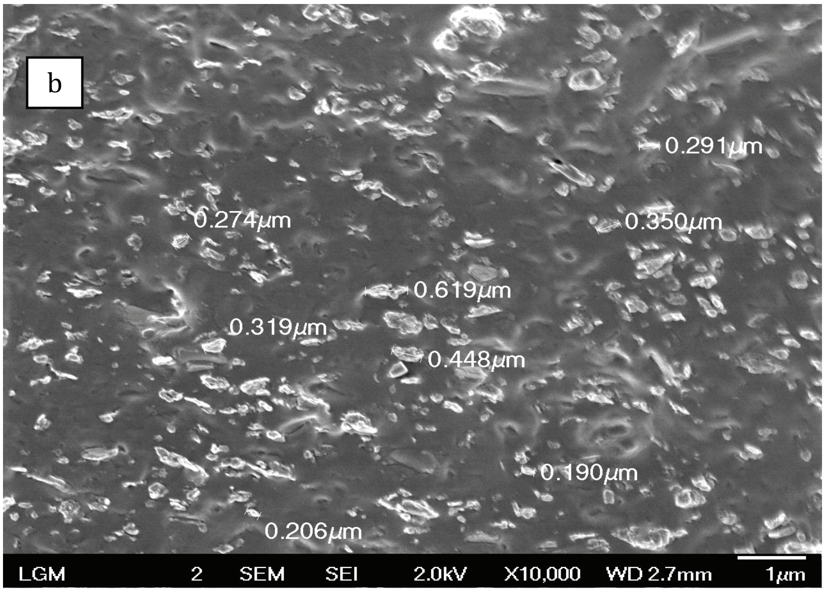


Figure 6(b). Fracture surface of MBSLC/MMT (5 p.h.r.) nanocomposite at high magnification (10,000X).

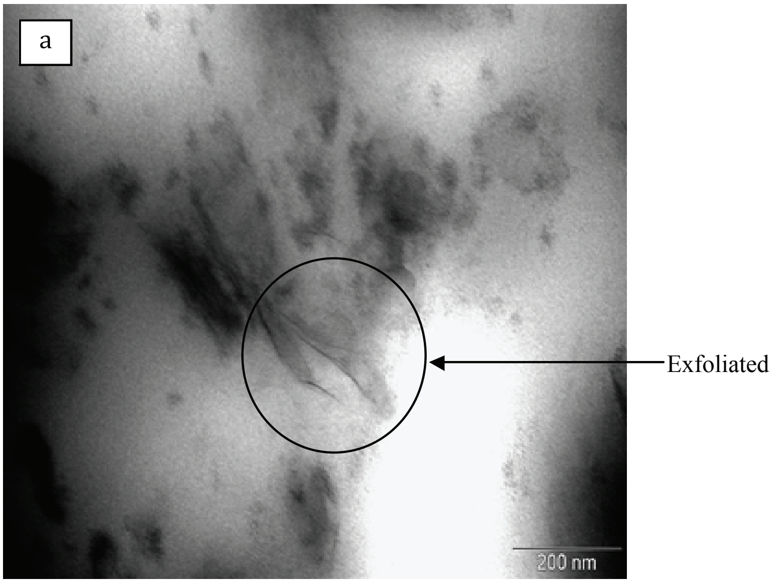


Figure 7(a). TEM micrograph of MBSLC/MMT (5 p.h.r.) nanocomposite at a high magnification (88, 000X).

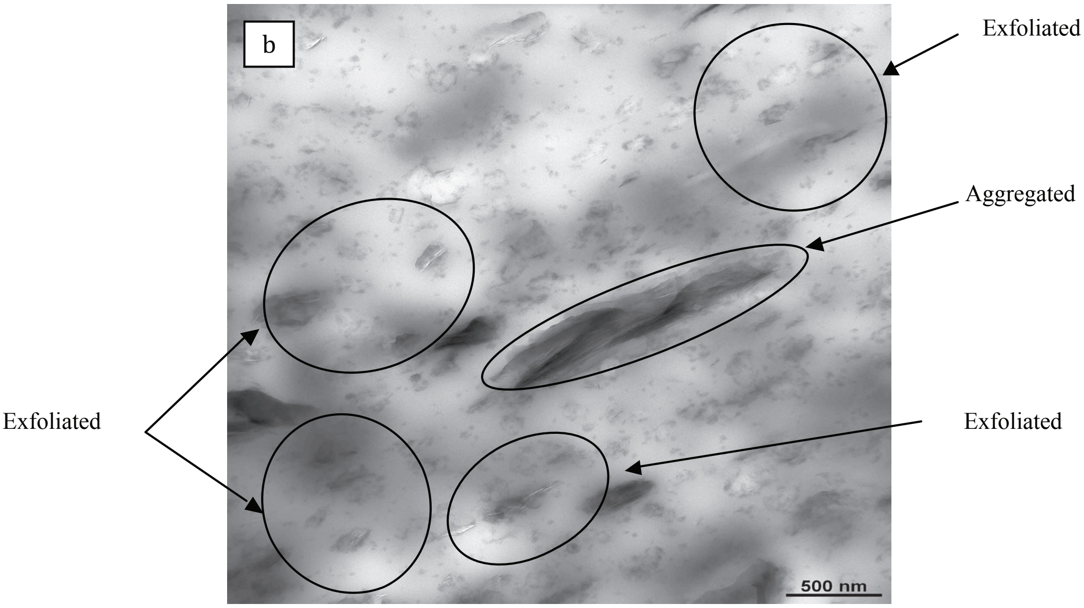


Figure 7(b). TEM micrograph of MBSLC/MMT (5 p.h.r.) nanocomposite at low magnification (43,700X).

nanocomposites prepared from the NRSLC possess a mixture of clay structures between the exfoliated and incomplete exfoliated dispersion state.

CONCLUSION

The NR/MMT nanocomposites have been successfully prepared by coagulating NRSLC with clay aqueous suspension. As compared to the nanocomposites prepared from standard latex centrifuged LC, NRSLC based nanocomposites exhibit shorter cure time and scorch time. It was noticed that MBSLC/MMT nanocomposites possess higher maximum torque and delta torque compared to those prepared from NRSLC. The improvement in mechanical properties such as the tensile strength, modulus, tear strength, hardness and compression set were also observed. In addition, the MBSLC/MMT nanocomposites possess lower air permeability measurements compared to the neat NR skim that suggests the improvement in barrier properties. It is believed that the enhancement of the mechanical and barrier properties in the nanocomposites is partly related to the homogenous dispersion of the layered clays within the smaller and more uniform latex particles in the NRSLC.

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