Effects of Layered Silicate Fillers and Their Surface Treatments in NR/BIIR Blend

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A R T I C L E I N F O

A B S T R A C T

In this study, the improvement in mechanical properties and abrasion resistance of natural rubber/bromobutyl rubber (NR/BIIR) blends were investigated when using different types of layered silicates as secondary fillers. Moreover, the effects of organophillic surface treatments and their synergistic effects with ENR compatibilizer were also studied. These fillers include montmorillonite clay, kaolin, bleaching clay, and talcum. We found that the secondary fillers could improve the properties of the rubber composites differently. Bleaching clay contributed to a dramatic increase in crosslink density, which could also increase the modulus and hardness of the composite. Montmorillonite clay could provide dramatic increase in abrasion resistance with low compression set, while kaolin was excellent in terms of tensile strength. With organophillic surface treatments, the silane-treated kaolin led to dramatic improvement in all aspects. Conversely, montmorillonite clay treated with octadecylamine contributed to significantly higher modulus and hardness, while losing its abrasion resistance and resilience. These results were opposite for bleaching clay. In this case, even though the composites of silane-treated kaolin obtained improved abrasion resistance and lower compression set, they suffered the drop in crosslink density, modulus, hardness and tensile strength.

1. Introduction

Due to its low air permeability, butyl rubber (IIR) has been used in various applications including footballs, tire inner liners and insulators of air-conditioned tubes, etc [1]. Nevertheless, as the cost of butyl rubber is considerably high compared to natural rubber (NR), NR is potentially blended with IIR to reduce cost. However, since the cure time of IIR is inconsistent with NR, inhomogeneous curing may cause phase separation inside these blends. In this regard, bromobutyl rubber (BIIR) has replaced IIR for the blends with NR [2]. The outstanding characteristics of NR are its high toughness and resilience; nevertheless, the drawback of NR is that it can be easily degraded by heat and ozone. Moreover, it also possessed low oil resistance and high gas permeability, which is undesirable in some gas storage applications. Generally, the presence of methyl groups serves to reduce the gas permeability of polymers. Butyl rubber is more saturated and has more methyl groups than natural rubber causing it to be twenty times less permeable to air [3]. Therefore, by blending NR with BIIR, some modifications should be incorporated to improve the properties of the NR/BIIR blends. To improve mechanical strengths of rubber, reinforcing fillers are commonly incorporated. Good choices of reinforcing fillers for abrasion resistance and gas barrier purpose are those with platelet structures. Among different kinds of platelet fillers, talcum and kaolinite are commonly used in rubber compounding formulation due to their abundance and low cost. Talcum is a hydrated magnesium silicate sheets with the chemical formula $Mg_3Si_4O_{10}(OH)_2$. The surfaces of these elementary sheets do not contain hydroxyl groups or active ions making it hydrophobic and inert [4]. This filler is generally used as processing aid, UV resistance, insulator and liquid barrier of rubber products [5]. On the other hand, kaolin consists of non-expandable and hydrophilic alumino–silicate layers. An individual kaolin particle has the shape of a hexagonal plate. In nature, these plates occur in stacks or "books" that exhibit varying degrees of stacking regularity. It is generally used as a semi–reinforcing filler and to reduce cost [6]. Beside talcum and kaolinite, montmorillonite clay has become of increasing interest especially in nanocomposite applications. This is mainly due to its ion-exchange capability and its expandability, which can create tremendous increase in the filler's surface area [4, 7]. Since the advent of nanocomposites, montmorillonite clays were widely investigated for their applications as nanofillers in polymers. Several reports were found on the applications of montmorillonite clay in natural rubber [8-12]. By melt compounding, even though the degree of exfoliation or intercalation

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was limited, its applications as abrasion resistance, gas barrier or in terms of property improvement still worth investigation. Bleaching clay, another type of layered silicate generally used for bleaching application was also considered here. In this paper, we investigate the effects of different layered silicates stated earlier as well as their surface modification on various properties of the natural rubber/bromobutyl rubber blend composites. The properties include tensile strength, surface hardness, compression set, abrasion resistance and gas permeability. In the past, epoxidized natural rubber has been used in various aspects including intercalation and exfoliation of organoclay in natural rubber or in natural rubber blend matrices [13-15], improving of blend compatibility [16], mechanical strengths [17-18], and gas permeability [19] In our previous study [20], the role of epoxidized natural rubber (ENR) was investigated as a compatibilizer in NR/BIIR blend. Here, we investigated the synergistic effects of surface treatment together with the use of ENR compatibilizer on improving several properties of NR/BIIR blend composites.

2. Experimental

2.1 Raw Materials

The natural rubber used in this experiment was STR-5L grade supplied by Yong Thai Rubber Co., Ltd. (Thailand). Bromobutyl rubber, MBTS and TMTD were provided by Multi-chemical Engineering, Co., Ltd. (Thailand), and the epoxidized natural rubber with 50 mol% epoxidation was obtained from San-Thap International Co., Ltd. Montmorillonite clay with the cation exchange capacity of 100 meq./100g. of clay, and kaolinite clay (kaolin) were kindly supplied by Kunimine (Japan) and Kentucky-Tennessee Clay (U.S.A.), respectively. Other chemicals (talcum, phenolic resin, paraffinic oil, paraffin wax, stearic acid, and zinc oxide) were kindly donated by Petch Thai Chemical Co., Ltd, Thailand.

2.2 Surface Modification of Layered Silicates

In this study, organophillic surface treatment of montmorillonite clay was carried out by cation-exchange reaction with octadecylamine, while those of kaolin and bleaching clay were carried out by silylation reaction. The procedures for both surface treatment methods are described below.

(a) Cation–exchange reaction of montmorillonite clay [21]

First, montmorillonite clay was swollen in deionized water at room temperature with continuous stirring overnight. Prior to the reaction, the dispersion was heated up to 70 °C for 1/2 hour. In a separate container, the protonated form of octadecylammonium ion was prepared by dissolving the octadecylamine (8% of clay) into 2.9 ml of HCl and 500 ml of water at 70 °C. The mixture was then poured into the clay dispersion under vigorous stirring for 4 hours at 70 °C to produce organoclay. The organoclay then underwent 3 cycles of consecutive centrifuging and washing by hot water at 70 °C and dried in a vacuum oven at 110 °C for 24 hrs.

(b) Silylation of kaolin and bleaching clay [22]

In this study, tetrasulfane silane (Si-69) was selected for silylation reactions of kaolin and bleaching clay due to the fact that Si-69 has already found applications as a compatibilizer for natural rubber with inorganic fillers. The structure of Si-69, shown in Figure 1, is composed of symmetric ethoxy groups, which were converted to silanol groups on hydrolysis, and nonhydrolyzable organic and sulphur groups that enables the coupling agent to bond with rubbers.
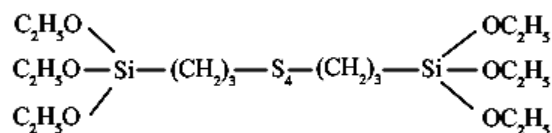
Figure 1: Structure of Bis(3–triethoxylpropyl)–tetrasulfane (Si-69).

First, Si-69 in the amount of 8% of the reinforcing fillers was hydrolyzed under continuous stirring for 1 hour in a mixture of 90% ethanol and 10% water. Acetic acid was used as a catalyst. Then, the silylation reaction was carried out by pouring the hydrolyzed Si-69 mixture into the clay dispersion under vigorous stirring for 24 hours at room temperature to produce organoclay. The organoclay were then washed and dried in a vacuum oven at 110 °C for 24 hrs.

2.3 NR/BIIR Composite Preparation

The compounding formulations of the NR/BIIR composites were listed in Table 1. Formulation A and B are for composites without and with ENR compatibilizer, respectively. The rubber compounds prepared according to formulas A and B were compounded in an open

two-roll mill at 70°C. During compounding, the rubbers were first masticated for 5–10 minutes before adding activators (stearic acid and zinc oxide). Then, the fillers were added together with DEG, paraffinic oil, paraffin wax, and phenolic resins. Curatives (MBTS, TMTD, and sulphur) were added last to prevent precuring. After compounding, the samples were then vulcanized in compression molds at 180°C.

Table 1: Formulations of the rubber compounds used in this study.

Ingredient (phr)[a]	A	B
Natural Rubber, NR	25	25
Bromobutyl Rubber, BIIR	75	75
Epoxidised Natural Rubber, ENR	-	10
Secondary Filler (treated/untreated)	10	10
Stearic acid	3	3
Zinc oxide	2	2
Silica	40	40
Phenolic resin	2	2
Paraffinic oil	7.5	7.5
Paraffin wax	2.5	2.5
DEG[b]	3.5	3.5
MBTS[c]	2	2
TMTD[d]	0.8	0.8
Sulfur	1	1
[a] *Parts per hundred parts of rubber* [b] *Diethylene glycol* [c] *Dibenzothiazole Disulphide* [d] *Tetramethyl thiuramdisulphide*		

2.4 Characterization

The surface areas of fillers were determined by the Brunauer-Emmett-Teller (BET) method on the Quantachrome (AUTOSORB-1) following ASTM D 3037-1978 standard test method, whereas the average particle sizes were measured by Mastersizer MS2000 (model APA2000) particle sizer. The X-ray diffraction patterns and the elemental compositions of the fillers were obtained from JEOL-LDX 3530 X-ray diffractometer and the Philips PW2404 XRF, respectively. The cure characteristics of the composites were measured using a Monsanto Moving Die Rheometer (Model MDR 2000) at 180°C. The presence of functional groups on the surfaces of both the montmorillonite clay and kaolin was verified by FTIR Perkin Elmer System 2000. The light source is in the mid-infrared range (4,000 – 400 cm^{-1}) with the resolution of 4 cm^{-1} using triglycine sulphate (TGS) detector. The inorganic compositions of the clays were analyzed by Philips PW2404 (wavelength dispersive) X–Ray Fluorescence Spectrometer (XRF).

The tensile stress–strain properties were measured according to ISO 37–1977(E) by Mini-tech Universal Testing machine, with type-1 dumbbell test specimens. Shore hardness and abrasion tests were measured by using Durometer Shore A according to ASTM 2240 and Hampden Abrasion Tester according to DIN 53516, respectively. Compression set measurement was performed following ASTM D395 and the gas permeability tests were carried out based on ASTM D 3985 using oxygen as the model gas.

The micrographs of the fractured surfaces of the composites were taken by a Joel scanning electron microscope (SEM). The fractured surfaces were coated with gold to prevent electrostatic charging during examination.

## 3. Results and Discussion

3.1 Filler characterizations

Table 2 reports the average particle sizes and BET surface area of fillers used in this study. As can be seen, the average particle size of montmorillonite clay is the smallest with the highest surface area, whereas talcum has the largest particle size with the lowest surface area. The elemental compositions of fillers used here were tested by X-ray Fluorescence (XRF). As reported in Table 3, major compositions of these fillers were consistent with their chemical structures reported in literature, where talcum was composed mainly of SiO_2 and MgO, and the clays, which were alumino-silicate in nature, consisted primarily of SiO_2 and Al_2O_3. Moreover, majority of the trace components in montmorillonite clay were Na+ and Mg^{2+}, corresponding to the ion-exchangeable species reportedly found in the interlayer spacing of expandable montmorillonite clays. [4, 12]. On the other hand, the majority of trace components in bleaching clay is potassium (K+). The XRD analyzes of the clays are shown in Figure 2. As can be seen, the diffraction pattern of montmorillonite clay indicated the characteristic peak of montmorillonite at $2\theta = 7.10°$ (interlayer spacing = 12.45 Å), whereas the pattern of kaolin revealed the obvious characteristic peak for kaolinite clay at $2\theta = 12.47°$ (interlayer spacing = 7.09 Å). On the other hand, the pattern of bleaching clay indicated that the clay consisted of illite ($2\theta = 8.96°$ and $17.91°$) and a smaller portion of kaolinite ($2\theta = 12.48°$). The interlayer space of illite is mainly occupied by potassium cations (K^+) consistent with the XRF result of the bleaching clay.

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Table 2: Average particle sizes and BET specific surface areas of fillers

Types of filler	Average Diameter (μm)	Specific Surface Area (m²/g)
Talc	16.66	3.18
Montmorillonite Clay	4.81	25.85
Kaolinite Clay	11.23	21.32
Bleaching Clay	5.74	4.22

Table 3: Oxide Analysis of Fillers by X-ray Fluorescence (XRF)

Compound	Composition (% by weight)			
	Talcum	Montmorillonite Clay	Kaolin	Bleaching Clay
SiO_2	61.4	64.33	53.20	75.20
Al_2O_3	0.14	23.95	43.70	18.30
Fe_2O_3	0.03	2.30	1.10	0.85
MgO	38.10	3.53	-	1.60
Na_2O	-	4.65	0.08	0.28
SO_3	-	0.30	0.31	-
CaO	0.31	0.59	0.02	0.07
TiO_2	-	0.18	1.10	0.07
K_2O	-	0.12	0.35	3.60
P_2O_5	0.02	-	0.10	-
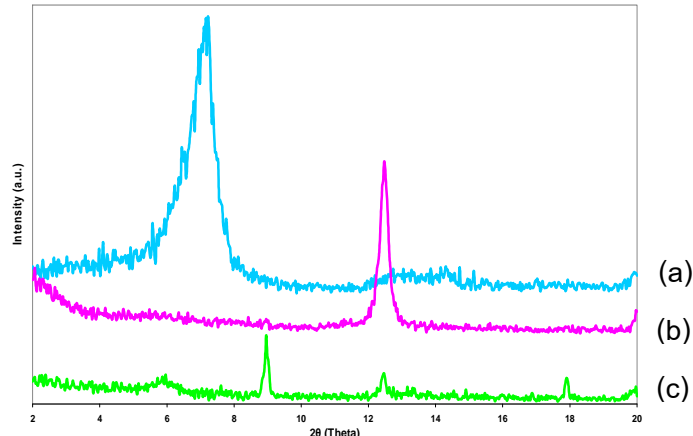
Figure 2: XRD patterns of (a) montmorillonite clay, (b) kaolin and (c) bleaching clay used in this study.

From the FTIR spectra of the three types of clays in Figure 3, the broad absorbance peaks at 900-1100 cm^{-1} of montmorillonite and bleaching clays are similar indicating similar rearrangement of Si-O and Al-O bonds of alumino-silicates. The differences are the absorbance peaks of adsorbed water at 3,400 – 3,500 cm^{-1} and 1,600 cm^{-1} appeared in montmorillonite clay but not in bleaching clay indicating the absence of adsorbed water in

bleaching clay. On the other hand, the absorbance pattern at 3,600 and 3,700 cm^{-1} of bleaching clay is similar to that of kaolin indicating similar pattern of surface hydroxyl groups. The characteristic perpendicular and in–plane Si–O stretchings of kaolin appeared at 1,100 cm^{-1} and 1,000 – 1,050 cm^{-1}, respectively, whereas the Al$_2$OH deformation occurred at 900 cm^{-1} [23].
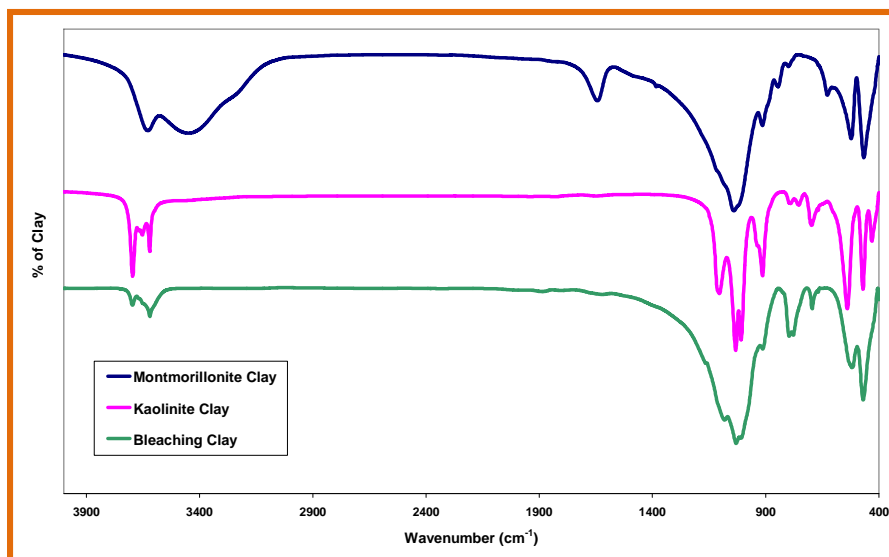

Figure 3: FTIR spectra of the same clays as in Figure 2

3.2   Organoclay characterization

After surface treatment, the expansion of the clay interlayer and the %coverage of coupling agents on the clay surfaces were determined by X-Ray diffraction and thermogravimetric analysis. The XRD patterns of the clays before and after surface treatment are shown in Figure 4. In Figure 4(a) the primary silicate of the pristine montmorillonite clay presents a diffraction peak at $2\theta = 7.097°$, corresponding to an interlayer distance (d) of 12.45 Å. After treated with octadecylamine, the diffraction peak was shifted to $2\theta = 5.003°$ (d = 17.65 Å), indicating an enlargement of the interlayer spacing due to the insertion of octadecylammonium ions between the interlayer. In Figure 4(b) and (c), on the other hand, after kaolin and bleaching clay were treated with silane, the diffraction peaks were at the same locations as those of the pristine clays but with much lower intensity. This insignificant expansion of the clays implies no insertion of the silane couling agent into the interlayer spaces. However, the lower intensity indicated that the dispersion of the aggregated structure might be improved.

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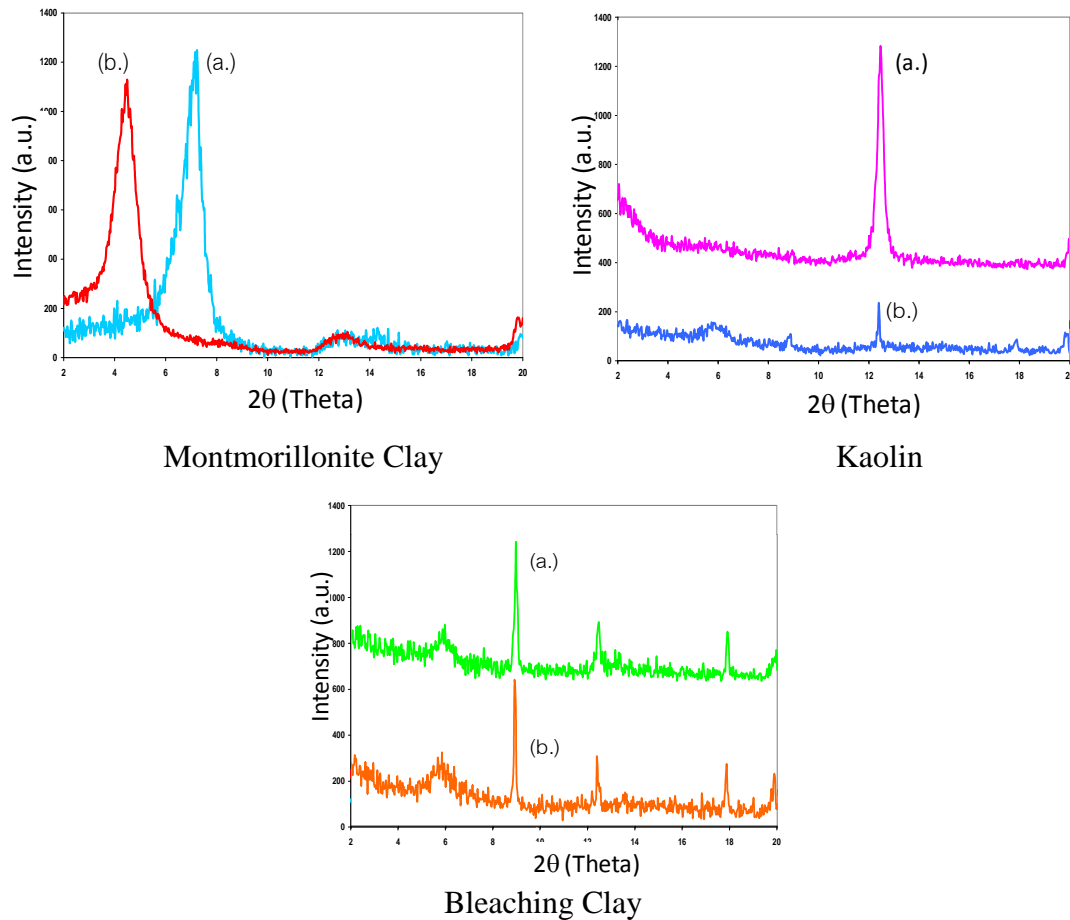
Figure 4: XRD patterns (a) before and (b) after surface modification of montmorillonite clay (top-left), kaolin (top-right) and bleaching clay (bottom)

The TGA thermograms of the same set of clays were used to calculate the %coverage of the organophillic compound on the clay surface/interfaces. We found that the %coverage of organophillic compound on montmorillonite clay was 26.5 %, whereas the %coverages of silane on kaolin and bleaching clay were almost undetectable by TGA. These results agree well with the XRD patterns. The high surface coverage of montmorillonite clay was because the coating of octadecylamine by cation-exchange reaction covered not only the outer surface of the clay but also the interlayer spaces. On the other hand, the low surface coverage of the silane-coated clays was due to the limited coating only on the outer surfaces.

3.3 The effects of clay types and surface treatments on the properties of NR/BIIR composites

The surface structures and the organophillic surface treatment of clays affected both the cure characteristics and mechanical properties of the NR/BIIR blends. The cure characteristics in table 4 are shown in terms of scorch time (ts_2), cure time (tc_{90}), and the maximum torque difference (ΔT_{max}). The cure time (tc_{90}) is denoted by the time when the torque value reaches 90% of the maximum torque and the maximum torque difference (ΔT_{max}), is the differences between the maximum torque (T_{max}) and the minimum torque (T_{min}). The magnitude of ΔT_{max} indicates the degree of crosslinking of the vulcanized rubber composites [24].

Table 4: Cure characteristics of the composites with different types of secondary fillers at 180°C

| Sample	ts_2	tc_{90}	T_{max}	T_{min}	ΔT_{max}
No Plate–like Filler	0.48	2.59	7.06	2.08	4.98
Talc	1.24	3.00	8.95	3.53	5.42
Mont.	1.15	3.29	9.29	3.78	5.51
(Treated Mont.)	(1.13)	(2.30)	(8.79)	(3.50)	(5.29)
Kaolin	1.19	3.29	9.43	4.10	5.33
(Treated Kaolin)	(1.33)	(5.26)	(9.50)	(4.20)	(5.30)
Bleaching Clay	0.55	3.06	11.39	3.90	7.49
(Treated B. Clay)	(1.21)	(4.20)	(10.14)	(3.25)	(6.89)

With secondary fillers (except for bleaching clay), the scorch times (ts_2) of the composites were roughly twice as long as those without a secondary filler. This was probably due to the obstruction from the platy fillers to form crosslink network within the rubber matrices. After surface treatments, the cure time of kaolin and bleaching clay were much longer than without surface treatment. This is most likely because the surface coverage of clays by silane partly deactivated the acceleration effects of metal oxides naturally presented in the clays. [25] On the other hand, the cure time of treated montmorillonite clay was shorter than that of the pristine clay since the ammonium ion present in the coupling agent also helped accelerating the curing reaction.[26] Nevertheless, the ΔT_{max} in Table 4 indicated that the crosslink density of all blend composites using treated secondary fillers were lower than those using the untreated fillers.

The mechanical properties of the same composites are shown in figure 5(a-c) in terms of modulus, tensile strength and elongation at break, respectively. As can be seen, without

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surface treatment, the composite of bleaching clay provided the highest modulus. However, with surface treatment, the modulii of the bleaching clay composite dropped significantly consistent with the drop in crosslink density. On the other hand, for kaolin and montmorillonite, surface treatments of those composites provided improved tensile modulus, where the highest modulus belongs to the composite of treated montmorillonite clay. The adverse effect of this high modulus was the drop in tensile strength and elongation at break. (This could be improved by lowering the clay loading.) Therefore, when considering the improvement in terms of tensile strength and elongation at break, the composite of treated kaolin could provide improved tensile strength, modulus, and elongation at break. The values of surface hardness of the composites in Figure 6(a) were roughly in proportion to the tensile moduli.
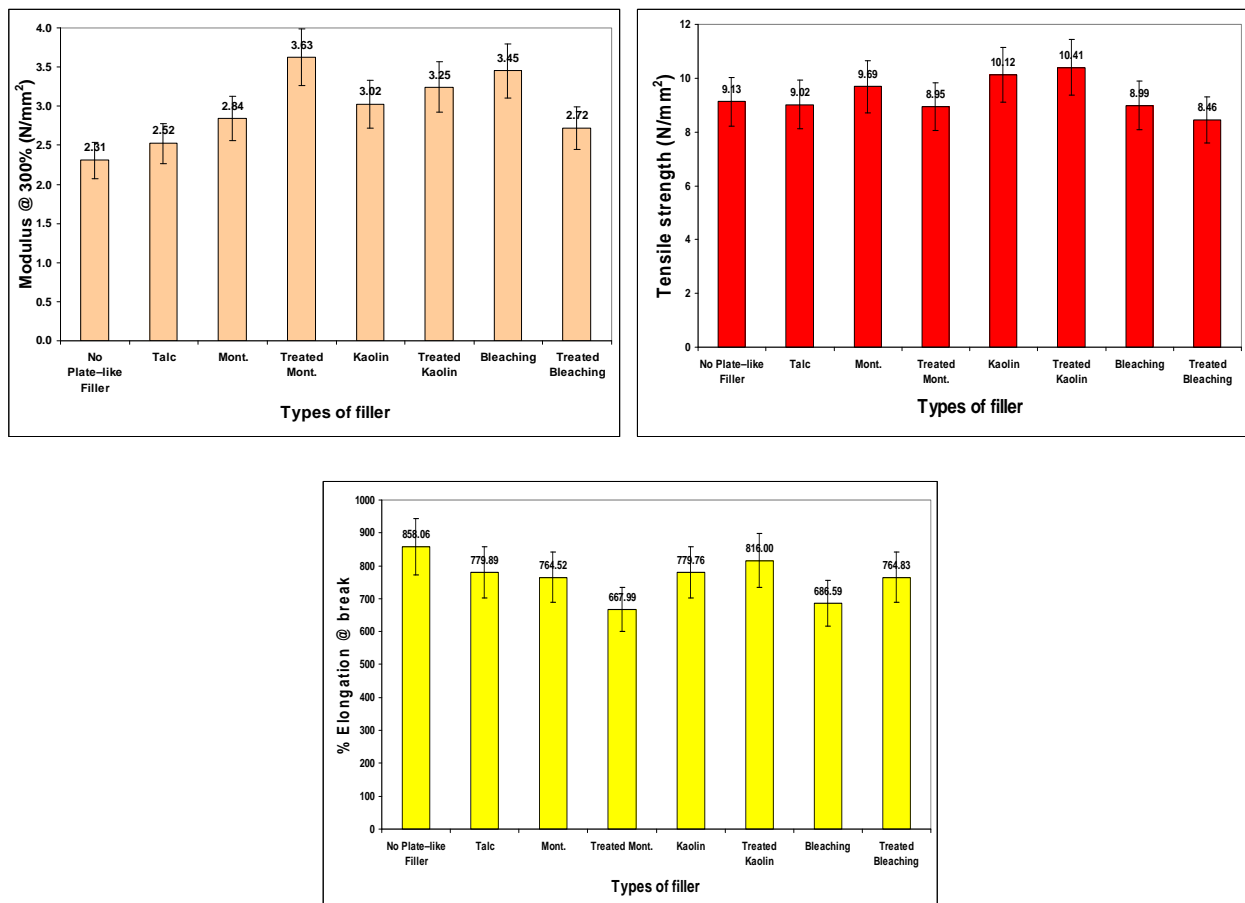
Figure 5: (top-left) Tensile modulus at 300% strain, (top-right) tensile strength and (bottom) elongation at break of NR/BIIR blend composites, where talcum, and pristine/treated montmorillonite clay, kaolin and bleaching clay were used as secondary fillers

(a)

(b)
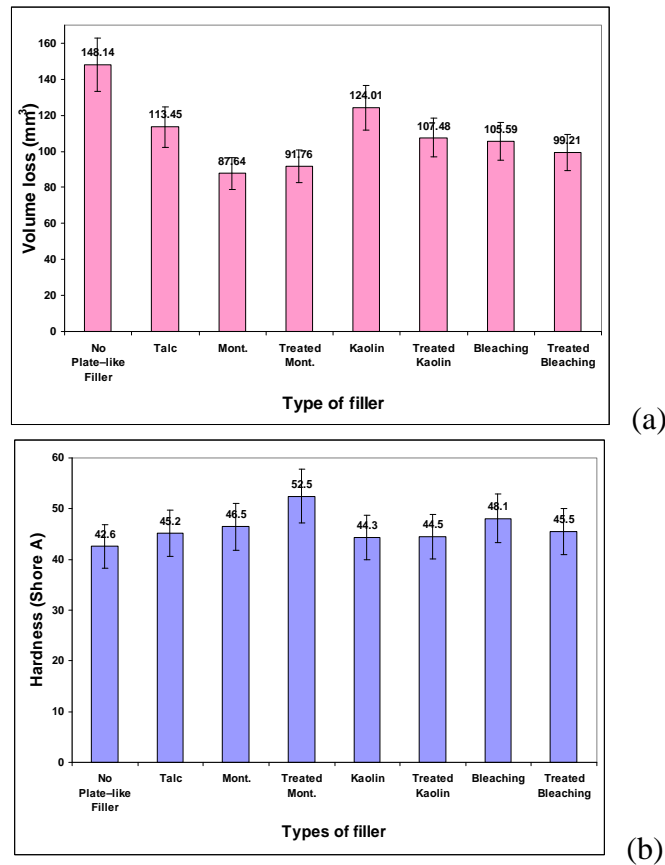
Figure 6: (a) Surface hardness and (b) abrasion loss of the same NR/BIIR blend composites as in Figure 5

Another interesting property is wear or abrasion resistance. It is quite clear in Figure 6(b) that the addition of any of these plate-like fillers could improve wear/abrasion resistance, where montmorillonite clay was outstanding in this aspect, followed by bleaching clay. Abrasion resistance of kaolin composite was not very good but was improved after surface treatment.

The dispersions of clays in the rubber blend matrices are indicated by the SEM images of fractured surfaces shown in figure 7 for montmorillonite and kaolin before and after surface treatment. It was noticeable that the clays were more compatible with the rubber matrices after surface treatments.

3.4 The synergistic effects of ENR compatibilizer and filler surface modification

The approach in improving filler/matrix compatibility could be carried out by using compatibilizer as well as chemically modifying the filler surfaces. Here, the synergistic

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effects of using 10 phr of ENR compatibilizer and filler surface treatment will be investigated. These effects were reported in terms of crosslink density, mechanical strength, abrasion resistance and gas permeability.


(a.)

(b.)

(c.)

(d.)
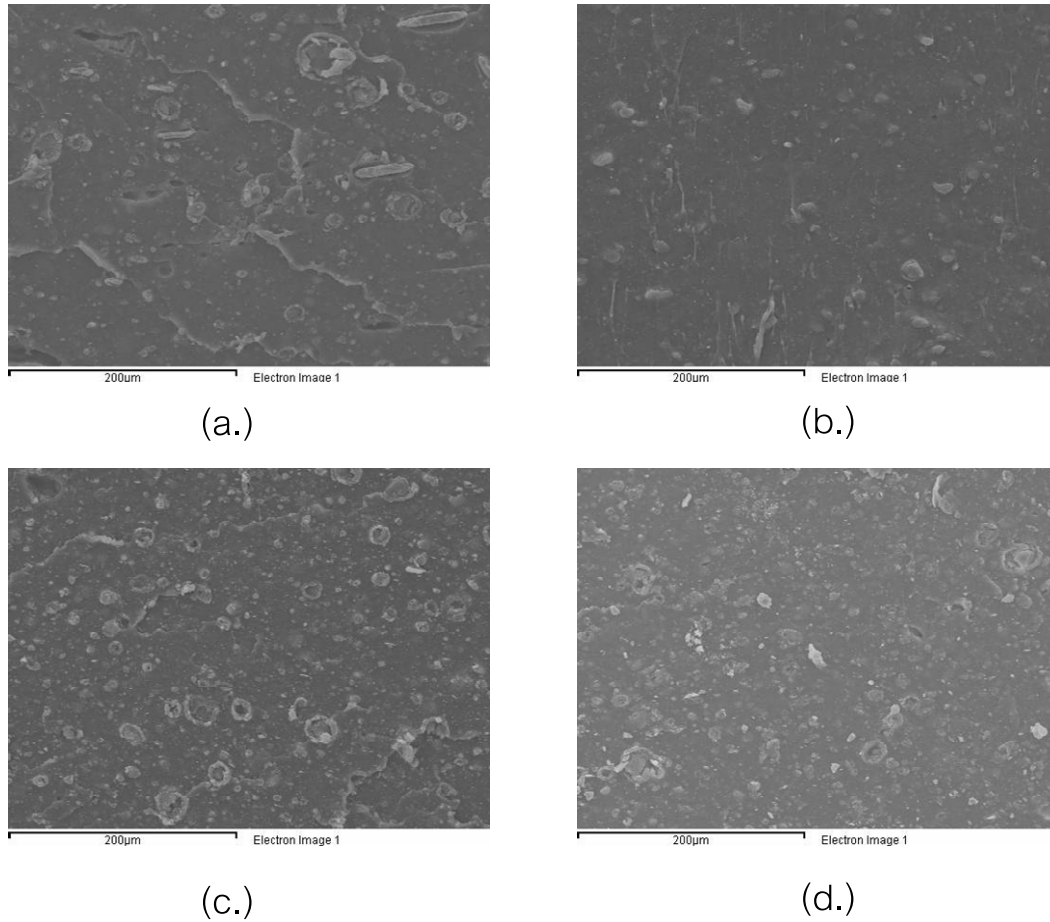
Figure 7: SEM micrographs of the NR/BIIR blend composites using (a) montmorillonite clay (b) surface-treated montmorilonite clay (c) kaolin (d) surface-treated kaolin as secondary filler

(a)

(b)
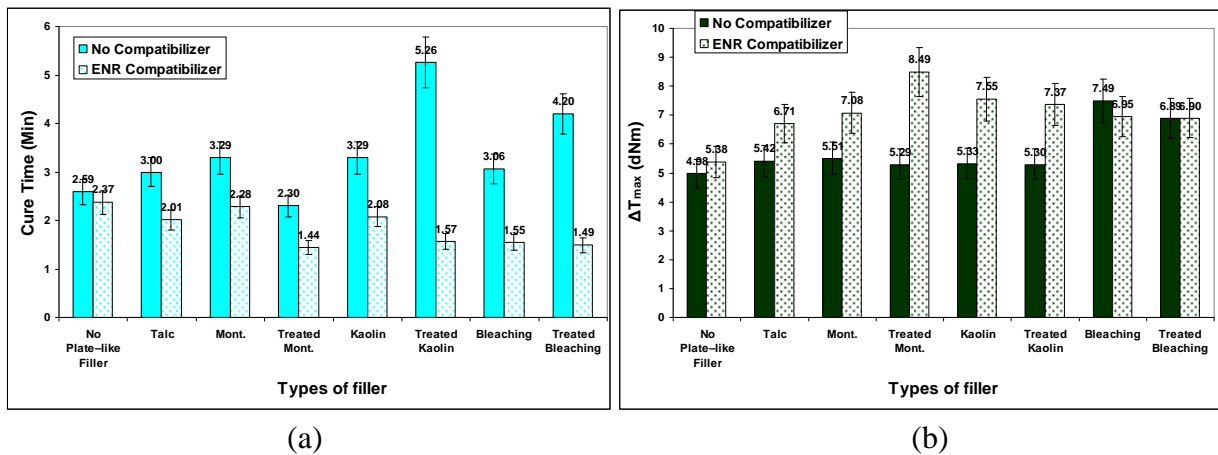
Figure 8: (a) Cure time and (b) ΔT_{max} of the same NR/BIIR blend composites as in Figure 5 with and without 10 phr of ENR compatibilizer

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With ENR compatibilizer, the cure characteristic changed in 2 aspects, which were the cure time and the crosslink density. Figure 8 showed that ENR compatibilizer could significantly shorten cure times, especially for the composites of silane-treated clays, and increased the crosslink density for most of the blend composites. This is because the epoxy ring in ENR activates the transformation of adjacent double bonds in the rubber molecules into free radicals. These radicals can quickly react and form additional crosslinks with sulphur. [27] The increase in crosslink density due to the addition of 10 phr ENR compatibilizer significantly outweighed the effects of filler surface treatment. This increase led in overall to higher modulus and lower tensile strength and elongation at break as shown in Figure 9 (a-c).
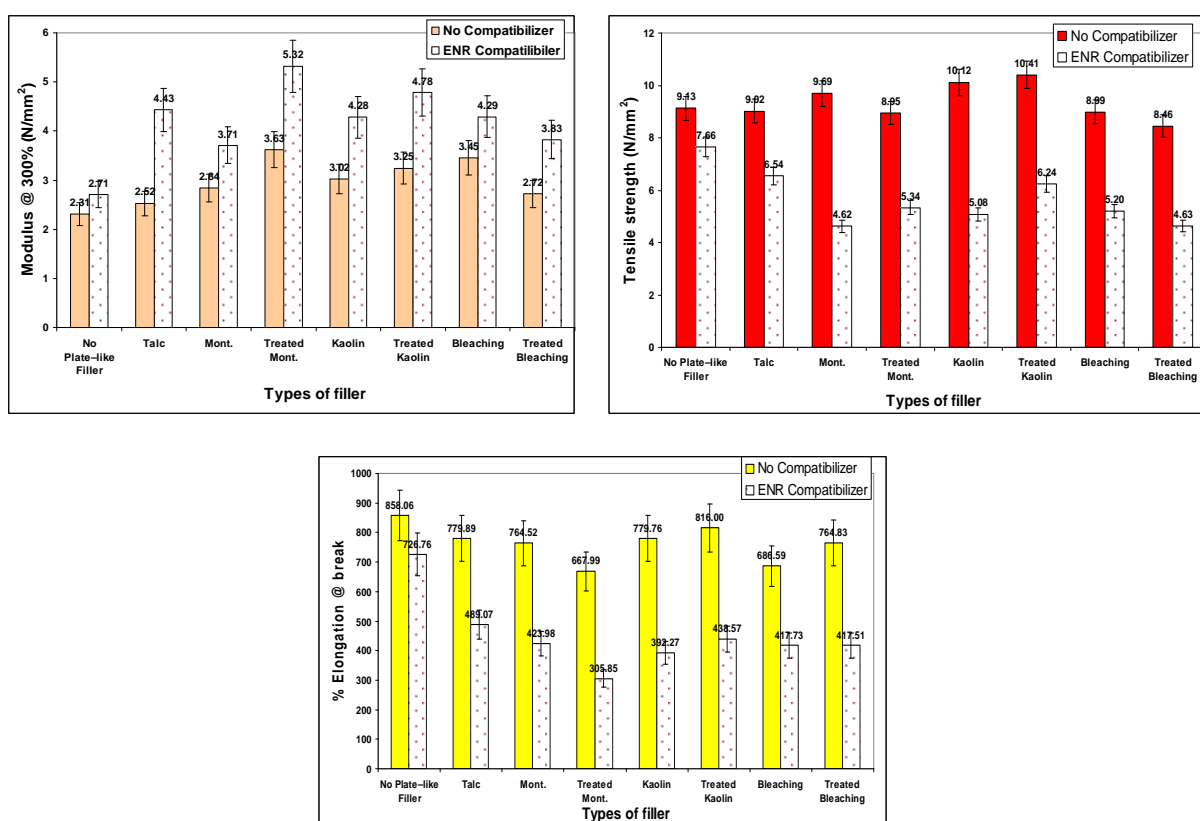
Figure 9: (Top-left) Modulus at 300% strain, (Top-right) Tensile strength, and (bottom) Elongation at break of the same NR/BIIR blend composites as in Figure 8

Figure 10a showed that the addition of plate-like fillers could in overall lead to lower compression set, where the treated bleaching clay was the best in this aspect. The addition of ENR compatibilizer to those treated clay composites could lower the compression set even future. For wear/abrasion resistance, as mentioned earlier, montmorillonite clay was the best

in this aspect but the surface treatment of the clay slightly worsen this feature (Figure 10b). The addition of ENR compatibilizer could significantly reduce abrasion and wear of the composite, and the wear was minimal when using ENR compatibilizer together with the surface-treated montmorillonite clay.

(a)   (b)
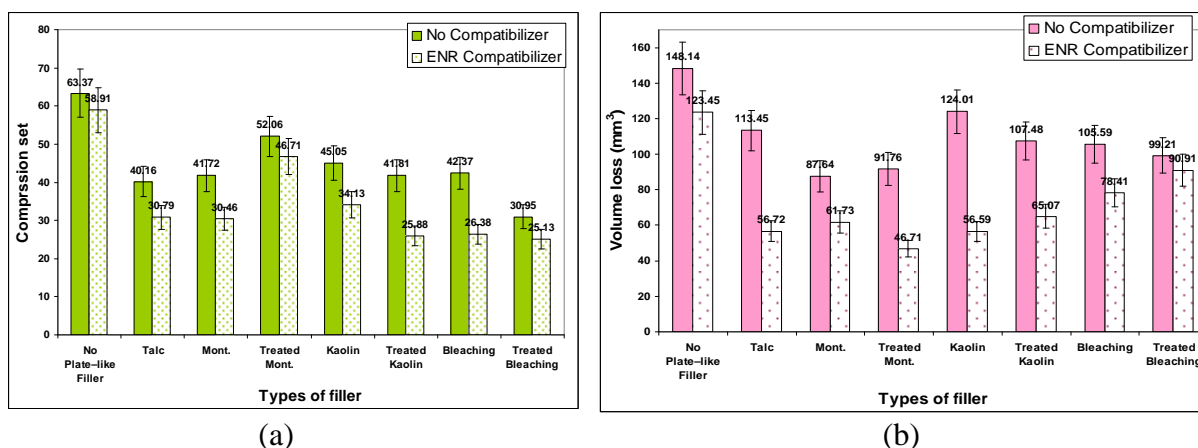
Figure 10 : (a) Compression set and (b) Abrasion loss of the same NR/BIIR blend composites as in figure 8

In terms of gas permeability, Table 5 shows the gas permeability of some selected blend composites. As can be seen, montmorillonite clay and kaolin, even with surface modification and ENR compatibilizer, could not reduce the gas permeation of the blend composites as much as talcum. In this case, though ENR could lower the gas permeability of unfilled NR/BIIR blend, it could not improve the gas permeability of NR/BIIR-talcum composite any further.

Table 5: Oxygen permeabilities of selected NR/BIIR blend composites.

Types of rubber composite	OTR (CC/m^{3}xDay)
BIIR	41.2
BIIR & NR	92.82
BIIR & NR & ENR	57.46
BIIR & NR-Talc	68.82
BIIR & NR & ENR-Talc	69.78
BIIR & NR-Treated Mont	118.32
BIIR & NR & ENR-Treated Mont	111.31
BIIR & NR-Treated Kaolin	117.31

4. Conclusion

The surface treatments of 3 types of plate-like fillers were investigated for the used as secondary fillers in NR/BIIR blend composites for the improvement in several properties. Those properties include tensile properties, surface hardness, abrasion resistance and compression set. Moreover, the synergistic effects of ENR compatibilizer together with surface treatment of the fillers were also studied. We found that the addition of plate-like fillers could significantly reduce the compression set and abrasion loss with an increase in modulus at high %strain. However, the different types of secondary fillers could in detail affect the final properties of the composites differently. Montmorillonite and bleaching clays, which were similar types of alumino-silicate, were outstanding in terms of high abrasion resistance with low compression set, where montmorillonite clay provided the highest abrasion resistance. The as-received bleaching clay provided high crosslink density, which led to high modulus and surface hardness. Kaolin, the conventional plate-like filler for rubber industries, was considered appropriate in the aspect of mechanical properties as it could provide high tensile strength with moderate modulus. The filler surface treatments could significantly affect the blend properties. It was found that the surface treatment of montmorillonite clay could significantly improve the tensile modulii and surface hardness of the blend composite with a drop in tensile strength and a slightly higher compression set. This trade-off in properties could supposedly be fine-tuned by using lower amount of clay loading. The silylation of kaolin could slightly improve all of the blend properties especially the abrasion loss, where the silylation of bleaching clay led to the lowest compression set but with lower mechanical properties. Regarding the synergistic effect of surface treatment and ENR compatibilizer, the effects of ENR compatibilizer were found to be very strong as it could significantly increase the blend crosslink density, lower the abrasion loss and compression set beyond those of the surface-treated clays. However, the increase in crosslink density here had an adverse effect on the tensile strength. Therefore, the addition of lower doses of ENR together with surface treatment of montmorillonite clay could be an interesting pathway to improve tensile strength, compression set and abrasion resistance of NR/BIIR blend composites.

5. Acknowledgements

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