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Maleated Natural Rubber로 조절된 Natural Rubber/Halloysite 나노 튜브 복합재료

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Maleated Natural Rubber Compatibilized Natural Rubber/Halloysite Nanotubes Composites

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Abstract: The properties of rubber composites depend strongly on the compatibility of the rubber matrix and particulate filler. The polarity difference between the two phases has always been the main concern. Natural rubber (NR) and halloysite nanotubes (HNT) are one of the examples of the incompatible system. In this regard, a suitable compatibilizer is recommended to mediate the interactions. In this study, the maleated natural rubber (MNR) with various amounts of maleic anhydride (MA) was introduced as a compatibilizer to this composite. By increasing MA contents, scorch and curing times were increased whereas the maximum torque and the torque differences exhibited the highest values at the MA content of 2 phr. Payne effect was also implemented to monitor their rubber-filler interactions. The MNR with 2 phr of MA exhibited the lowest filler-filler interaction as shown by a lower decrement of storage modulus at high strain. This rubber composite also exhibited the optimum tensile and tear strengths. It is clearly highlighted that application of the MNR with a suitable MA amount enables to increase the rubber-filler interaction significantly and therefore improve a HNT dispersion. Hence, the use of MNR provided the great potential to compatibilize NR and HNT.

Keywords: natural rubber, maleated natural rubber, halloysite nanotubes, Payne effect.

Introduction

Improving the performance of rubber can be achieved by adding small amount of nanofillers and this technique has drawn considerable attention during the last decades.[1-3] An obvious enhancement of physical and other related properties of rubber depends greatly on several factors such as the filler aspect ratio, the degree of dispersion, and the alignment of the particulates. Halloysite nanotube (HNT) is the nanofiller that has been recently available in many types of matrix.[4-7] This is because of the very special characteristic that is formed by surface weathering of aluminosilicate minerals. The surface chemistry of HNT is similar to clay, making this material incompatible with the non-polar rubber such as NR. Scientists have been trying to solve this drawback by several approaches in order to improve their compatibility. These included a very common method like using the silane coupling agents[8] as well as using the compatibilizers,[9] and adjusting the methods of preparation.[10]

Addition of compatibilizer to incompatible system has greatly influenced the overall structure of the composites. Most used compatibilizers were based on modified rubber which is prepared by introducing some functional groups to increase its polarity. In this regards, higher polarity of rubber is achieved and it is expected to increase the compatibility between non-polar rubber and HNT. One of the well-known methods has been the grafting of maleic anhydride (MA) onto the rubber molecule. For example, Pasbakhsh *et al.*[11] utilized EPDM-g-

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MA to compatibilize between EPDM and HNT. It was obvious that EPDM-*g*-MA reduced a tendency of HNT agglomeration and hence improved the HNT dispersion. This was described to be due to a better interaction between the hydroxyl groups on HNT surface and succinic anhydride groups of the EPDM-*g*-MA. Similar approach was also carried and found in the literature.[12,13] They also proposed possible interaction gained between the filler and modifier. Another example of using modified rubber to improve the compatibility between non-polar rubber and HNT was the use of carboxylated styrene butadiene rubber reported by Du *et al.*.[10] It was shown that strong interfacial bonding of rubber and HNT was formed, making the HNT dispersed uniformly and even individually in the rubber matrix. The mechanical properties, especially the modulus and hardness, are significantly increased by introducing this technique. From these examples together with the structure's point of view, the interaction between NR and HNT can be made possible by introduction of the modified rubber.

In this study, modified rubber was specially focused towards the use of maleated natural rubber or MNR. Based on the chemical structure of MNR, it was anticipated to enhance the compatibility of these two components especially at the outer layers of HNT (silanol and/or siloxane groups). To date, no reports have been published concerning to the use of MNR as a compatibilizer in the HNT filled NR composites. The study focused mainly on the curing, mechanical properties and dynamic properties of the composites. The findings obtained in this work will lead to the scientific perspective on the role of MNR as a compatibilizer for NR/HNT composites and extend to be source of detailed information for manufacturing the rubber products containing the HNT in the system.

Experimental

Materials. STR 5 L was the grade of NR used as a main matrix both in compounding the composite and preparing the MNR, it was manufactured by Chalong Latex Industry Co., Ltd., Thailand. MA was used to graft it onto NR molecule, it was obtained from Sigma-Aldrich (Thailand) Co., Ltd. Bangkok, Thailand. HNT was mined and supplied by Imerys Ceramics, New Zealand. HNT consists of the following components, e.g., SiO_2 (51.415 wt%), Al_2O_3 (34.15 wt%), Fe_2O_3 (0.3 wt%), TiO_2 (0.08 wt%) as well as MnO, CaO, MgO, K_2O and Na_2O as traces. Other related properties of this HNT are listed in Table 1.[14] The curing activators namely ZnO and stearic acid were purchased from Global Chemical Co., Ltd., Samut Prakan, Thailand and Imperial Chemical Co., Ltd., Bangkok, Thailand respectively. *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS) as accelerator, was purchased from Flexsys America L.P., West Virginia, USA, and sulfur as vulcanizing agent, was purchased from Siam Chemical Co., Ltd., Samut Prakan, Thailand.

Table 1. Typical Analysis Data of HNT Relative to the Formation of Polymer Composites[14]

HNT properties	Values
Dominant particle shapes	Long and thin, short and stubby, tubular, spherical and plate-like
Pore shape	Cylindrical
Length	100-3000 nm
Outer diameter	50-200 nm
Inner diameter	15-70 nm
Aspect ratio (L/D)	12
Mean particle size in aqueous solution	143 nm
BET surface area	22.1 m^2/g
Pore space	14%
Lumen space	10.7%
Density	2.14 g/cm^3
Average pore size	93.1 Å

Preparation of MNR. Grafting of MA e.g., 1-8 phr onto NR was done by mixing the NR with MA in a Brabender Plasticorder at 145 °C at a rotor speed of 60 rpm under normal atmosphere. The mixing was last for 10 min. The resulting rubber was purified by reprecipitation only for the purpose of characterization by FTIR. The resulting MNR was then purified to confirm grafting of MA onto NR. This was carried out by dissolving the rubber sample in toluene at room temperature for 24 h and then at 60 °C for 2 h, the soluble part was collected and precipitated in acetone. The sample was dried in a vacuum oven at 40 °C for 24 h. The purified MNR was finally characterized for FTIR spectrum.

Preparation of NR/HNT Composites. Table 2 lists the main ingredients used for preparing the rubber composites, in which the main matrix used was separate accordingly. The entire amounts of additives were mixed in a Brabender (Plastograph® EC Plus, Mixer W50EHT 3Z) and just after the dumping, the compounds were passed through a two-roll mill to avoid excess heat. The compounds were then compressed into certain shapes using a hydraulic hot press, with the vulcanizing times obtained by a moving-die rheometer (MDR) as described later.

Table 2. Compounding Ingredients Used for Preparation of the Composites

Ingredients	Amount (phr)
NR	90
MNR*	10
ZnO	5
Stearic acid	1
CBS	2
Sulfur	2
HNT	10

Remark: MNR used was compounded separately according to the MA contents.

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR). The FTIR spectra of MNR were analyzed using a Bruker FTIR spectrometer (Tensor27) with a smart durable single bounce diamond in the ATR cell. Each spectrum was recorded in transmission mode after 32 scans per spectrum, with 4 cm^{-1} resolutions from 4000 to 400 cm^{-1}.

Measurement of Curing Characteristics. The curing characteristics of the composites were determined using an MDR (Rheoline, Mini MDR Lite) at 150 °C. Torque, scorch time (t_{s2}) and curing time (t_{c90}) were determined according to ASTM D5289.

Measurement of Mechanical Properties. The samples were cut into a dumbbell shape according to ASTM D412. The tensile tests were carried out with a universal tensile machine (Tinius Olsen, H10KS) at a cross-head speed of 500 mm/min. This is to determine 100% modulus, 300% modulus, tensile strength and elongation at break. Further, the tear strength of the composites was also tested using the same machine by following the ASTM D624 with a cross-head speed of 500 mm/min. The tear strength recorded was the average of five repeated tests for each compound.

Dynamic Properties. The dynamic properties of the NR/HNT and MNR compatibilized NR/HNT composites were studied using a Rubber Process Analyzer model D-RPA 3000 (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany). The composite sample was cured at 150 °C based on the curing time observed from Rheoline Mini MDR Lite (Prescott Instrument Ltd., UK). Then, temperature was cooled down until 60 °C, frequency 10 Hz and varying strains in the range of 0.56 to 90%. The raw outputs in term of storage modulus (G') and damping characteristic (tan δ) were recorded whereby the rubber-filler interaction of the composites were monitored through the Payne effect. Payne effect can be calculated according to the equation below;

$$\text{Payne effect} = G'_i - G'_f \tag{1}$$

Where G'_i is the G' at 0.5% strain and G'_f is the G' at 90% strain. Higher Payne effect indicates lower rubber-filler interaction.

Scanning Electron Microscopy. The morphology of the rubber sample was screened by a scanning electron microscope (Quanta 400) to gain the detailed information on the dispersion of HNT filler in both NR and MNR. To electrostatic charge during scanning, fractured samples were coated with gold palladium prior to be scanned.

Results and Discussion

Functionalities of Maleated Natural Rubber. FTIR spectrum of MNR at various MA contents is shown in Figure 1 where the peak assignments were listed in Table 3. As for the unmodified NR, the characteristic peaks are found at around 2960, 2920 and 2850 cm^{-1}, indicating the CH stretching vibrations of carbon-carbon double bond in NR. Other important peaks are at 1664 and 835 cm^{-1}, associated with the stretching vibrations of C=C bonds and out of plane deformations of =C-H groups, respectively. When NR was grafted by MA, a broad and intense characteristic band at a wavenumber of 1787 cm^{-1} and a weak absorption band at 1875 cm^{-1} were observed. These bands can be assigned to grafted anhydride, which are due to symmetric (strong) and asymmetric (weak) C=O stretching vibrations of succinic anhydride rings, respectively.

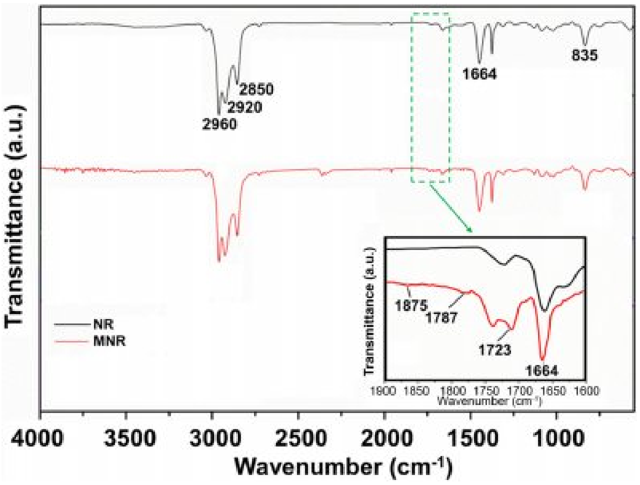

Figure 1. FTIR spectra of NR and MNR at 8 phr of MA.

Table 3. Observed Peaks and Respective Assignments of MNR

Wavenumbers (cm^{-1})	Assignments
2960	–C–H stretching vibration of carbon-carbon double bond
2920	CH_2 stretching vibration of –C=C–
2850	CH stretching vibration of –C=C–
1875	C=O stretch of succinic anhydride (weak)
1787	C=O stretch of polymeric anhydride (weak)
1723	C=O stretch, carbonyl group
1664	C=C stretching vibration
835	Out-of-plane bending vibration of C–H in the –CH=CH– group

These bands were responsible to the presence of succinic anhydride groups grafted onto NR molecules. Moreover, there was an important peak captured at wavenumber of 1723 cm^{-1} due to the formation of carbonyl groups of opened ring structure succinic anhydride. This is because a high level of grafted maleic anhydride tends to react with moisture during drying and storage. The peaks seen in this study were quite similar to the previous results in the literature.[13,15]

Cure Characteristics. The curing curves of the NR/HNT in the absence and presence of MNR as a compatibilizer are shown in Figure 2 where the summarized results were listed in Table 4.

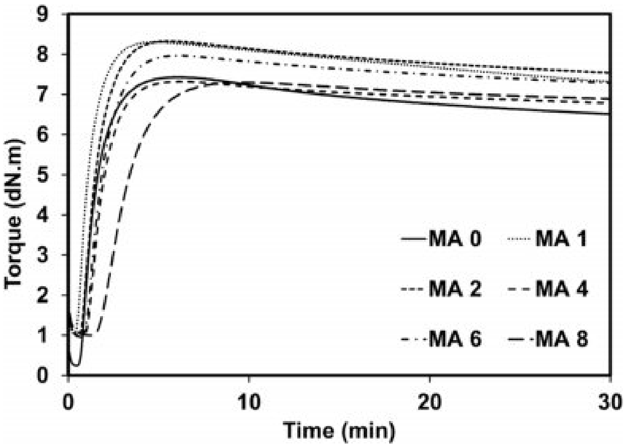

Figure 2. Curing curves of NR/HNT composites in the absence and presence of MNR as a compatibilizer.

The minimum torque (M_L) slightly decreased upon the MA content in MNR, M_L is known to be a representative of compound's viscosity. Introducing the MNR has caused to increase the M_L. During the preparation of MNR, the maleated crosslinks can be formed which has led to increase a gel part in MNR. This later resulted to increase the compound's viscosity of the composite. Similar observation was also found by Nakason *et al.*[13] and Sahakaro and Beraheng,[15] they also explained the same reason behind such finding. Further increase in MA content has given M_L more or less the same values. However, it is interesting to highlight that the maximum torque (M_H) and torque difference ($M_H - M_L$) were observed differently. Both values increased up to 2 phr of MA contained in MNR and then decreased after this level. The increment of these values indicate higher extend of crosslinking and/or interaction between the NR and HNT. The proposed interaction between NR and HNT is illustrated in Figure 3. There are two possible interactions formed in the composite either through opened ring and/or cyclic structures. Grafting of the succinic anhydride groups onto NR molecules of the MNR enabled to increase polarity of rubber and made it compatible to the HNT. Pasbakshs *et al.*[11] also proposed similar interaction forming from the hydroxyl groups of HNT and succinic anhydride groups of EPDM-*g*-MA. Considering the decrease of M_H and $M_H - M_L$, it could be due to the higher level of self-crosslink (maleated crosslink) in the MNR especially at higher level of

Table 4. Curing Characteristics of NR/HNT Composites in the Absence and Presence of MNR as a Compatibilizer

Compound	M_L (dN.m)	M_H (dN.m)	M_H-M_L (dN.m)	t_{s1} (min)	t_{c90} (min)	CRI (min^{-1})
MA 0	0.25	7.43	7.18	0.84	2.81	50.76
MA 1	1.03	8.31	7.28	0.62	2.24	61.73
MA 2	0.98	8.33	7.35	0.90	2.83	51.81
MA 4	0.98	7.97	6.99	1.25	3.16	52.36
MA 6	1.00	7.30	6.30	1.16	3.24	48.08
MA 8	0.95	7.33	6.38	2.09	5.20	32.15

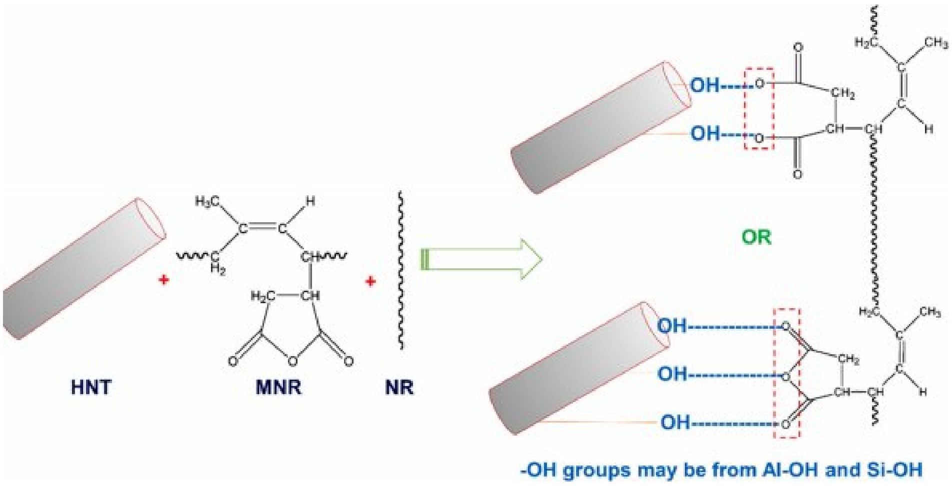

Figure 3. Possible interaction between NR and HNT in the presence of MNR as a compatibilizer.

MA. As more crosslink was formed, less succinic anhydride groups were available to mediate the interaction between NR and HNT.

As for the vulcanizing reaction, introducing the MNR has lengthen the vulcanizing process. This was monitored though the scorch (t_{s2}) and curing (t_{c90}) times. It is simply due the presence of acids from ring opening of succinic anhydride groups. Any chemical substance that gives the rubber compound more acidity will lead to an adsorption of accelerator[16,17] and delay the reactivity of accelerators.

Dynamic Properties. Dynamic properties of the composites were carried out using Rubber Process Analyzer. This is to investigate the storage modulus and the Payne effect. Figures 4 and 5 illustrate the storage modulus and the Payne effect of NR/HNT composites in the absence and presence of MNR as a compatibilizer. It can be seen that the storage modulus of all compounds showed constant values at low strain region but slightly decrease when the strain is higher than 50%. This is the common phenomenon happens to the viscoelastic material due to the molecular stability of the rubber. In addition to that, the Payne effects of all composites were also estimated from the difference between the storage modulus at low strain and high strain amplitude.[18,19] The level of Payne effect of the NR/HNT compound was found to be 231.49 kPa where the Payne effect was comparatively reduced against the MA contents, i.e., 182.47, 157.86, 176.71, 161.14 and 135.52 kPa respectively for MA contents at 1-8 phr consecutively. This is a good indication that the interaction between NR and HNT was improved. The lower Payne effect is responsible to be due to the lower filler-filler interaction.[20] This finding is very good

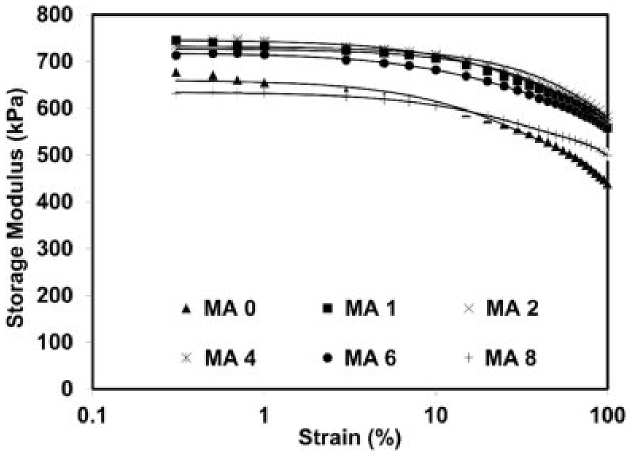

Figure 4. Storage modulus of NR/HNT composites in the absence and presence of MNR as a compatibilizer.

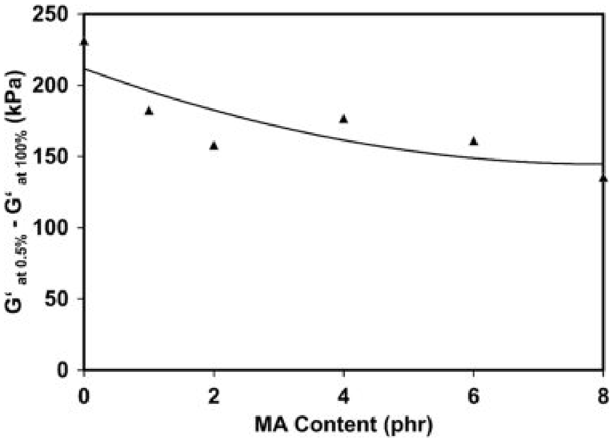

Figure 5. Payne effect of NR/HNT composites in the absence and presence of MNR as a compatibilizer.

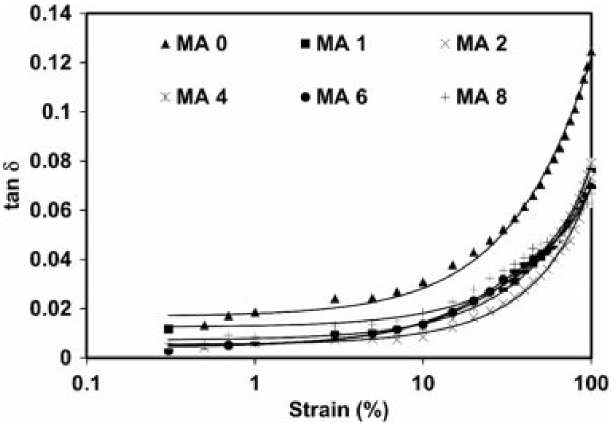

Figure 6. Damping characteristic (tan δ) of NR/HNT composites in the absence and presence of MNR as a compatibilizer.

agreement to the state of cure observed in the previous study.

Dependence of damping characteristic (tan δ) as functions of strain is shown in Figure 6. Considering the composite without the addition of MNR as a compatibilizer. It was found that highest damping value was observed. High damping indicates low elastic response over dynamic condition. However, when the MNR was added as a compatibilizer, it is obvious that the composites exhibited low damping characteristics, suggesting that a considerable degree of mobility was exhibited. This is simply due to the better interaction between rubber and filler through the use of MNR as the main rubber matrix in the system. The compatibility of non-polar rubber and HNT increases an interfacial adhesion and results in an improved elastic property of the composites.

Mechanical Properties. To confirm more on the compatibility of NR and HNT, mechanical properties are the good indication. Tensile properties and tear strength of the NR/HNT composites in the absence and presence of MNR as a compatibilizer are listed in Table 5. Tensile strength was found to be higher when MNR was added to the composite and the value increased up to 2 phr of MA content. Higher tensile strength observed is responsible to their high levels of rubber-filler interaction. Such increment is definitely attributed to an improved degree of compatibility between rubber and HNT in the presence of MNR which was described earlier in Figure 3. A further increment of MA content also leads to a reduction of tensile strength due to a formation of maleate network[12] as discussed earlier. As a result, the stress concentration point was observed at the interacting point, creating catastrophic failure in the rubber samples while stretching. This also caused the same phenomenon to the elongation at break of the composites.

The strong interaction of the NR and HNT has made the tensile modulus (stresses at 100% and 300% strains) higher especially at high concentration of MA. As more MA was grafted to the NR, a possibility of self-crosslink was formed, resulting in stiffer and harder composites. In addition to this, the tear strength was also carried out to monitor the strength of the composites. Similar optimum content of MA was also observed for the tear strength. Again, this is simply to an improvement of the compatibility between the NR and HNT, higher energy was then highly required to tear the sample.

Scanning Electron Microscopy. The fractured samples after testing the tensile properties were used to observe the micro-fractured surface. The image obtained can be used to correlate with the tensile strength. The tensile fractured surfaces of the NR/HNT composites in the absence and presence of MNR as a compatibilizer are shown in Figure 7. Figures 7(A) and 7(B) show the tensile fractured surface of the composites with the control formulation and the use of MNR as a compatibilizer. Better dispersion of HNT was seen when the MNR was added to the composite. This may be attributed to an improved compatibility between NR and HNT. Higher compatibility has reduced the possibility of HNT to interact each other. As a result, the dispersion was improved, leading to an increase in resistance to crack propagation and thus giving higher tensile strength. However, when higher amount of MA was used in the MNR e.g., MA contents at 6 and 8 phr respectively (see Figures 7(C) and 7(D)). The HNT tended to agglomerate each other due to their filler-filler interaction as observed

Table 5. Mechanical Properties of NR/HNT Composites in the Absence and Presence of MNR as a Compatibilizer

Compound	Tensile strength (MPa)	Elongation at break (%)	M100 (MPa)	M300 (MPa)	Tear strength (N/mm)
MA 0	18.31 ± 1.85	640.36 ± 16.67	1.00 ± 0.01	2.50 ± 0.05	31.8 ± 0.20
MA 1	20.33 ± 1.47	640.67 ± 13.13	0.98 ± 0.02	2.44 ± 0.02	34.2 ± 0.31
MA 2	22.05 ± 1.41	647.71 ± 41.42	1.00 ± 0.01	2.56 ± 0.01	35.7 ± 0.26
MA 4	21.89 ± 1.50	637.00 ± 24.99	1.00 ± 0.01	2.62 ± 0.03	35.1 ± 0.22
MA 6	18.70 ± 0.97	624.18 ± 20.42	0.95 ± 0.02	2.46 ± 0.02	35.0 ± 0.16
MA 8	17.23 ± 0.26	561.12 ± 25.37	1.08 ± 0.02	3.00 ± 0.02	34.1 ± 0.55

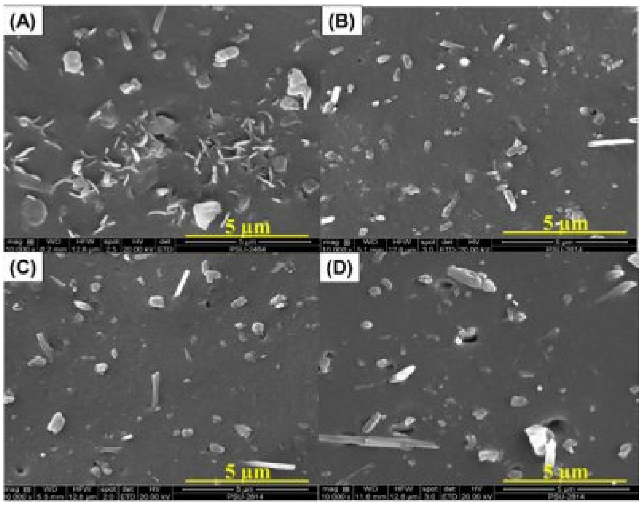

Figure 7. SEM images obtained from tensile fractured surfaces of NR/HNT composites in the absence and presence of MNR as a compatibilizer. i.e., Reference (A); MA 2 phr (B); MA 4 phr (C); MA 8 phr (D) at 10000× magnifications.

from the higher Payne effect. Such agglomeration is simply due to low compatibility between NR and HNT caused by the self-crosslinked MNR. Similar observations were previously reported on changes of microfractured surfaces against the addition of other fillers filled NR composites in the presence of compatibilizer.[21,22]

Conclusions

The aim of this study was to use MNR as compatiblizer for NR/HNT composites. It can be seen that the overall properties of the composites were clearly enhanced when MNR was used as a compatibilizer. MNR has very special functional group that can form hydrogen bonding with the hydroxyl groups available on the HNT inner and outer surface. The obtained interaction is possible to enhance the mechanical properties such as tensile strength, modulus and tear strength of the composites which is again verified by the reduction of Payne effect observed from the dynamic properties. It has been clearly highlighted in this present work that the use of MNR resulted in an enhanced rubber-HNT interaction and reduced filler-filler interaction which provides great benefit to the mechanical and dynamical properties. This finding will lead to the scientific understanding on the role of MNR as a compatibilizer for NR/HNT composites and can be source of useful information for manufacturing the rubber products based on this composites. To some extent, this could lead to a modification of processing method without requiring the use of silane coupling agent which is complicated and costly.

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