



# Article Maleated Natural Rubber/Halloysite Nanotubes Composites

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**Abstract:** In this study, maleic anhydride (MA) grafted natural rubber (NR), known as maleated natural rubber (MNR), was melt-prepared with the MA content varied within 1–8 phr. MNR was used as the main matrix, with Halloysite Nanotubes (HNT) as a filler, in order to obtain composites with improved performance. The compounds were investigated for their filler–filler interactions by considering their Payne effect. On increasing the MA content, scorch and cure times increased along with maximum torque and torque difference. The MNR with 4 phr of MA exhibited the least filler–filler interactions, as indicated by the retention of the storage modulus after applying a large strain to the filled compound. This MNR compound also provided the highest tensile strength among the cases tested. It is interesting to highlight that MNR, with an appropriate MA content, reduces filler–filler interactions, and, thereby, enhances the HNT filler dispersion, as verified by SEM images, leading to improved mechanical and dynamical properties.

Keywords: natural rubber; maleated natural rubber; maleic anhydride; Halloysite Nanotubes

# 1. Introduction

Comparatively small loading levels of nanofillers in rubber matrices have drawn considerable attention during recent decades [1]. The physical properties of rubber can be clearly improved by this means. Such improvements depend on several factors, such as the filler aspect ratio, the degree of dispersion, and the filler orientation. Halloysite Nanotubes (HNT) are interesting nanofillers that have recently become available [2–4]. A HNT is a unique and versatile nanomaterial that is formed by the physical weathering of aluminosilicate minerals, and is composed of aluminum, silicon, hydrogen and oxygen. A HNT has two interlayer surfaces, one with aluminum hydroxide (Al-OH) groups located inside the tubes, and the other with siloxane (Si-O-Si) groups that cover the outer surfaces of the HNT.

Due to the unique surface chemistry of HNT, the compatibility of natural rubber (NR) with HNT is of interest, and several studies have sought to overcome their incompatibility. They have used modified rubbers as compatibilizers, [5] coupling agents [6], and adjusted the steps of preparation [7]. The application of a compatibilizer has been observed to affect the overall structure of a composite. As for the modified natural rubber, the improved compatibility of NR with HNT was obtained through certain functional groups, i.e., maleic anhydride (MA). Pasbakhsh et al. [8] used MA grafted onto ethylene propylene diene rubber (EPDM-g-MA) for compatibility with HNT. It has been demonstrated that the HNT filler agglomerates less, and has a finer dispersion in the presence of EPDM-g-MA. This has been attributed to reactions between hydroxyl groups on HNT surfaces and succinic anhydride available at the EPDM-g-MA. Similar observation was also found by Ismail et al. [9], who proposed

interactions between hydroxyl groups in paper sludge and MA groups of maleated natural rubber (MNR). From a structural point of view, the interactions of NR with HNT can be made possible by introducing this type of modified natural rubber.

The aim of this study is to find the same solution, as it has been shown to provide remarkable properties to the composites. Therefore, the use of MNR as the matrix for improved compatibility with HNT filler was proposed. Based on the chemical structure of MNR, it was expected to have improved compatibility between the succinic anhydride group of MNR and silanol and/or siloxane groups of HNT, and to have improved other related properties of the composites. To date, no prior report has been published on detailed investigations concerning the use of MNR as a matrix with HNT filler. In this study, curing characteristics, mechanical properties, and dynamic properties were investigated and discussed. This study will improve the scientific understanding of how MNR could influence the properties of rubber/HNT composites, and will provide useful information for preparing rubber products based on MNR/HNT composites.

## 2. Materials and Methods

# 2.1. Materials

The Standard Thai Rubber (STR) 5L as the main natural rubber (NR) grade used for preparing the composites. It was purchased from Chalong Latex Industry Co., Ltd., Thailand. The halloysite nanotubes (HNT) was supplied by Imerys Tableware Asia Limited, New Zealand. The main components in the HNT were SiO<sub>2</sub> (49.5 wt%), Al<sub>2</sub>O<sub>3</sub> (35.5 wt%), Fe<sub>2</sub>O<sub>3</sub> (0.29 wt%), and TiO2 (0.09 wt%), with traces of CaO, MgO, K<sub>2</sub>O and Na<sub>2</sub>O. Maleic anhydride was supplied by Sigma-Aldrich (Thailand) Co., Ltd., Bangkok, Thailand. The activators zinc oxide (ZnO) and stearic acid were purchased from Global Chemical Co., Ltd., Samut Prakan, Thailand, and Imperial Chemical Co., Ltd., Bangkok, Thailand, respectively. The accelerator, N-cyclohexyl-2-benzothiazole sulfenamide (CBS) was bought from Flexsys America L.P., West Virginia, USA, and sulfur was purchased from Siam Chemical Co., Ltd., Samut Prakan, Thailand.

# 2.2. Preparation of MNR

The grafting of MA onto NR was prepared by mixing NR with MA in an internal mixer (Brabender Plasticorder) at a temperature of 145 °C for approximately 10 min with a rotor speed of 60 rpm. The MA contents varied within 1–8 phr. The resulting MNR was then purified to confirm the 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 a Fourier Transform Infrared Spectroscopy (FTIR) spectrum.

### 2.3. Preparation of Rubber Composites

Table 1 lists the main ingredients used for preparing the rubber composites, in which the main matrix used was separated accordingly. The total amounts of additives were mixed in a Brabender (Plastograph<sup>®</sup> EC Plus, Mixer W50EHT 3Z, Duisburg, Germany), and, just after the dumping, the compounds were passed through a two-roll mill to avoid excess heat. The compounds were then compressed into specific shapes using a hydraulic hot press, with the vulcanizing times obtained by a moving-die rheometer (MDR), which is described later.

Ingredient	Amount (phr)			
8	Control	MNR		
NR	100	-		
MNR *	-	100		
ZnO	5	5		
Stearic acid	1	1		
CBS	2	2		
Sulfur	2	2		
HNT	10	10		

Table 1. Compounding ingredients used in the composites.

Remark: \* MNR used was compounded separately according to the MA content (e.g., 1-8 phr).

## 2.4. Observation of Functionality Changes Using 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 with 32 scans per spectrum and 4 cm<sup>-1</sup> resolution from 4000 to 550 cm<sup>-1</sup>.

#### 2.5. 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 ( $ts_2$ ), and curing time ( $tc_{90}$ ) were determined according to ASTM D5289.

#### 2.6. 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, Pennsylvania, USA) at a cross-head speed of 500 mm/min. This was 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.

## 2.7. Dynamic Properties

The dynamic properties of the NR/HNT and MNR/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 from Rheoline Mini MDR Lite (Prescott Instrument Ltd., Gloucestershire, England). Then, the sample was cooled down to 60 °C, and varying strains in the range from 0.5% to 100% were applied at a frequency of 10 Hz. The raw outputs storage modulus (G') and damping characteristic (tan  $\delta$ ) were recorded, and the rubber–filler interactions in the composites were monitored through the Payne effect. The Payne effect can be quantified as follows:

Payne effect = 
$$G'_{f} - G'_{i}$$
 (1)

where  $G'_{f}$  is G' at 100% strain, and  $G'_{i}$  is G' at 0.5% strain. A larger Payne effect indicates poorer rubber–filler interactions.

#### 2.8. 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 produce electrostatic charge during scanning, fractured samples were coated with gold palladium prior to be scanned.

# 3. Results and Discussion

#### 3.1. Functionalities of Maleated Natural Rubber

The FTIR spectra and the peak assignments for MNR at various MA contents are shown in Figures 1 and 2, and the peak assignments are also listed in Table 2. Considering the FTIR spectra of the purified MNR, an intense and broad characteristic band at wavenumber 1787 cm<sup>-1</sup> and a weak absorption band at 1875 cm<sup>-1</sup> confirmed the existence of succinic anhydride groups grafted onto the NR molecules. The observed bands were responses to the symmetric and asymmetric carbonyl (C=O) stretching vibrations of succinic anhydride rings. Moreover, there was an important peak captured at wavenumber of 1723 cm<sup>-1</sup> due to the formation of carbonyl groups of opened ring structure succinic anhydride. The peaks seen in this study were quite similar to previous results seen in the literature [10,11].



Figure 1. FTIR spectra of maleated natural rubber prepared at various maleic anhydride contents.



Figure 2. FTIR spectra in wavenumber range 1900–1600 cm<sup>-1</sup> of NR and MNR at 8 phr of MA.

Wavenumber cm <sup>-1</sup>	Assignment
2900	C-H stretch of NR
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 stretch of NR
835	C-H out of plane bend of NR

Table 2. The observed peaks and their assignments for MNR samples.

#### 3.2. Curing Characteristics

The curing curves of the NR/HNT and MNR/HNT composites are shown in Figure 3, with the results summarized in Table 3. The minimum torque  $(M_L)$  slightly increased with the MA content in MNR, and  $M_{\rm L}$  is known to represent the compound's viscosity. A further increase in MA concentration decreased the grafted MA content [12]. The MNR was melt-prepared, giving better contact with the rubber molecules than occurs in the solution state, as described by Nakason et al. [10]. A further increase of MA decreased the grafting efficiency, indicating the formation of maleate crosslinks under shear at an elevated temperature. This matches the higher M<sub>L</sub> observed. A similar pattern was also found for the maximum torque ( $M_H$ ) and for the torque difference ( $M_H - M_L$ ) of the composites. This could be caused by differences in HNT dispersion and by different extents of crosslinking. Because these two torque values are known to represent the degree of crosslinking and/or the interactions within the composite system [13], this clearly indicates that a lower degree of crosslinking may be present due to acidity in the nature of maleic anhydride. As for the vulcanizing reaction, the MNR/HNT compounds display significantly longer scorch and cure times than the NR/HNT compounds. This is simply due the acidity in the nature coming from the ring opening reaction of succinic anhydride groups. Any chemical substance that makes the rubber compound more acidic will cause adsorption of accelerators [14] and retard the reactivity of accelerators.



Figure 3. Tensile strength and elongation at break of NR/HNT and MNR/HNT composites.

Compound	M <sub>L</sub> (dN.m)	M <sub>H</sub> (dN.m)	$M_H$ - $M_L$ (dN.m)	t <sub>S1</sub> (min)	t <sub>c90</sub> (min)	CRI (min <sup>-1</sup> )
MA 0	0.25	7.43	7.18	0.84	2.81	50.76
MA 1	0.22	7.63	7.41	2.92	6.40	28.74
MA 2	0.32	7.82	7.50	4.24	9.71	18.28
MA 4	0.38	7.77	7.39	5.14	13.05	12.64
MA 6	0.58	7.34	6.76	5.29	15.39	9.90
MA 8	0.58	6.25	5.67	5.46	19.16	7.30

Table 3. Curing characteristics of NR/HNT and MNR/HNT composites.

#### 3.3. Mechanical Properties

Figure 4 shows the stress–strain curves of the NR/HNT and MNR/HNT composites. The stress and strain values appear to differ between the NR and MNR as a matrix. From the stress–strain curves, it is possible to estimate the change point of the strain for each of the samples. Clearly, the strain at the onset of the stress upturn for the MNR/HNT composites is much lower than that of the NR/HNT composite, and the onset strain decreases with increasing MA content. This observation indicates that the use of MNR affects the stress–strain behavior of NR and lowers the strain at the onset of the stress upturn. Higher compatibility between MNR and HNT is responsible for these findings. Further, the area underneath the stress–strain curve was examined to confirm the compatibility of rubber and the filler. This indicates the toughness of a material [15]. The largest area underneath the curve corresponds to the greatest toughness. The MNR/HNT composites showed a greater area underneath the stress–strain curve than the NR/HNT composites, and, therefore, greater toughness.



Figure 4. Stress-strain curves of the NR/HNT and MNR/HNT composites.

To focus in more detail, the tensile strength and elongation at break are plotted in Figure 5. The tensile strength increased when the concentration of MA increased. This is comparatively higher than for the NR/HNT composite. An increment in the tensile strength of the MNR/HNT composites is definitely caused by the improved compatibility of rubber and HNT. Grafting the succinic anhydride groups onto the NR molecules of the MNR enabled an increase in the polarity of the rubber and made it compatible with the HNT by forming the interactions between the succinic anhydride groups (either in the form of an opened ring or a cyclic structure) and the hydroxyl groups on the HNT surfaces. The formation of such interactions are seen and postulated in Figure 6. Similar interactions between the hydroxyl groups of HNT and the maleic anhydride groups have been discussed recently, such as in the case of EPDM-g-MA versus HNT by Pasbakhsh et al. [8].



Figure 5. Tensile strength and elongation at break of NR/HNT and MNR/HNT composites.



-OH groups may be from AI-OH and Si-OH

Figure 6. Possible interactions between MNR and HNT.

A further increase of the MA content also reduces the tensile strength since a maleate network may also be formed, and this would create a less uniform network structure [10]. Another possible reason may be the lower degree of crosslinking of the composites: a higher MA content can increase the acidity in nature of the MNR, leading to reduce the extension of crosslinking. This was clearly explained in  $M_H$  and  $M_H - M_L$ , reported in the preceding section. There was a similar effect observed in the elongation at break of the MNR/HNT composites. The strong interactions of NR and HNT can be confirmed from the stresses at 100% and 300% strains (see Figure 7). It can be seen that the stresses at 100% and 300% elongations (M100 and M300) increased with the MA content. As more MA was grafted onto the NR, more interactions took place, resulting in stiffer and harder composites. The reinforcement index (i.e., the ratio of modulus at 300% strain to modulus at 100% strain) is also embedded in Figure 7. Here, it can be seen that the reinforcing index gradually increased with the MA content. This is attributed to the higher compatibility between rubber and the filler when MNR was used as matrix. However, the lower tensile modulus and reinforcing index at a higher amount of MA may be simply due to the lower degree of crosslinking, as related to the torque difference found in

the previous result. Furthermore, the tear strength showed a remarkable improvement with the MA content, as can be seen in Figure 8. The improved tear strength is due to the strong interactions of MNR and HNT as well as to the improved HNT dispersion in the rubber matrix.



Figure 7. Tensile modulus and reinforcing index of NR/HNT and MNR/HNT composites.



Figure 8. Tear strength of NR/HNT and MNR/HNT composites.

## 3.4. Dynamic Properties

The dynamic properties of the composites were determined using a Rubber Process Analyzer to investigate the storage modulus and the Payne effect. Figures 9 and 10 illustrate the storage modulus and the Payne effect of the NR/HNT and MNR/HNT composites. It can be seen that the storage modulus of all compounds was constant in the low-strain region, but decreased slightly with strains higher than 50%. This is common with viscoelastic materials and is due to the molecular stability of rubber. In addition to that, the Payne effect was estimated from the difference between the storage moduli at small and large strain amplitudes [16,17]. The level of Payne effect in the NR/HNT compound was 0.231 MPa and this decreased with the MA content to 0.174 MPa, 0.150 MPa and 0.160 MPa, with respect to the MPS loadings of 2–8 phr, in this order. This is a good indication that the interactions between MNR and HNT were improved. A lesser Payne effect indicates fewer filler–filler interactions [18]. However,

higher Payne effect at higher amount of MA was linked to the lower degree of crosslinking observed previously. The damping characteristics (tan  $\delta$ ) as functions of strain are shown in Figure 11. It is obvious that the composites had lower damping characteristics with the addition of MA in the MNR, indicating a considerable degree of molecular mobility. This is simply due to the better interactions between rubber and the filler when using MNR as the main rubber matrix. The good compatibility with the HNT filler increases the adhesion at interface, resulting in an improvement in the elastic properties of the composites.



Figure 9. Storage moduli of NR/HNT and MNR/HNT composites.



Figure 10. Payne effect of NR/HNT and MNR/HNT composites.



**Figure 11.** Damping characteristics (tan δ) of NR/HNT and MNR/HNT composites.

#### 3.5. Scanning Electron Microscopy

Figures 12 and 13 show the tensile fractured surfaces of the NR/HNT and MNR/HNT composites. With low magnification in the images, the surface roughness of the composites was captured and is discussed subsequently. The scanning electron microscope (SEM) images of the composites with the NR and MNR as a matrix are shown in Figure 12A, B. Figure 12B shows a rougher surface and more matrix tearing lines than Figure 12A. This might be simply due to a higher rubber–filler interaction when the MNR was replaced in the formulation, increasing resistance to the propagation of cracks and thus providing a higher tensile strength in comparison to the NR/HNT composite. When a high MA content was grafted onto the NR (see Figure 12C,D), the roughness became more visible, indicating coherence of the rubber and filler, and, hence, the improved mechanical properties. In particular, Figure 12C shows that the highest tensile strength matched a uniformly homogenous pattern of roughness throughout the sample.



**Figure 12.** Scanning electron microscope (SEM) images of the tensile fracture surfaces of NR/HNT composites in the presence of MNR/HNT as dual compatibilizers: reference (**A**), MPS 0 phr (**B**), MPS 0.5 phr (**C**), and MPS 1.5 phr (**D**), all at 100× magnification.



**Figure 13.** SEM images of the tensile fracture surfaces of NR/HNT composites in the presence of MNR/HNT as dual compatibilizers: reference (**A**), MPS 0 phr (**B**), MPS 0.5 phr (**C**), and MPS 1.5 phr (**D**), all at 10,000× magnification.

To assess the dispersion of HNT throughout the rubber matrix, SEM images were taken at 10,000× magnification and are shown in Figure 13. In Figure 13A, the agglomeration of HNT is seen on the fractured surface of the NR/HNT composite. When the NR matrix was replaced with MNR (Figure 13B), no agglomeration is seen due to good compatibility of the filler with the matrix. Moreover, the dispersion of HNT improved with the increased MA content. The homogeneity of the composites was significantly improved, especially when 4 phr and 8 phr MA was grafted onto NR (Figure 13C,D). The improved dispersion of HNT is clearly responsible for the improved tensile strength and tear strength, with more energy needed to break the samples. A better dispersion of HNT throughout the matrix increased the stress at a given strain. Similar observations on changes of microfractured surfaces with other fillers in NR composites in the presence of a compatibilizer have been reported previously [19].

## 4. Conclusions

The overall properties of the composites clearly improved when MNR was used as the main matrix of the HNT filled composites, when compared to those with plain NR. MNR has very special functional groups that can form hydrogen bonds with the hydroxyl groups available on the inner and outer surfaces of HNT. These interactions enhanced the tensile strength, modulus, and tear strength of the composites, and were corroborated by the decrease in Payne effect quantified from dynamic measurements. In this work, it has been clearly highlighted that the use of MNR improved HNT–rubber interactions and reduced filler–filler interactions, which benefits the mechanical and dynamical properties of the rubber composites. Therefore, MNR is a potentially alternative matrix for compatibility with the polar HNT surfaces, and could also improve the processing behavior without requiring the addition of a silane coupling agent, which is considered a complicated and costly method.

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### References

- 1. Arrighi, V.; McEwen, I.; Qian, H.; Prieto, M.S. The glass transition and interfacial layer in styrene-butadiene rubber containing silica nanofiller. *Polymer* **2003**, *44*, 6259–6266. [CrossRef]
- Ismail, H.; Pasbakhsh, P.; Fauzi, M.A.; Bakar, A.A. Morphological, thermal and tensile properties of halloysite nanotubes filled ethylene propylene diene monomer (EPDM) nanocomposites. *Polym. Test.* 2008, 27, 841–850. [CrossRef]
- 3. Jia, Z.; Luo, Y.; Guo, B.; Yang, B.; Du, M.; Jia, D. Reinforcing and flame-retardant effects of halloysite nanotubes on LLDPE. *Polym. Plas. Technol. Eng.* **2009**, *48*, 607–613. [CrossRef]
- 4. Vahedi, V.; Pasbakhsh, P.; Chai, S.-P. Toward high performance epoxy/halloysite nanocomposites: New insights based on rheological, curing, and impact properties. *Mater. Des.* **2015**, *68*, 42–53. [CrossRef]
- 5. Paran, S.; Naderi, G.; Ghoreishy, M. XNBR-grafted halloysite nanotube core-shell as a potential compatibilizer for immiscible polymer systems. *Appl. Surf. Sci.* **2016**, *382*, 63–72. [CrossRef]
- Rooj, S.; Das, A.; Thakur, V.; Mahaling, R.; Bhowmick, A.K.; Heinrich, G. Preparation and properties of natural nanocomposites based on natural rubber and naturally occurring halloysite nanotubes. *Mater. Des.* 2010, *31*, 2151–2156. [CrossRef]
- 7. Du, M.; Guo, B.; Lei, Y.; Liu, M.; Jia, D. Carboxylated butadiene–styrene rubber/halloysite nanotube nanocomposites: Interfacial interaction and performance. *Polymer* **2008**, *49*, 4871–4876. [CrossRef]
- 8. Pasbakhsh, P.; Ismail, H.; Fauzi, M.A.; Bakar, A.A. Influence of maleic anhydride grafted ethylene propylene diene monomer (MAH-g-EPDM) on the properties of EPDM nanocomposites reinforced by halloysite nanotubes. *Polym. Test.* **2009**, *28*, 548–559. [CrossRef]
- 9. Ismail, H.; Rusli, A.; Rashid, A.A. Maleated natural rubber as a coupling agent for paper sludge filled natural rubber composites. *Polym. Test.* **2005**, *24*, 856–862. [CrossRef]
- 10. Nakason, C.; Kaesaman, A.; Supasanthitikul, P. The grafting of maleic anhydride onto natural rubber. *Polym. Test.* **2004**, *23*, 35–41. [CrossRef]
- 11. Sahakaro, K.; Beraheng, S. Reinforcement of maleated natural rubber by precipitated silica. *J. Appl. Polym. Sci.* **2008**, *109*, 3839–3848. [CrossRef]
- 12. Nabil, H.; Ismail, H.; Azura, A. Recycled polyethylene terephthalate filled natural rubber compounds: Effects of filler loading and types of matrix. *J. Elast. Plas.* **2011**, *43*, 429–449. [CrossRef]
- 13. Rattanasom, N.; Saowapark, T.; Deeprasertkul, C. Reinforcement of natural rubber with silica/carbon black hybrid filler. *Polym. Test.* **2007**, *26*, 369–377. [CrossRef]
- 14. Coran, A. Chemistry of the vulcanization and protection of elastomers: A review of the achievements. *J. Appl. Polym. Sci.* 2003, *87*, 24–30. [CrossRef]
- 15. Nun-anan, P.; Wisunthorn, S.; Pichaiyut, S.; Nathaworn, C.D.; Nakason, C. Influence of nonrubber components on properties of unvulcanized natural rubber. *Polym. Adv. Technol.* **2020**, *31*, 44–59. [CrossRef]
- 16. Payne, A.; Whittaker, R. Low strain dynamic properties of filled rubbers. *Rubb. Chem. Technol.* **1971**, 44, 440–478. [CrossRef]
- Kaewsakul, W.; Sahakaro, K.; Dierkes, W.K.; Noordermeer, J.W. Cooperative effects of epoxide functional groups on natural rubber and silane coupling agents on reinforcing efficiency of silica. *Rubb. Chem. Technol.* 2014, *87*, 291–310. [CrossRef]

- 18. Rooj, S.; Das, A.; Stöckelhuber, K.W.; Wang, D.-Y.; Galiatsatos, V.; Heinrich, G. Understanding the reinforcing behavior of expanded clay particles in natural rubber compounds. *Soft. Mat.* **2013**, *9*, 3798–3808. [CrossRef]
- Waesateh, K.; Saiwari, S.; Ismail, H.; Othman, N.; Soontaranon, S.; Hayeemasae, N. Features of crystallization behavior of natural rubber/halloysite nanotubes composites using synchrotron wide-angle X-ray scattering. *Intern. J. Polym. Anal. Charac.* 2018, 23, 260–270. [CrossRef]



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