Influence of nanofiller types on morphology and mechanical properties of natural rubber nanocomposites

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Abstract Natural rubber (NR) nanocomposite containing different types of filler, i.e., nanoclay (clay) and cellulose nanofiber (CNF) were prepared in this study. The masterbatches of NR with 5 parts per hundred parts of rubber of nanofiller were firstly prepared by using the latex mixing method, followed by compounding on two roll mill and compression molding to obtain NR nanocomposite specimens. The unfilled NR sample was also prepared for comparison. Morphological properties of NR nanocomposites were investigated by using transmission electron microscopy, while the mechanical and dynamic properties were studied by using a universal tensile testing machine and dynamic mechanical analyzer (DMA). It was found that the clay with platelet morphology was uniformly dispersed, while the long and flexible CNFs were aggregated and poorly dispersed. The greater improvement of modulus at various strains was achieved from CNF filled NR nanocomposites, while the highest tensile strength was obtained from the clay filled nanocomposite. As compared to the clay containing nanocomposite, the addition of CNF markedly decreased the tensile strength and elongation at break of the NR due to poor dispersion of CNF. However, a significant improvement in mechanical properties at low strain was obtained when the CNF was used as filler due to high degree of fiber entanglement, as suggested by DMA observation.

1. Introduction
Natural rubber (NR) is a flexible material used extensively in a variety of applications such as tires, dipped goods, adhesives, rubber thread, foam, conveyor belts, hoses, gaskets, footwear, and engine mounts, because of its unique characteristic. However, the NR is rarely used in its pure form as it is too weak to fulfil a practical application requirement due to lack of hardness, strength and wear resistance. Basically, one of classical ways to achieve property improvement of NR is simply accomplished by adding reinforcing fillers. In the past, when the NR was reinforced with nanofillers such as nanoclay (clay), graphene, carbon black, and cellulose nanofiber (CNF), etc. showed a great potential for producing a wide variety of high value products. Among these materials, the clay and CNF have been receiving a lot of attention in the
research and industrial sectors due to their economical and environmental attentions. However, the comparative study of the NR nanocomposites reinforced with clay and CNF are limited. To understand the influence of filler geometry on morphology and mechanical properties of NR nanocomposites, the NR filled with clay or CNF were prepared. In previous studies [1,5], it was found that the maximum property enhancement was attained at 5 parts per hundred of rubber (phr) for both types of filler. Therefore, in this study, the NR was mixed with two different nanofillers at a fixed concentration 5 phr to fabricate the NR nanocomposites. The experimental observations on the microstructure of the clay/NR and CNF/NR nanocomposites as well as their mechanical properties were compared. The unfilled NR was also prepared as a reference.

2. Experimental

Two different kinds of NR masterbatches were prepared via the latex mixing method. Suspension of clay (Kunipia-F®, Kunimine Industries Co. Ltd., Tokyo, Japan) or CNF (Nanoforest-S, Chuetsu Pulp and Paper Co. Ltd., Tokyo, Japan) in water was added into NR latex (HA-NR latex, Yala Latex Co. Ltd., Yala, Thailand). The NR and nanofiller were mixed thoroughly under vigorous stirring at ambient temperature for 30 min, and dried at 50°C for 3 days to obtain the clay/NR and CNF/NR masterbatches containing 5 phr nanofillers. The unfilled NR was also prepared using the same procedure and used as a reference. For the preparation of NR and their nanocomposites, the dried NR and masterbatches of NR nanocomposites were masticated and mixed with paraffinic oil (China Petrochemical International Co. Ltd., Shanghai, China), and 2,2,4-trimethyl-1,2-dihydroquinone (TMQ, Lanxess AG, Cologne, Germany) in an internal mixer (CT internal mixer, Chareon TUT Co., Ltd., Samutprakan, Thailand) at a temperature of 50°C with a rotor speed of 60 rpm for 10 min. The obtained NR and NR nanocomposite compounds were mixed with dicumyl peroxide (DCP, Wuzhou International Co. Ltd., Shenzhen, China) on a two-roll mill. The compounds were then hot-pressed at 90% cure in a mold for 8 min at 160°C. the samples were cut into test specimens for microscopic analysis and mechanical property measurement.

3. Results and discussion

Dispersion of nanofillers (clay and CNF) in the NR nanocomposites is shown in Figure 1(A) and (B). From Figure 1(A), it is seen that the clay particles with intercalated structure where the NR chains intercalated into interlayer space of the clay tactoids [1], shown as a dark line, were homogeneously dispersed in the NR matrix (lighter region). Moreover, some of the clay remained as aggregated particles or tactoids having average thickness and length of about 22 ± 16 nm and 158 ± 87 nm, respectively. In the case of CNF/NR nanocomposite (Figure 1(B)), there were different grades of CNF aggregations, ranging from small aggregate (i.e., fiber-like structure) to large aggregate (i.e., spherical-like one). The average thickness of CNFs was about 132 ± 74 nm while the average length was approximately 1-3 µm. It is also observed from the TEM image (Figure 1 (B)) that the CNFs were highly entangled. The CNFs are long and flexible nanofibers, and they have a high density of hydroxyl groups present on their surfaces, therefore the CNFs are easily entangled and interact through hydrogen bonding, leading to forming CNF aggregates of different shapes and dimensions [2-5].

![Figure 1. TEM images of NR nanocomposites: (A) clay/NR, and (B) CNF/NR nanocomposites.](image)

Figure 2. shows the stress-strain curves of the NR and its nanocomposites, and the values of modulus at 100% strain, tensile strength and elongation at break are tabulated in Table 1. It is seen that the inclusion
of nanofiller influence
do the stress-\strain behaviour of NR. The addition of clay altered the stress-strain
curves of NR by a slowly increase of stress at low strain and sharply increase of stress at high strain due
to collaborative strain-induced crystallization [1]. On the other hand, the CNF/NR nanocomposite did not show any evidence of such process during tensile testing. As compared to the unfilled NR, the addition of clay slightly increased the stiffness (i.e., Young’s modulus and 100% modulus), and considerably increased tensile strength. The increased stiffness caused a reduced flexibility of the clay/NR nanocomposite. The good dispersion of clay in the NR matrix would be responsible for this enhancement. The addition of CNF markedly decreased both the tensile strength and elongation at break of the NR due to large aggregation and poor dispersion of CNF in the NR matrix, as already shown in Figure 1(B). Therefore, the large CNF aggregate acted as a rubber network defect, which lowered the mechanical properties of the NR [6-7]. However, it is very interesting to mention that the incorporation of CNF significantly enhanced the Young’s modulus and 100% modulus of the NR. The enhancement was about 119% and 150% over that of the clay/NR nanocomposite, respectively. It was believed that the entanglement between CNF-CN and CNF-NR imparted the rigidity of the NR nanocomposite, which increased the Young’s modulus and 100% modulus of NR. This explanation was later confirmed by DMA result.

**Figure 2.** Stress-strain curves of NR and their nanocomposites.

**Table 1.** Young’s modulus, 100% modulus, tensile strength, and elongation at break of NR and their nanocomposites.

| Samples     | Young’s modulus (MPa) | 100% Modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|-------------|------------------------|--------------------|------------------------|------------------------|
| NR          | 0.0033                 | 0.24±0.03          | 3.64±0.85              | 759±16                 |
| Clay/NR     | 0.0054                 | 0.35±0.01          | 9.81±0.39              | 672±11                 |
| CNF/NR      | 0.0118                 | 0.90±0.03          | 2.38±0.16              | 293±11                 |

**Figure 3.** Variation of (A) storage modulus (log G’) and (B) loss tangent (Tan δ) as a function of temperature for NR and their nanocomposites.
Table 2. Storage modulus ($G'$) at 25°C, degree of entanglement and maximum loss tangent ($\tan \delta_{\text{max}}$) of NR and their nanocomposites.

| Samples   | Log $G'$ at 25°C (MPa) | Degree of entanglement (mole/cm$^3$) | $\tan \delta_{\text{max}}$ |
|-----------|------------------------|-------------------------------------|-----------------------------|
| NR        | 5.79                   | 4.623x10$^{-5}$                     | 2.55                        |
| Clay/NR   | 6.13                   | 7.181x10$^{-5}$                     | 2.65                        |
| CNF/NR    | 6.30                   | 1.476x10$^{-4}$                     | 1.64                        |

Figure 3 shows storage modulus ($G'$) and loss tangent ($\tan \delta$) as a function of temperature for the NR and their nanocomposites. Their corresponding values, i.e., degree of entanglement are also tabulated in Table 2. The degree of entanglement was calculated by using: Degree of entanglement = $E'/6RT$ [8], where $E'$ is the storage modulus obtained from the plateau region, $R$ is the universal gas constant and $T$ is the absolute temperature. From both Figure 3 and Table 2, the incorporation of both fillers increased $G'$ at 25°C and the improvement was even more evident for the NR reinforced with CNF (Figure 3(A)), indicating that higher stiffness was obtained from the CNF filled NR nanocomposite. In addition, the lowest $\tan \delta$ peak was found in the CNF/NR nanocomposite, indicating that the higher interactions at the interface between the NR matrix and CNF nanofillers. This was attributed to the CNF has higher surface area to interact with NR than clay. High interactions between NR and nanofiller would effectively restrict the mobility of the NR chains near the interface region, lowering the ability of sample to dissipate energy, resulting in lowering the peak height of $\tan \delta$. From Table 2, it was seen that the degree of entanglement value was increased with adding nanofillers, and the increment was more pronounced when the CNF was used as a nanofiller. The higher degree of entanglement in the CNF/NR nanocomposite further substantiated the increase of storage modulus and mechanical properties in the CNF/NR nanocomposites at low strain [9-10].

4. Conclusions
The nanocomposites containing 5 phr nanofiller were successfully prepared by using the latex mixing method. Based on the obtained results, it was found that the clay with platelet morphology was uniformly dispersed, while the long and flexible CNFs were aggregated and poorly dispersed. The greater improvement of modulus at various strains was achieved from the 5 phr CNF filled NR nanocomposites, while the highest tensile strength was obtained from the 5 phr clay filled nanocomposite. The addition of CNF markedly decreased the tensile strength and elongation at break of the NR due to poor dispersion of CNF. However, a significant improvement in 100% modulus was obtained from the 5 phr CNF/NR nanocomposite due to higher degree of entanglement in CNF/NR nanocomposite, as suggested by DMA.

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