

## Preparation and Characterization of Rubber/Clay Nanocomposite Using Skim Natural Rubber Latex

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## 스킴천연고무 라텍스를 이용한 고무/점토 나노복합체의 제조 및 특성

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**ABSTRACT :** A new route for making rubber/clay nanocomposites was suggested based on skim natural rubber latex (SNRL), which is a protein rich by-product obtained during the centrifugal concentration of natural rubber (NR) latex. NR/acrylonitrile butadiene rubber (NBR) based nanocomposites were prepared from SNRL and NBR latex of 26 % acrylonitrile content by blending of aqueous dispersion of organoclay (OC) followed by coagulation, drying, mill mixing and vulcanization. X-ray diffraction(XRD) studies revealed that NR/NBR blend nanocomposites exhibited a highly intercalated and exfoliated structure, especially for NBR-rich blends. Dynamic mechanical studies showed that more compatible behavior was observed for NBR-rich blends. The 25/75 NR/NBR blend nanocomposite showed the best mechanical properties.

**요약 :** 천연고무(NR) 라텍스의 원심분리 농축과정의 부산물인 고농도 단백질 함유 스킴 천연고무라텍스(SNRL)를 이용한 고무/점토 나노복합체의 새로운 제조방법을 제시하였다. SNRL과 26% 아크릴로니트릴 함량의 NBR 라텍스의 혼합물에 수분산 유기화 점토(OC)를 첨가하여 혼합하고, 건조 후에 밀혼합과 가황공정을 거쳐 NR/아크릴로니트릴 부타디엔 고무(NBR) 나노복합체를 제조하였다. X-선 회절(XRD) 연구를 통하여 제조된 NR/NBR 블렌드 나노복합체는 층간 삽입이 높은 삽입형과 일부 박리형을 나타내는 것으로 밝혀졌고, 특히 NBR 상이 많은 블렌드에서 그 효과는 더 크게 나타났다. 동적기계적 거동 분석결과 NBR 상이 높은 블렌드가 상용성이 더 높은 것으로 나타났다. NR/NBR 25/75 블렌드가 가장 우수한 기계적 강도를 나타내었다.

**Keywords :** skim natural rubber, latex, NR, NBR, nanocomposites, clay

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## I. Introduction

Natural rubber (NR) latex obtained from *Hevea Braziliensis* tree finds extensive use for its unique properties like strength, elasticity and durability. Rubber is present in the latex as a colloidal dispersion of spherical or pear shaped particles with size in the range of 50 Å to 3 μm in an aqueous serum.<sup>1</sup> A surface film consisting of various types of lipids and proteins provide colloidal stability to the dispersion.<sup>1</sup> Ordinary NR latex needs to be concentrated by centrifugation to increase its dry rubber content (DRC) and to convert it into a homogeneous and easily transportable item suitable for the production of satisfactory latex based goods. During this process a protein rich serum called skim latex containing 4-10% DRC is released whose disposal is an issue of ecological importance. The low particle size of the rubber and the presence of higher proportion of non rubber ingredients in skim latex make its coagulation more difficult and markedly affect the properties of rubber hydrocarbon recovered. Normally rubber is recovered either by spontaneous or acid coagulation,<sup>2</sup> or by use of quaternary ammonium salts.<sup>3</sup> Use of ammonium stearate enhances the formation of a firmer coagulum. The protein content of skim latex is generally reduced by enzymatic protein hydrolysis.<sup>1</sup> A creaming process using inorganic salts in presence of enzymes has been reported for production of good quality skim rubber.<sup>4</sup>

For several decades the properties of natural rubber had been improved either by blending with synthetic rubbers or by use of proper fillers. Acrylonitrile butadiene rubber (NBR) is a material of immense interest due to its excellent resistance to oil or solvent resistance, easy processability and moderate cost. Extensive work had been carried out in blends of natural rubber with specialty rubbers such as NBR and ethylene propylene diene monomer rubber (EPDM).<sup>5</sup> But in most of the cases best combination of properties have not been achieved as there were problems related to unequal cross-

linking and filler migration.<sup>6-9</sup> Blends of NR and NBR are expected to be highly useful in a variety of automobile gaskets and seals and also in dairy applications where the material is required to be capable of resistant to swelling by butter, fat etc., and yet have the strength required by service conditions. This is of interest when use of reinforcing black fillers is not practical because of the need to meet food contact regulations. Appropriately compounded NR/NBR blends are expected to give cost effective products that satisfy such demands. The recent approach in fillers had been to use nanosize fillers at reduced quantities for enhancement of properties.<sup>10,11</sup> Carbon black and silica with particle size of 10-30 nm still remain the most accepted fillers for reinforcement in NR. Much effort is now being carried out to replace carbon black or silica by a new class of clay filler.<sup>12-14</sup> This clay mineral, also called 1,2 silicate, has very small particle size with plate like structure of dimensions around 100x100x1 nm. This filler is made to be more like hydrophobic by treatment with cationic surfactants which at the same time increase the interlayer distance of the silicate layers. Such modified clay show unique reinforcement characteristics as polymer molecules can travel into the interlayer spacing of clays.<sup>15-18</sup> Clay is added to rubber in the solution form, latex stage or by dry mixing.<sup>19-22</sup> Mixing clay dispersions in the latex followed by coagulation has been shown recently as a more environmentally friendly and simple process to obtain rubber nanocomposites.<sup>23</sup> Excellent dispersion of chemicals with minimum molecular weight reduction is possible by addition of chemicals to the emulsion stage of polymers before further processing.<sup>24</sup>

Skim latex is produced in large quantities in latex centrifuging factories and it is environmentally desirable to process it. However the potential of it as an excellent source of NR is yet to receive appropriate attention and this material has not so far been exploited for the development of nanocomposites.

In this paper a new route for production of

NR/NBR blend nanocomposites from a comparatively cheap source of skim natural rubber latex which is the by-product during NR production.

## II. Experimental

### 1. Materials

The skim latex was obtained from Southland Latex Company Ltd, Thailand. The specifications of skim latex used are shown in Table 1. The acrylonitrile butadiene rubber latex (48C40 grade), 43 % total solids content, containing 26% acrylonitrile content (AN) was supplied by Synthomer Limited, Harlow, England. Natural montmorillonite modified with a quaternary ammonium salt (organoclay (OC), Cloisite-15A®), was supplied by Southern Clay Products, Inc. Texas, USA. The other chemicals used were commercial rubber grade chemicals.

**Table 1. Characteristics of Skim Latex Investigated**

Parameter	Value
Dry rubber content	4.81 wt%
Ammonia content	0.49 wt%
pH	10.6

### 2. Preparation of rubber clay nanocomposite

The skim latex was mixed with surfactant and alkali at definite concentrations and blended with the required proportion of NBR latex to have dry rubber content in the ratio of 25/75, 50/50 and 75/25 NR/NBR, for a definite period of time as reported earlier.<sup>25</sup> During this time, creaming of latex took place and DRC of the creamed fraction increased to 9.6%, 11.5 % and 16.3% respectively for NR/NBR 75/25, 50/50 and 25/75 blend ratios, with the separation of an aqueous serum layer that could be easily removed. The creamed NR/NBR latex blend mixed with a 30 % aqueous dispersion of organoclay at the required concentration was coagulated by adding a formic acid to get a consolidated

**Table 2. Compounding Recipe**

Ingredients	% of NR in NR/NBR blends			
	75	50	25	0
Rubber	100	100	100	100
ZnO	5	5	5	5
Stearic acid	1	1	1	1
Antioxidant	1	1	1	1
Sulfur	2.13	1.75	1.38	1.0
CBS <sup>1)</sup>	1.1	1.3	1.5	1.7
MBTS <sup>2)</sup>	0.1	0.2	0.3	0.4
TMTD <sup>3)</sup>	0.4	0.2	-	-

<sup>1)</sup> N-cyclohexyl-2-benzothiazole sulfonamide,

<sup>2)</sup> Benzothiazyl disulfide

<sup>3)</sup> Tetramethylthiuram disulfide

coagulum. The coagulated mass was washed with distilled water until the free acid was completely removed, and then dried in an air oven at 70 °C for 24 hr. On addition of acid, the latex coagulated as a consolidated mass and the dried rubber had a pale yellow color. The dried coagulum was mixed with all the required compounding ingredients as shown in Table 2. The rubber compounds after mixing were vulcanized at 150 °C to their optimum cure time determined using oscillating-disk rheometer (ODR, Alpha Technologies, USA). The vulcanization was carried out at 150 °C using a hydraulically operated press with electrically heated platens.

### 3. Characterization

Particle size of rubber latex was determined using a particle size analyzer model Microtrach, UPA 150, USA, using light scattering technique, which measures the quantity of light at predetermined angles scattered by the particles. The XRD evaluation of the d-spacing between the silicate layers was by using Bragg's law<sup>26</sup> given below.

$$n\lambda = 2d \sin \theta \quad (1)$$

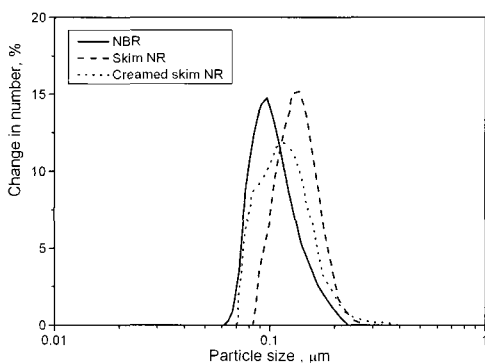
The XRD data between 2 and 10° were obtained at 4° min<sup>-1</sup> on a diffractometer (Rigaku 2500 PC,

Japan) with Cu-K $\alpha$  radiation (wave length 1.54 Å) at a generator voltage of 40 kV and a generator current of 40 mA. Transmission electron microscopy (TEM) images were taken from cryogenically microtomed ultra thin sections using a Zeiss TEM (model: EM 912 Omega H-800) operating at 120 kV. The tensile strength of the samples were tested using a tensile tester, model LRX plus, Lloyd Instruments, U.K, at 500 mm /min, as per ASTM D 412. The damping characteristics and the elastic modulus of the samples were carried out using a dynamic mechanical analyzer (DMA) at a frequency of 10 Hz at a heating rate of 2 °C/min. The glass transition temperature of the samples was determined using a DSC-2910, TA Instruments, at a heating rate of 10 °C/min in N<sub>2</sub> atmosphere.

### III. Results and Discussion

#### 1. Particle size of latex

The particle size distributions for neat skim latex, creamed skim latex and NBR latex, are shown in Figure 1. The particle size varies from 0.094 to 0.630  $\mu\text{m}$  for pure skim latex and from 0.079 to 0.578  $\mu\text{m}$  for creamed skim latex. The particle size recorded by NBR latex is comparatively lower. There is a considerable size reduction for skim latex particles after creaming as more than 14 % of the particles recorded a size lower than the smallest



**Figure 1.** Particle size distribution of skim NR latex, creamed skim NR latex and NBR latex.

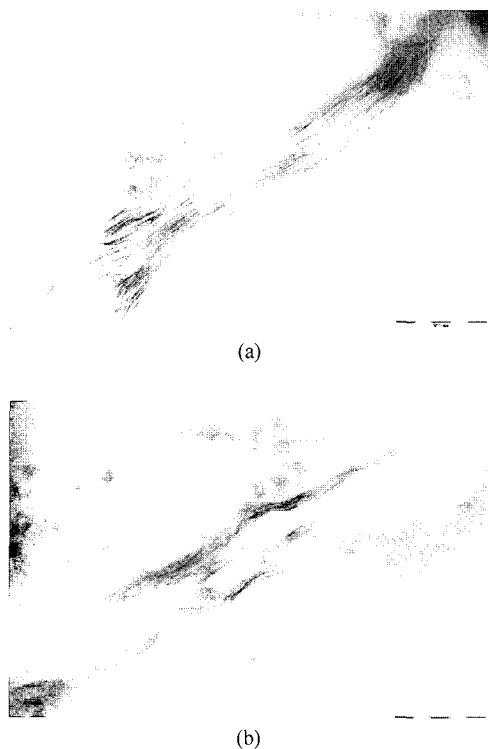
detected particles of pure skim rubber latex. Particle size obtained here is in close agreement with the earlier reported values on particle size of skim latex, which is shown to be about 0.1  $\mu\text{m}$ <sup>8</sup> or in the range of 0.072 to 0.995  $\mu\text{m}$ .<sup>27</sup> This is below the average particle size of fresh latex since larger particles are known to readily separate into concentrated fraction. The particle size of fresh *Hevea* latex was shown to have a bimodal distribution with a mean diameter of 1.07  $\mu\text{m}$ <sup>28</sup> and in some cases a lower size range of 0.08 to 0.75  $\mu\text{m}$ .<sup>29</sup> The colloidal stability of skim latex is attributed to the presence of adsorbed proteins and fatty acid soap anions. During the process of creaming it is expected that the proteins undergo hydrolysis. The reduction in size of the particles could be attributed to this process because the protein envelope that surrounds the rubber particle has been reported to be approximately 100 Å thick.<sup>30</sup> It should be noted that the particle size of NR latex is reduced to a size very close to that of NBR latex after creaming and hence expected to have excellent dispersion as compared to blends of NBR and concentrated NR latex. Hence use of skim latex is advantageous in blending with synthetic latex.

#### 2. Dispersion of clay

The change in the basal spacing for blend nanocomposites as represented by a change in the position of the peak from that of pure organoclay is shown in Table 3. The basal spacing of 001 plane for Cloisite 15A<sup>®</sup> is 3.20 nm corresponding to a  $2\theta$  value of 2.76.<sup>31</sup> The basal spacing of organically modified MMT increases in all the rubber clay nanocomposites showing that there is a pronounced insertion of NR or NBR molecules in the clay galleries leading to the formation of a highly intercalated matrix. The intergallery distance of OC increases to 47.95 and 43.68 for pure NR and NBR, respectively at a loading of 5 phr. The OC in NR matrix gives a higher intercalation in spite of NBR being more polar. The blends show a higher level of intercalation than NBR. In addition to the

**Table 3. X-ray Diffraction Data**

Sample	$2\theta$ (degree)	d-space (Å)
OC	2.76	31.96
NR with 5 phr OC	1.84	47.95
75/25 NR/NBR with 5 phr OC	1.90	46.43
50/50 NR/NBR with 5 phr OC	1.76	50.13
25/75 NR/NBR with 5 phr OC	1.9	46.43
NBR with 5 phr OC	2.02	43.68

**Figure 2.** TEM images of (a) 25/75 and (b) 50/50 NR/NBR nanocomposites.

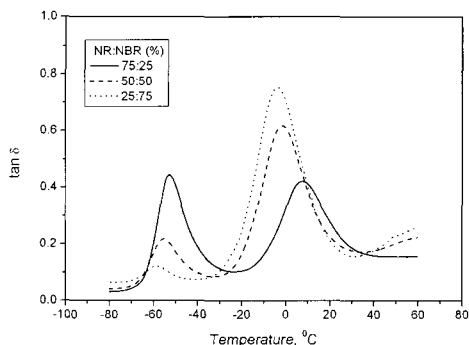
polarity, level of intercalation is known to be drastically affected by the cure systems employed for vulcanization.<sup>32</sup> The interlayer distance can also be reduced if the intercalant is partially removed for the reaction of sulfur amine complex formation during vulcanization<sup>33-35</sup> or can be increased if the cross linking of rubber takes place inside the galleries. The other conditions remaining same the variation in intercalation is attributed to the level

of vulcanization achieved by the different curatives.

More accurate information on the level of dispersion of clay in NR/NBR blend matrix is derived from TEM micrographs shown in Figure 2. The TEM images of NR/NBR blend nanocomposites with 5 phr OC, in which silicate layers are shown as dark lines, display that even though in some areas the silicate layers are stacked up, they are also exfoliated to some degree in other areas for blends of 25/75 and 50/50 NR/NBR blend composition. However, comparatively better dispersion of clay is observed for 50/50 blend, which displays well-dispersed structure showing mostly intercalated along with exfoliated structure. Thus NR chains due to their very high segmental mobility are able to intercalate into the gap and cause exfoliation along with NBR chains that are expected to intercalate clay easily due to its polar nature.

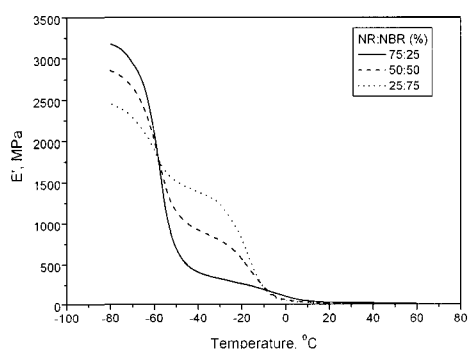
### 3. Dynamic mechanical property

Figure 3 gives the damping behavior for the NR/NBR blends containing 5 phr of OC. As expected, there is appearance of two  $T_g$ s corresponding to the individual phases of the blend components indicating micro-level homogeneity. However it is interesting to observe that with increase in the amount of NBR, the  $T_g$  of both NR and NBR phases shifts to lower temperatures, and the transition zone becomes more broadened, and simultaneously the difference of  $\tan \delta$  peak temperatures

**Figure 3.**  $\tan \delta$  vs. temperature for NR/NBR blends with 5 phr OC.

**Table 4. Glass Transition Temperature from DMA and DSC**

Samples	Glass Transition Temperatures (°C)		
	DSC	DMA	Temperature difference between $T_{gS}$ (°C) based on DMA
25/75/5	-64.2, -20.99	-57.3, -3.5	53.8
50/50/5	-64.0, -18.80	-55.5, -0.8	55.4
75/25/5	-61.48, -11.72	-52.9, +7.1	60.0

**Figure 4.** Storage modulus vs. temperature for NR/NBR blends with 5 phr OC.

for the two rubbers gets reduced. Table 4 summarizes the glass transition temperatures ( $T_g$ ) evaluated from DMA along with those from DSC.

Figure 4 gives the variation of storage modulus as a function of temperature. Clear two transitions are observed when the NR content is 75%, however the transition zone decrease as the NBR content in the blend increases. It is generally known that the formation of molecular-level mixing occurs when

the  $T_{gS}$  corresponding to individual rubbers are closer.<sup>36-39</sup> From this observation it can be inferred that the NBR-rich blends tend to form more homogeneous mixture in a molecular level. This will lead to enhanced mechanical properties, which will be described in the following section.

#### 4. Mechanical property

The physical properties of NR/NBR blends with and without OC are shown in Table 5. A considerable improvement in the overall mechanical properties like tensile strength and elongation at break is observed with the addition of OC, and this improvement is higher for NBR-rich blends. Excellent mechanical properties are observed for 25/75 NR/NBR blend with 5 phr of OC. The mechanical properties of blend are not only governed by factors related to level of vulcanization in both the phases and fine dispersion of filler, but also by the type of crosslinks where a comparatively lower strength is recorded for mono-sulfide crosslinks. The clay is expected to form a fine dispersion during the stages of its preparation and blending with latex before coagulation due to the high shear forces involved.<sup>40</sup> Due to problems arising from unequal distribution of crosslinks during vulcanization<sup>5</sup> there can be a phase separation and it is expected that this becomes more prominent when NBR content is low probably due to preferential cure of NR phase. However when NBR content in the blend is high the phase separation is less conspicuous as was discussed earlier from observations on  $T_g$  measurement. Thus, the 25/75 NR/NBR blend nanocomposite has a more

**Table 5. Mechanical Properties**

Property	NR/NBR/OC (wt%/wt%/phr)							
	75/25/0	75/25/5	50/50/0	50/50/5	25/75/0	25/75/5	0/100/0	0/100/5
100% Modulus, MPa	2.28	2.89	2.25	2.48	2.71	3.23	1.9	2.26
200% Modulus, MPa	3.6	4.0	3.2	3.41	3.90	4.2	2.5	3.11
300% Modulus, MPa	4.5	5.4	4.60	4.64	4.80	5.3	3.4	4.34
Tensile strength, MPa	8.58	9.16	10.0	10.9	13.1	16.9	7.90	12.15
Elongation at break, %	400	450	410	440	450	500	440	500

uniformly cured matrix with a finer dispersion of clay leading to enhanced mechanical properties.

#### IV. Conclusions

From skim natural rubber latex, a by-product from NR manufacturing, a simple and environmentally friendly procedure was suggested for the production of natural rubber/acrylonitrile butadiene rubber latex nanocomposites. Based on the XRD and TEM results, NBR-rich blends lead to an increase of the interlayer space of OC resulting in highly intercalated rubber/clay nanocomposites. The clay was exfoliated to some degree in 50/50 and 25/75 NR/NBR blends based on TEM images. The glass transition temperature shifted to higher temperature ranges with the increase in proportion of NR in the blend. Better mixing was observed for NBR-rich blends. The best mechanical properties were observed for 25/75 NR/NBR blend nanocomposite.

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