Blending in Latex Form of Natural Rubber and Nitrile Latices: A Preliminary Study of Morphology and Mechanical Properties

N. Moonprasith, K. Suchiva, and O. Tongcher
National Metal and Materials Technology Center
114 Thailand Science Park, Paholyothin Rd., Klong1, Klong Luang, Pathumthani 12120 Thailand.

Abstract
The mechanical properties, morphology and oil swelling of natural rubber (NR) latex and acrylonitrile-butadiene rubber (NBR) latex blends were studied in various ratio; 100:0, 75:25, 50:50, 25:75 and 0:100. It was found that the latex blends were uniformly mixed both in the latex form and in the resulting thin film. Morphology of the blend films in sub-microscales is characterized by SEM. All films showed that, the particles in dispersed phase retain their original sizes and shapes, and phase separations between NR and NBR are in the range of sub-micrometer to few micrometers (which is relatively small in comparison to melt blend). Blend films were stained with osmium tetroxide (OsO₄) to yield a dark NR phase. The NR/NBR latex blends were dried, mixed with vulcanizing agents, and subsequently vulcanized. Mechanical and chemical properties of the vulcanisates were examined. As expected, when the content of nitrile was increased, the oil swelling and hardness (Shore A) properties of these blends increased with the increment of NBR content, but decreasing in tensile strength.

Key words: rubber blend; morphology; acrylonitrile-butadiene rubber; vulcanization

1. Introduction
Blending is a plausible and simple mean to develop new materials in a relatively short time and with low costs of investment [1]. Natural rubber (NR) has excellent mechanical properties and heat build-up but poor oil resistance [2]. It has been commercially available and exploited in a variety of manufacturing products such as tyre, bulb seal, o-ring, gasket, bumper, and fender. On the other hand, acrylonitrile-butadiene rubber (NBR) is known for its superior properties in oil resistance, ozone and chemical resistance [2], it is hence chosen to be blended with NR in this experiment. Melt blends have been employed industrially, but a certain level of blend compatibility is achieved despite of great efforts on blend improvements via technical and mechanical tunings [3, 4]. Sirisinha et. al [5] studied properties of the blend of NR/NBR as a function of blending conditions and blend ratios. It was found that blend morphology is a significant factor, which has an impact on chemical and mechanical properties. With the increase of blending time, the size of NR dispersed phase decreased, resulting in an enhancement of oil resistance. In addition, they reported that rotor speed did not have much effect on phase morphology, and thus oil resistance of the blends. The blend certainly shows the greatest improvement of oil resistance when NBR forms a continuous phase. Therefore, oil resistance of the blends is improved with an increase of NBR component. In this study, development of phase morphology with blend ratio and its effects on oil resistance properties will be investigated, and the resulting chemical and mechanical properties will be studied accordingly.

2. Experimental
2.1 Materials
High ammonia NR latex with a dry rubber content of 60.03% was kindly supported by Thai Rubber Latex Co.,Ltd. Thailand and acrylonitrile-butadiene rubber or NBR latex (Perbunan N Latex VT-LA) was obtained from Bayer Thai Co.,Ltd with 45% acrylonitrile content and both latices were used as received. The particle size of NR and NBR latices were measured using particle size analyzer (Autosizer S4700, Malvern). The average particle sizes of NR and NBR latex were 700.0 nm and 240.4 nm, respectively. The zeta (ζ) potential of the dispersion was determined using the electrophoretic technique (Zetasizer 4, Malvern). The zeta potential of NR latex was -43.5 mV, and NBR latex was -49.1 mV.

2.2 Compounding and vulcanization procedures NR latex and NBR latex were readily mixed together for 10 minutes at an ambient temperature with the following blending ratios: 100:0, 75:25, 50:50, 25:75, 0:100 (w/w; based on dry rubber content). The latex blend films were formed by spin coating technique with spin speed 3,000 rpm for 60 seconds. Then, the blending films were dried, stained with osmium tetroxide (OsO₄) and investigated their morphology by SEM. For compounding, water in latex blends was removed by evaporation and the dried blends were compounded in Banbury-type internal mixer of 365 cm³ with a fill factor of 0.7, and a rotor speed 40 rpm, at 60°C for 12 minutes. The compounded blend was then sheeted on a cool two-roller mill and compression-molded into 2 mm-thick sheet. The cure characteristics were determined by Moving Die Rheometer (MDR) at 150°C and curing time was obtained from the time needed to obtain a 90 % cure (t₉₀). Vulcanization was finally carried out by compression technique.

2.3 Characterization
SEM technique was used to investigate the morphology of the unvulcanized blend films. Tensile strength, % elongation at break, 100% modulus and 300% modulus of the vulcanized samples were measured by an Instron 1011 tensile tester with a crosshead speed of 500 mm/min and full-scale load cell of 500 N in accordance with ASTM D 638. Oil resistance was observed by immersion the test specimens (vulcanized blend) in motor oil at room temperature for 168 h (ASTM D 471-79). The
hardness (Shore A) of the vulcanized blends was also monitored.

![Fig.1](image_url)

**Fig.1 SEM images of the NR:NBR thin films from latex blends;**
(a) NR:NBR 75:25 (b) NR:NBR 50:50 (c) NR:NBR 25:75

3. Result and Discussion

NR and NBR latices were blended by mechanical stirring without applying any special treatments. Blend films were prepared by spin coating technique. Morphology studies were carried out using SEM without being compounded and vulcanized. Furthermore, properties of NR/NBR vulcanized blends were examined for various compositions of NR and NBR with and without aging.

**Phase Morphology**

Fig.1a shows the SEM image of the NR/NBR blend with the ratio of 75:25. It is found that NR was the major continuous phase and NBR formed a dispersed phase with retaining their sizes and shapes approximately. When the ratio of NBR increases to about half by weight, the phase morphology was quite difficult to interpret. In our observation, NR is still a continuous phase and NBR is a dispersed phase. At the weight ratio of NR:NBR 25:75, NR displayed as dispersed phase and NBR was a matrix phase as expected (Fig.1c). From these observations, we can summarize that a high composition in the blend display a continuous phase morphology, and the small content of the rubber latex will be a dispersed phase. However, at an equal weight ratio, phase morphology will depend on each pair of latex blend and in this experiment, NR and NBR, NR is a continuous phase.

**Tensile Properties**

The mechanical properties of the vulcanized NR/NBR blends are shown in Table.1. The effects of blend composition of NR/NBR on tensile properties before and after heat aging are shown in Fig.2. It can be seen that tensile strength of NR/NBR blends exhibited increases in tensile strength with increasing NR content in the blends until it reaches the maximum of pure NR. Elongation at break also shows a similar behavior i.e. the value increases as NR content is higher. In other words, the elongation at break of Vulcanized NR was depressed by addition of NBR. Heat aging can naturally lower tensile strength for the blends of all compositions. This was to be expected since the heat aging normally caused degradation of the rubber.

**Oil-Resistant Properties**

Influences of blend ratio on oil resistance of NR/NBR blends are shown in Fig.4. It can be seen that blend ratio has a significant effect on oil resistant properties of the blends. From Fig.4, the percentage of oil swelling is decreased almost linearly as the content of NBR is higher in the blend composition, but at 50:50 NR:NBR, graph is non linear (may be cause from NR was likely continuous phase that it just slightly coated on NBR surface but not enough to be a continuous phase cause of poor oil resistance and tensile properties, too) while that of 75:25 NR:NBR is the lowest (in fact, it should be the highest for 100%NR while lowest for 100%NBR).

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<th>Table.1 Physical properties of NR/NBR blendsa</th>
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<td>NR:NBR</td>
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a The surface of NBR sheet after compression molding was damaged (due to contiguity), hence its tensile property can not be examined.

b Mass change in Motor Oil at 25°C for 168 h.
4. Conclusion

Tensile properties of the blends are generally improved with the increasing NR component because of good mechanical properties of NR. The blend ratio has significant effects on oil-resistant and tensile properties of NR/NBR blends. The 75%, 50% and 25% NBR content is the better oil resistance than pure natural rubber. The 50:50 NR:NBR is a poor oil resistance and tensile strength (less than it should be by observed oil swelling graph from 75% to 25% was assumed as linear that 50% is skipped off) as it should be that might effect from phase formation (assume phase formation behavior of gum rubber as the latex blend). Oil-resistance enhancement is attributed to the polar nature of NBR. When the content NBR increased, oil swelling and hardness properties are enhanced.

References: