

## Effect of Low Molecular Weight Natural Rubber on Mixing and Vulcanized Properties of Low Energy Processing Natural Rubber (Kesan Berat Molekul Rendah Getah Asli ke atas Pencampuran dan Sifat Tervulkan Pemprosesan Tenaga Rendah Getah Asli)

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### ABSTRACT

*Compounding of natural rubber (NR) requires high energy due to the high viscosity characteristic of NR. In order to reduce the viscosity, low molecular weight of NR (LNR) latex was prepared from field latex by using oxidative phenyl hydrazine/O<sub>2</sub> system. LNR latex was mixed with high ammonium NR latex at 3, 5 and 10 phr to provide low energy processing NR (LEPNR). Viscosity molecular weights (M<sub>v</sub>) of obtained LNR were 42.59, 18.42 and 6.66 kg/mol, respectively. It was found that the maximum Mooney viscosities and ML 1+4@100°C of LEPNRs were significantly decreased with a decrease of M<sub>v</sub> of LNR and an increase of LNR content as well. Specific mixing energy consumptions for mastication step and carbon black incorporation step in Brabender Plasticorder were characterized. The results showed that the mixing energy consumption decreased with an increase of LNR content and a decrease of M<sub>v</sub> of LNR. Furthermore, an addition of LNR lowered the viscosity of the compounded rubber, slightly shortened the scorch time, and significantly changed the cure time. Although LNR dropped 50% and 100% modulus of vulcanized rubber, it slightly effected the tensile strength of the vulcanized rubber.*

*Keywords: Low molecular weight NR; natural rubber; provide low energy processing NR*

### ABSTRAK

*Pengkompaunan getah asli (NR) memerlukan tenaga yang tinggi kerana ciri kelikatan tinggi getah asli. Dalam usaha untuk mengurangkan kelikatan, berat molekul rendah getah asli (LNR) getah diperbuat daripada lateks ladang dengan menggunakan sistem oksidatif fenil hidrazin/O<sub>2</sub>. LNR getah bercampur dengan ammonium tinggi getah asli getah pada 3, 5 dan 10 phr untuk menyediakan NR pemprosesan tenaga yang rendah (LEPNR). Kelikatan berat molekul (M<sub>v</sub>) yang diperolehi LNR masing-masing adalah 42.59, 18.42 dan 6.66 kg/mol. Didapati kelikatan maksimum Mooney dan ML 1+4@100°C LEPNRs telah menurun dengan ketara dengan penurunan sebanyak M<sub>v</sub> daripada LNR dan peningkatan kandungan LNR juga. Tenaga penggunaan pencampuran tertentu untuk langkah pengunyahan dan karbon hitam disebatikan dalam Brabender Plasticorder telah dicirikan. Keputusan kajian menunjukkan bahawa penggunaan tenaga pencampuran menurun dengan peningkatan kandungan LNR dan penurunan M<sub>v</sub> daripada LNR. Tambahan pula, penambahan LNR menurunkan kelikatan getah kompaun, memendekkan masa pembakaran dan dengan ketara mengubah masa memvulkan. Walaupun LNR menurunkan modulus sebanyak 50% dan 100% getah tervulkan, ia memberi sedikit kesan pada kekuatan tegangan getah tervulkan.*

*Kata kunci: Getah asli; berat molekul yang rendah NR; memberikan pemprosesan getah asli tenaga yang rendah*

### INTRODUCTION

Natural rubber (NR) has worthy properties for manufacturing of various products. In order to improve an ease of processing, vulcanization, performance of the products and reduce cost of rubber product reinforcement filler, non-reinforcement and additive are mixed in NR. Since NR is a high molecular weight polymer having tough and high viscosity, it requires high energy to compound the NR. Moreover, high shear two roll mill or internal mixer machine is essential to soften the NR for well mixing with additive and filler. In addition, storage hardening also affects the processing because it causes and increase of

viscosity. The viscosity of polymer can be reduced by an addition of plasticizer. The plasticized polymer consumes low energy during mixing and processing. Applying this concept, low energy processing natural rubber (LEPNR) could be prepared. External plasticization is an alternative method to reduce the viscosity of NR by applying and appropriate amount of plasticizer. For example, low molecular weight NR (LNR) is prepared by using an oxidative phenyl hydrazine/O<sub>2</sub> system (Nor & Ebdon 1998). Besides, the structure of LNR is similar to that of NR and co-vulcanized NR. In this work, the factors that affect the efficiency of production of LEPNR were studied.

## MATERIALS AND METHODS

### PREPARATION AND CHARACTERIZATION OF LNR LATEX

Field NR was diluted to 30% DRC and stabilized with 5 phr sodium dodecyl sulfate. Then, LNR was prepared by oxidative chain scission of NR backbone using phenyl hydrazine/O<sub>2</sub> system (Nor & Ebdon 1998). The reaction was carried out at 70°C and compression air flow rate of 0.3 L/min. Intrinsic viscosity ( $[\eta]$ ) was characterized by dilution series using and Ubbelohde capillary viscometer at 30°C when toluene was used a solvent. Viscosity average molecular weight (M<sub>v</sub>) of LNR was calculated by using Mark-Houwink–Sakuyada equation (Young & Lovell 1992).

### PRODUCTION OF LEPNR

High ammonium NR (HANR) latex was blended with LNR latex at 0, 3, 5 and 10 phr, respectively, followed by casting in a tray and drying at ambient condition. Completely dried LEPNR appeared as colorless film.

### MOONEY VISCOSITY DETERMINATION

Mooney viscosity of NR was determined by using Alpha MV2000™. Mooney viscometer at 100°C for 4 min with a preheating step for 1 min and large rotor was use for measuring ML 1+4 @100°C.

### CHARACTERIZATION OF MIXING PROPERTIES

Mixing properties of LEPNR were studied through characterization of carbon black incorporation. Mixing was carried out in the Brabender Plasticorder and using Cam Blade Rotor with fill factor of 0.7 at rotor speed of 40 rpm and initial temperature of 50°C. The rotor stopped after rubber mastication for 2 min to load 40 phr of carbon black master batch and restarted after 1 min. Then, the

rubber was subjected to mix for 10 min. Specific energy consumption, E<sub>esp</sub>, of mixing both mastication step and carbon black incorporation step were calculated by using Evolution mixing torque data (Dimier et al. 2004).

### MECHANICAL PROPERTIES OF VULCANIZED NR

Compounded NR recipe containing NR, carbon black, zinc oxide (ZnO), stearic acid, N-tert-Butyl-2-Benzothiazolesulfena-mide (TBBS) and sulfur (S) was shown in Table 1. The mixture was compounded in a Brabender Plasticorder. Cure characteristic of the compounded rubber was determined by using alpha MDR 2000™ Moving Die Rheometer. Vulcanized NR sheets were prepared by compression molding. Tensile strength was carried out on Instron 5960 universal testing machine according to ASTM D412. The cross head speed was 500 mm/min and all samples were tested at room temperature.

## RESULTS AND DISCUSSION

### MOLECULAR WEIGHT OF LNR

The M<sub>v</sub> of LNR containing 30% DRC field NR latex was treated by using phenyl hydrazine/O<sub>2</sub> system at various phenyl hydrazine concentration at given reaction time as shown in Table 2. It can be seen that the molecular weight of natural rubber sharply decreased similar to previously reported by Nor and Ebdon (1998).

### EFFECT OF LNR ON MOONEY VISCOSITY OF LEPNR

Mooney viscosities of LNR were measurement shown in Figure 1. The results illustrated that decreasing of Mooney viscosity (MU) of NR was achieved by an addition of LNR. It can be seen that the initial or the maximum Mooney viscosity (Max. MU), Mooney viscosity ML 1+4 @100°C and area under Mooney viscosity curve obviously decreased when LNR with M<sub>v</sub> of 42.59, 18.42

TABLE 1. Formulation of compounded NR

	phr
NR	100
Carbon black	40
ZnO	5
Stearic acid	2
TBBS	1
S	2

TABLE 2. M<sub>v</sub> of prepared LNR

Phenyl hydrazine phr	Reaction time hour	M <sub>v</sub> of LNR kg/mol
0.0	0.0	546.1
3.50	5.0	42.59
10.0	15.0	18.42
20.0	15.0	6.66

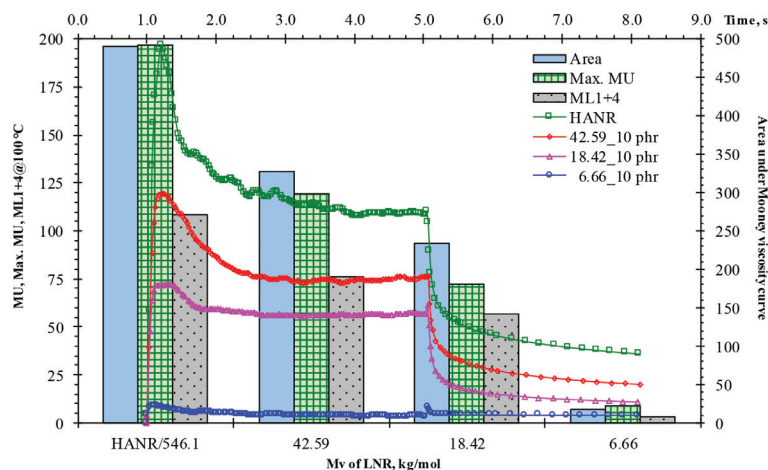


FIGURE 1. Effect of molecular weight of LNR on Mooney viscosity curve of LEPNR where content of LNR 10 p hr

and 6.66 kg/mol, respectively, were added in NR at 10 phr. Furthermore, addition of LNR with Mv of 6.66 kg/mol at 10 phr dramatically decreased Mooney viscosity of LEPNR. Mooney viscosity of LEPNR decreased correspondingly as shown in Figure 2 when LNR was added at 0, 3.0, 5.0 and 10 phr, respectively, however, the efficiency of plasticization depended upon the molecular weight of LNR. In addition, specific energy consumptions shown in Figure 3 indicated that at 3.0 and 5.0 phr of LNR with Mv of 42.59 and 18.42 kg/mol were less efficiency. On the other hand, LNR with Mv of 6.66 kg/mol showed better plasticization efficiency than that of LNR with Mv of 42.59 and 18.42 kg/mol. This method could control viscosity of NR, which improved mixing properties and energy consumption in the processing. The mixing lumps at the end of the mixing process were illustrated in Figure 4.

#### EFFECT OF LNR ON CURE PROPERTIES OF LEPNR

Figure 5 shows that all the scorch times TS 1.0 is longer than 1.30 min. This duration time was long enough to process the LEPNR. The results showed that an addition of LNR did not significantly decrease the scorch time of LEPNR. However, a greater decrease was observed when LNR with Mv of 6.66 kg/mol was used. This trend similar to the report of Wonkam et al. (2000) that studied the effect of deoxidized LNR on nitrile/butadiene rubber based mixes. Considering the cure curve, it was found that the cure rate increased when viscosity of compounded rubber decreased. The reason is that rubber molecule segments attached with curing agent were easier to move, therefore the probability of reaching appropriate curing sites on other molecule segments per unit time increased. Thus, rubber scorch occurred within shorter time.

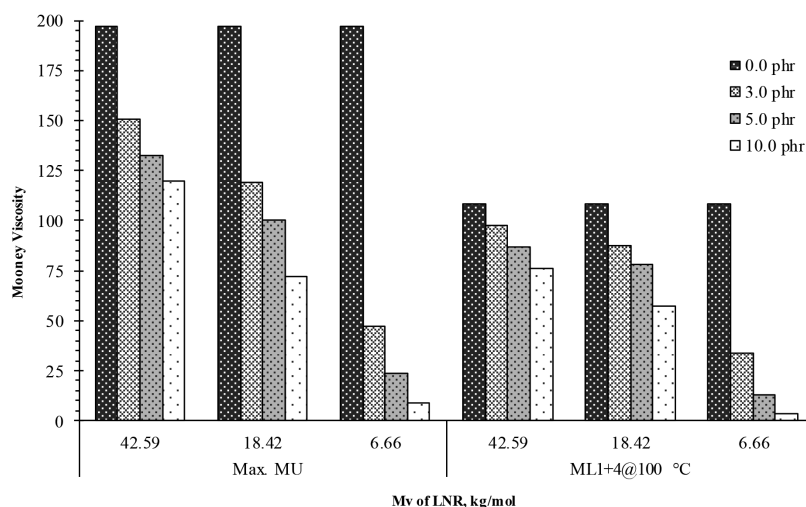


FIGURE 2. Effect of molecular weight and content of LNR on Mooney viscosity of LEPNR

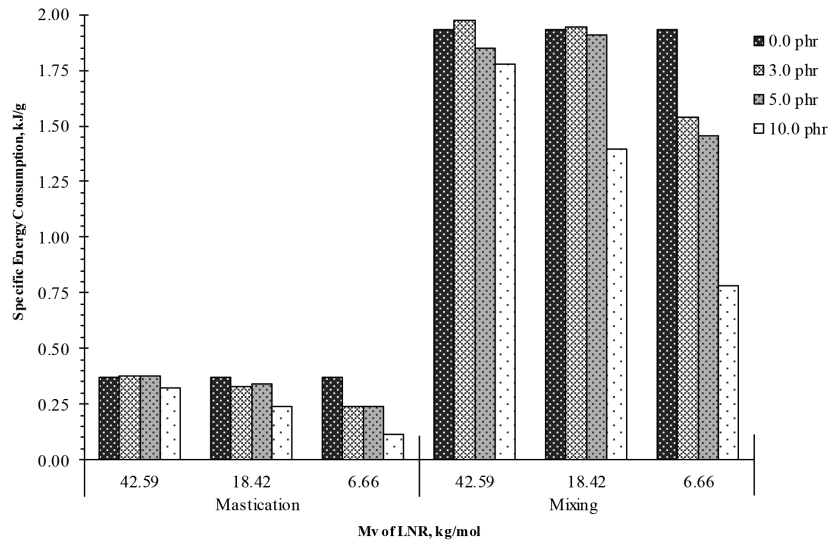


FIGURE 3. Specific energy consumption on mastication stage and carbon black mixing stage in Brabender; speed 40 rpm, regular temperature 50°C for 10 min

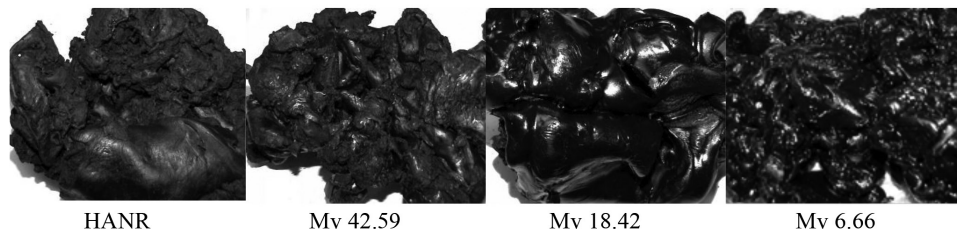


FIGURE 4. Photographs of mixing lump of whole rubber and mixing lump containing LNR with Mv of 42.59, 18.42 and 6.66 kg/mol 10 phr and carbon black 40.0 phr in Brabender for 10 min

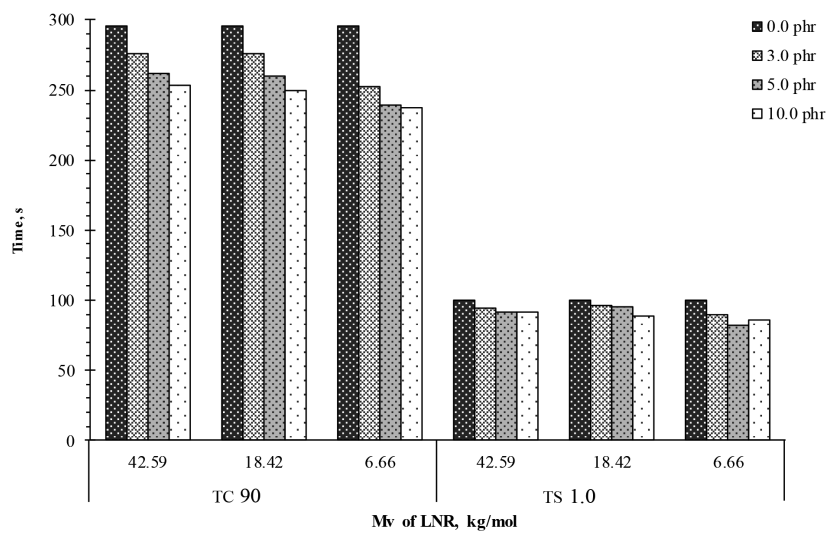


FIGURE 5. Scorch time, TS 1.0 and cure time, TC 90 of LEPNR at 155°C for 10 min

The results also showed that the optimum cure time TC 90 obviously decreased when LNR contents increased. LNR with Mv of 42.59 and 18.42 kg/mol dropped the TC90 in the same degree when the same content of the LNR was added. LNR with Mv of 6.66 kg/mol showed stronger effect to TC90 compared with other LNRs.

#### EFFECT OF LIQUID NATURAL RUBBER ON VULCANIZED PROPERTIES

Effect of LNR on modulus at 50% and 100% strain of vulcanized LEPNR is shown in Figure 6. It exhibited that the trends of both moduli at 50% and 100% strain decreased when LNR content increased. Modulus of vulcanized compounded LNR significantly decreased compared with vulcanized neat NR. The tendency of modulus also decreased as the molecular weight of LNR decreased. LNR

with lower molecular weight affected more significantly to the modulus than the higher molecular weight. It was believed that LNR with lower molecular weight was more effective plasticize, therefore, promoted the mobility of rubber molecules. Tensile strength and elongation at break of vulcanized NR were presented in Figures 7 and 8, respectively. The results showed a slight variation with molecular weight of LNR and LNR contents. The range of tensile strength was -2.5 to -1.1 MPa except for LNR with molecular weight of 6.66 kg/mol at 10 phr, where the difference was -6.7 MPa compared to neat vulcanized rubber. Tensile strength decreased as LNR content increased and molecular weight of LNR decreased. Nevertheless, elongation at break of LEPNR insignificantly increased as an amount of LNR increased and slightly increased as molecular weight of LNR decreased. However, it was noted that the vulcanized rubber compounding with 10 phr LNR

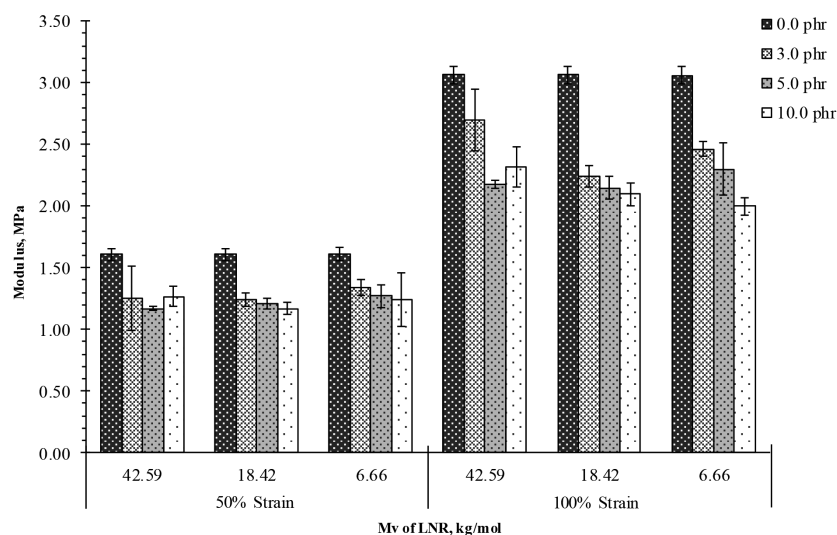


FIGURE 6. Modulus at 50% and 100% strain of vulcanized LEPNR

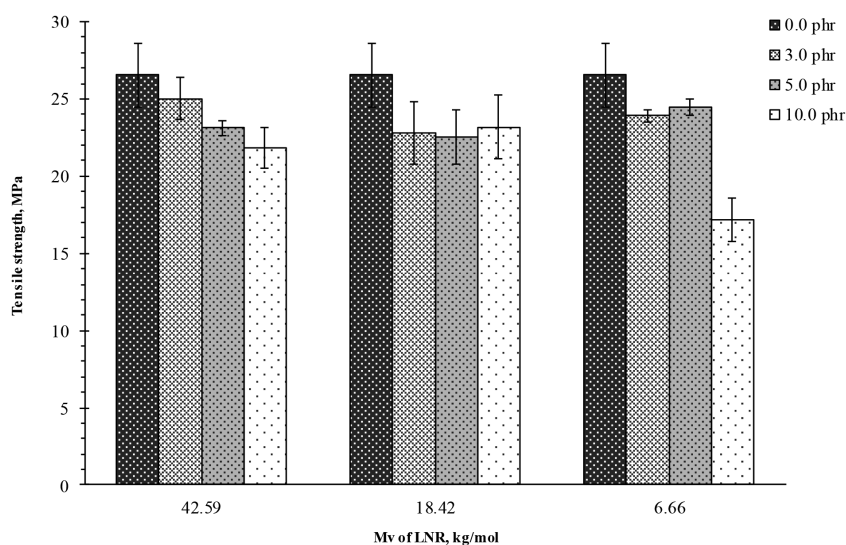


FIGURE 7. Tensile strength of vulcanized LEPNR



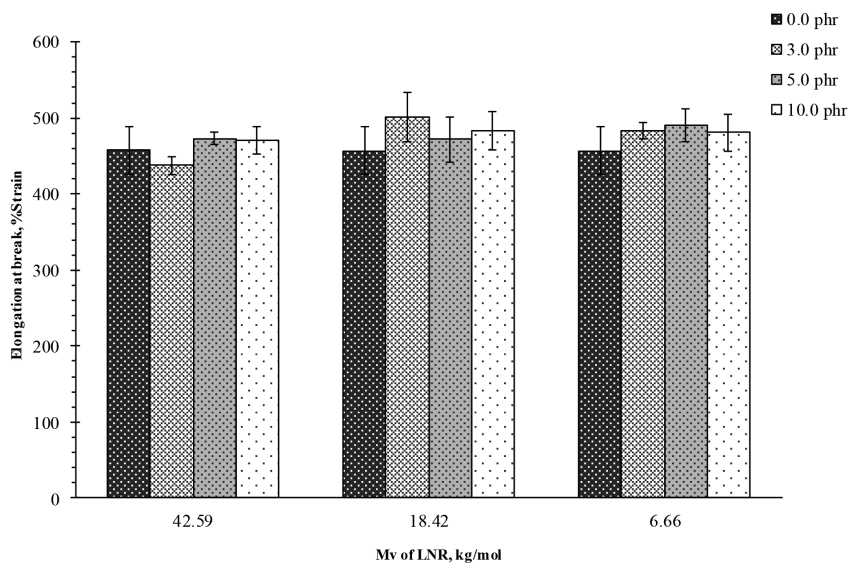


FIGURE 8. Elongation at break of vulcanized LEPNR

with Mv of 6.66 kg/mol was the softest compared to other vulcanized LEPNRs. This vulcanized rubber may be used in specific application since it is extra soft and highly capable to absorb energy.

#### CONCLUSION

LNR with Mv of 42.59, 18.42 and 6.66 kg/mol were prepared by using phenyl hydrazine/O<sub>2</sub> system and used as plasticizer to manufacture LEPNR. The efficiency on decreasing Mooney viscosity of LNR increased as Mv of LNR decreased and LNR content increased. Besides, the LNR improve mixing properties of NR by reducing energy consumption during mixing process, scorch time and cure time. Tensile strength and elongation at break slightly decreased compared with neat rubber vulcanized NR. Furthermore, an addition of LNR with molecular weight of 6.66 kg/mol at 10 phr, extra soft vulcanized LEPNR was obtained. Thus, mixing and vulcanized properties of LEPNR depended on molecular weight and content of LNR that used as plasticizer.

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