

The molecular weight (MW) and molecular weight distribution (MWD) of NR from different age and clone *Hevea* trees

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Abstract

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NR-latex was tapped from different age and clone *Hevea* trees. The latex of virgin started from 3 years trees was transesterified to reduce the branching molecules. The molecular weight (MW) and molecular weight distribution (MWD) of rubber molecules were measured using a gel-permeation chromatography (GPC). It was found that variation in MW and MWD of natural rubber depended on the age and clone of rubber tree. An increased age of rubber clone BPM 24 (3, 5 and 8 years) and KRS 156 (1, 15 and 25 years) also increased the MW and MWD of rubber. Nine different clones of 8 months young virgin trees (NATAWE 208, AVROS 2037, RRIC 6, GT-1, PR 255, PR 261, KRS 156, BPM 24 and RRIM 600) showed a unimodal distribution with a small variation in MW and narrow MWD. On the other hand, those regularly tapped mature trees (NATAWE 208, AVROS 2037, RRIC 6, GT-1, PR 255, PR 261 and KRS 156) aged 25 years, showed a great variation in MW and MWD. The \bar{M}_w value of NR showed a great variation from about 10^4 to 10^6 . The polydispersity (\bar{M}_w / \bar{M}_n) was between 2 and 11.

Key words : *Hevea* tree, natural rubber, latex, MW, MWD, clone

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บทคัดย่อ

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น้ำหนักโมเลกุลและการกระจายของน้ำหนักโมเลกุลยางธรรมชาติที่มีอายุและพันธุ์ต่าง ๆ กัน

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นำยางธรรมชาติจากต้นยางฮีเวียที่มีอายุและพันธุ์ต่างกัน โดยอายุตั้งแต่ 3 ปีขึ้นไป และเปิดกรีดครั้งแรก ได้ผ่านการสลายโครงสร้างหมู่เอสเทอร์เพื่อลดโครงสร้างโมเลกุลที่เป็นกิ่งก้านสาขา จากการตรวจวัดน้ำหนักโมเลกุล (MW) และการกระจายของน้ำหนักโมเลกุลของยาง (MWD) ด้วยเครื่อง gel-permeation chromatography (GPC) พบว่า MW และ MWD ของยางมีความแปรปรวนขึ้นกับอายุและพันธุ์ยาง ยางที่นำจากต้นยาง พันธุ์ BPM 24 (3, 5 และ 8 ปี) และพันธุ์ KRP 156 (1, 15 และ 25 ปี) พบว่า เมื่อดต้นยางมีอายุเพิ่มขึ้น MW และ MWD มีค่าเพิ่มขึ้น ส่วนยางจากต้นอ่อนอายุ 8 เดือนที่ไม่เคยเปิดกรีดมาก่อน 9 พันธุ์ (NATAWE 208, AVROS 2037, RRIC 6, GT-1, PR 255, PR 261, KRS 156, BPM 24 and RRIM 600) มีการกระจายน้ำหนักโมเลกุลแตกต่างกันเล็กน้อย ลักษณะการกระจายของน้ำหนักโมเลกุลเป็นแบบ unimodal ส่วนยางจากต้นยางที่เจริญเติบโตเต็มที่ อายุ 25 ปี และมีการกรีดยางตามปกติ (NATAWE 208, AVROS 2037, RRIC 6, GT-1, PR 255, PR 261 and KRS 156) พบว่า MW และ MWD มีความแปรปรวนกว้าง น้ำหนักโมเลกุลเฉลี่ยโดยน้ำหนัก (\bar{M}_w) มีค่าอยู่ระหว่าง 10^4 - 10^6 และสัดส่วนการกระจายของน้ำหนักโมเลกุลเฉลี่ยโดยน้ำหนักและโดยจำนวน (\bar{M}_w/\bar{M}_n) มีค่าอยู่ระหว่าง 2-11

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Natural rubber derived from species of *Hevea brasiliensis* tree is a high molecular weight polymer with a wide molecular weight distribution range. The great variation of their MW and MWD depends on clones and age of rubbers tree as well as soil and climate conditions of plantation. The molecular weight of natural rubber is of great importance for the processability of rubber product. The physical properties of the obtained rubber, such as modulus, tensile strength, tear strength, etc can also be remarkably widely dependent on the MW and MWD of rubber. The MW and MWD determinations of rubber have been carried out by osmometry, light scattering, solution viscometry and gel-permeation chromatography (GPC). Bristow *et al.* (1977) and Westall (1968) first found that natural rubber might have a bimodal MWD based on solvent fractionation. Subramaniam (1972) used GPC to measure the MWD of freshly tapped natural rubber latex and confirmed that the distribution of natural rubber was generally bimodal. It is also reported that the low molecular weight fraction of nineteen clonal rubbers varied

upto 40 %. Hager *et al.* (1976) found that \bar{M}_n of six-month-old seedlings was 6×10^4 with a very broad distribution. Mature virgin trees rubber was transesterified in order to remove ester groups, which can cause the forming of branch-points to the rubber molecules (as hard gel), and to produce linear rubber molecules (Tangpakdee *et al.*, 1997).

The MW and MWD of rubber obtained from different clones of young and mature trees and from an aged series of rubber trees was interesting. Thus, this work attempted to show the MW and MWD of different ages and clones of virgin *Hevea*-NR tree, which have been never tapped before, together with regularly tapped rubber trees, using GPC measurement.

Materials and Methods

Materials

The fresh *Hevea* latices used were obtained from young and mature trees grown in southern of Thailand. The latices of different ages and clones were collected from a smallholder plantation and

from an experimental plantation in Yala and Pattani Provinces. BPM 24 aged of 3, 5 and 8 years and KRS 156 aged of 1 and 15 years were first time tapped to characterize the MW and MWD of rubber. The measurement of MW and MWD was also performed for 8 months virgin seedling trees of 9 clones (NATAWE 208, AVROS 2037, RRIC 6, GT-1, PR 255, PR 261, KRS 156, BPM 24 and RRIM 600). As a control, 7 clones of mature trees (NATAWE 208, AVROS 2037, RRIC 6, GT-1, PR 255 and PR 261) aged of 25 years were regularly tapped.

Methods

After tapping, all fresh latices were preserved with 2 %w/v sodium dodecyl sulphate and were strained with a 60-mesh strainer before coagulating the latex with acetone. Dried rubbers from the first tapped started from 3 years virgin trees, were transesterified before measuring the MW and MWD by GPC. Transesterification of rubber was carried out by dissolving 2 g of purified rubber in 100 ml-dried toluene for overnight. Freshly prepared sodium methoxide (1 M) in methanol was then added into the solution. The transesterification reaction was proceeded in the dark under nitrogen atmosphere at room temperature at room temperature for 3 hours. After the reaction, the rubber solution was concentrated with a rotary evaporator at 50°C followed by re-precipitation with methanol. The transesterified rubber was dried *in vacuo* at room temperature.

The MW and MWD of rubber were measured using gel-permeation chromatography (GPC) in serial combination. Two columns having exclusion limits of 2.0×10^7 and 5.0×10^4 were used.

THF was used as an eluent with a flow rate of 0.5 ml/min. The measurement was at 35°C. The columns were calibrated with commercially obtained styrene standards of known molecular weight.

Results and Discussion

NR latices from different virgin trees, aged from 3 years, clones of BPM 24 (aged 3, 5 and 8 years) and KRS 156 (aged 15 years), were transesterified because rubber molecules contain high and low MW that can form gel easily after tapping. This could be due to some abnormal rubber groups such as aldehyde, epoxide or lactone (Gregg *et al.*, 1973). Allen and Bristow (1963) have also reported that gel phase in NR composes of small crosslinked latex particles. This cross-link or branch-points might be composed of phospholipids (Tangpakdee *et al.*, 1997). Tangpakdee and Tanaka (1997) also confirmed that the transesterified rubber is a linear molecule by using NMR analysis of the chain end group.

The rubber from young seedling trees and regularly tapped trees show no any gel formation. Therefore, the transesterification of these rubbers was not necessary. The content of fatty acid, phosphorus atom and gel was reduced markedly by transesterification. Transesterification was controlled to break down the branch points, forming by factional terminal groups, and would not cause chain scission in the rubber molecules (Tangpakdee *et al.*, 1997).

Natural rubber usually contains a very high molecular weight fraction in a wide range of MWD. RRIM 600 virgin trees aged from 1 to 7 years

Table 1. MW and MWD of RRIM 600 aged 1-7 years.

Ages (Years)	$\overline{M}_n * 10^{-5}$	$\overline{M}_w * 10^{-5}$	$\overline{M}_w / \overline{M}_n$
1	1.06	3.34	3.15
2	1.31	5.26	4.03
3	1.46	9.50	6.51
4	0.89	7.08	8.82
6	1.03	10.0	9.71
7	1.16	11.9	10.2

showed uni- and bi-modal MWDs. (Kovuttikulrangsie, 1999). The virgin seedling trees, aged 1 and 2 years, showed a unimodal MWD, while those aged from 3 to 7 years showed a skewed unimodal MWD which the low MW peak was smaller than that of the high MW peak. The \bar{M}_w of RRIM 600 virgin tree showed a dramatic increase from 3.3×10^5 to 1.2×10^6 as the rubber tree age increased. However, the \bar{M}_n was not substantially change (about 8.9×10^4 to 1.3×10^5). The polydispersity (\bar{M}_w/\bar{M}_n) of young to mature virgin trees was remarkably wide, ranging from 3 to 10 (Table 1) whereas that from seedling trees was narrow and increased with tree-age.

BPM 24 virgin trees aged 3, 5 and 8 years (Figure 1) showed a dramatic increase in MW due to the biosynthesis mechanism of the *Hevea* tree. The MW of growing trees showed an incline towards a higher molecular weight region. KRS 156 virgin trees aged 1 and 15 years as well as BPM 24 showed a similar unimodal MWD (Figure 2), while regularly tapped trees of KRS 156, aged 25 years showed as a skewed unimodal distribution with a shoulder in the high molecular weight region. It was suggested that the low molecular weight fraction consisted of linear polymers, while the high molecular weight was composed of branched molecules (Fuller *et al.*, 1990). Long fatty acid chain groups esterified to rubber molecule

have been found to associate with branching (Tanaka *et al.*, 1993). KRS 156 of young and mature virgin trees showed the \bar{M}_w dramatically increased (from 2.6×10^5 to 2.1×10^6), while the \bar{M}_n of rubber was slightly increased (from about 9.2×10^4 to 2.4×10^5) as the age of rubber trees increased. The polydispersity also gradually increased from 2 to 9.

Nine different clones of 8 months seedling tree (NATAWE 208, AVROS 2037, RRIC 6, GT-1, PR 255, PR 261, KRS 156, BPM24 and RRIM600) showed almost the same unimodal distribution (Figure 3). While the peak distribution of RRIC 6 and GT-1 appeared to split out due to some branching molecules formation. However, the position of the peak was located in the low molecular weight region and was a small variable which appeared from 10^4 to 10^5 depending on the clones of rubber trees. The polydispersity (\bar{M}_w/\bar{M}_n) was of a rather narrow range, from 2 to 6, for all the rubber clones studied.

Similarly, the seven clones of 25 years mature trees (NATAWE 208, AVROS 2037, RRIC 6, GT-1, PR 255, PR 261 and KRS 156) showed approximately the same MWDs shapes (Figure 4) (Kovuttikulrangsie, 1999). However, the MW and MWD were remarkably higher than those of seedling trees. Although most heights of MW peaks also appeared in the low molecular weight region,

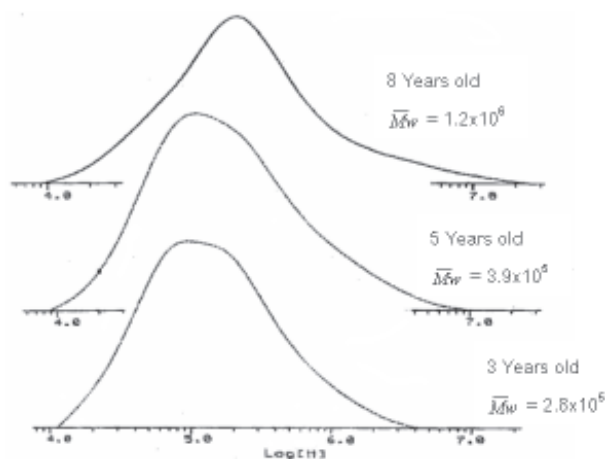


Figure 1. The MW and MWD of BPM 24

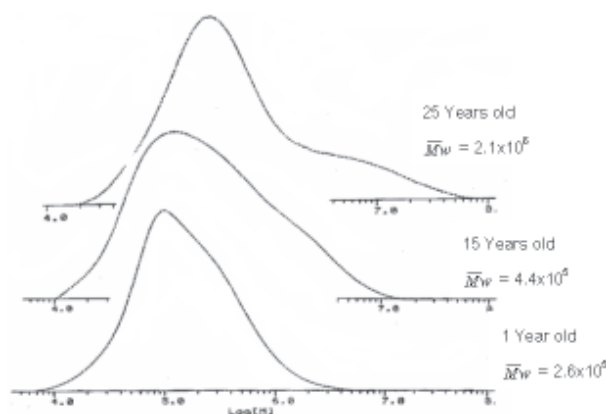


Figure 2. The MW and MWD of KRS 156

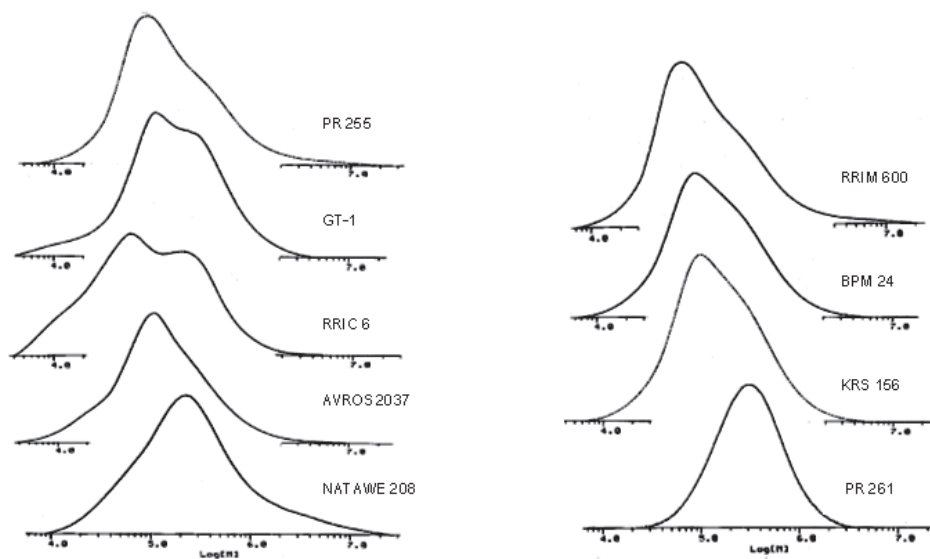


Figure 3. The MW and MWD of NR from different 9 clones of seeding trees aged 8 months.

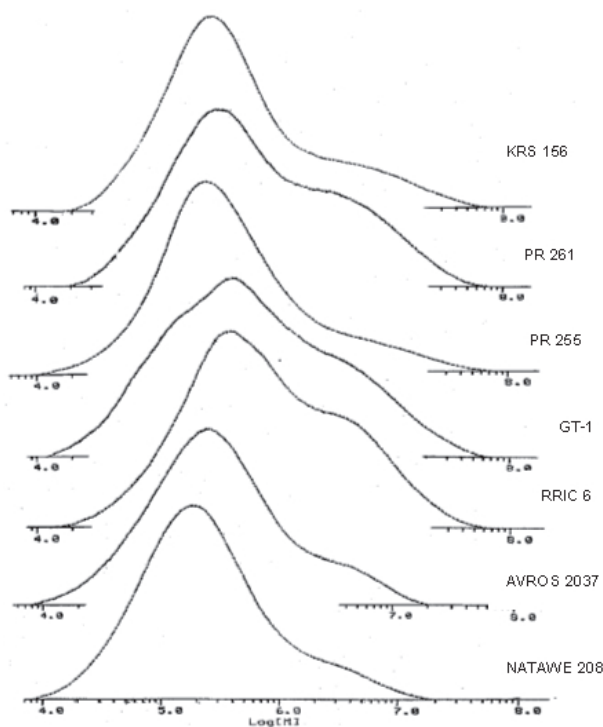


Figure 4. The MW and MWD of NR from 7 different matured clones, aged 25 years.

the actual value of molecular weight showed great variation depending on the clone from which the rubber was obtained. The \bar{M}_w showed an immense variation from 6.8×10^5 to 2.9×10^6 and the \bar{M}_n was

small, varying from about 1.2×10^5 to 3.2×10^5 . The molecular weight distribution (MWD) showed a remarkably wide range from 5 to 11 (Table 2).

Although the shapes of distribution curves

Table 2. MW and MWD of NR from 7 clones matured trees aged 25 years.

Clones	$\bar{M}_n * 10^{-5}$	$\bar{M}_w * 10^{-5}$	\bar{M}_w / \bar{M}_n
NATAWE 208	1.20	6.79	5.65
AVROS 2037	1.42	9.15	6.44
RRIC 6	3.21	26.0	8.11
GT-1	2.26	24.9	11.0
PR 255	2.06	17.0	8.23
PR 261	3.04	28.9	9.51
KRS 156	2.43	21.2	8.70

of rubber from all clones are different, the molecular weights range was approximately the same, i.e., 10^4 to 10^6 . In the case of commercial latex production, the rubber latex was a mixture of different clone rubber latices, therefore large variations in MW and MWD were reduced. However, during processing and storage of raw rubber during manufacture, the MW and MWD of rubber might be changed depending on clone of rubber.

Conclusions

The MW and MWD of natural rubber showed a great variation depending on age and clone of rubber trees. The transesterified rubber of growing tree showed a skewed unimodal distribution. The rubber from young trees gave a unimodal MWD with a lower MW than that of mature trees. Different clones of rubber were found to give variations in MW and MWDs. The commercially used rubbers of different ages and clones of *Hevea* trees, clearly indicated a large variation in MW, between 10^4 and 10^6 with a remarkably wide range of MWD from 2 to 11.

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mental plantation garden in Yala.

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