

# The rheological properties of masticated natural rubbers and their linear viscoelastic predictions

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**Abstract** Premastication of natural rubber (NR) is a common process to ease the incorporation of fillers and chemicals. This research studied the changes in molecular structure, molecular weight (MW), and linear viscoelastic (LVE) properties of the standard Thai NR block grade STR5L, which is the low contamination grade, after mastication for 20 min at 40, 70, and 100 rpm, respectively. The MWs of unmasticated and masticated NRs were quantified by size exclusion chromatography. The “dual constraint” model, which is known to provide good predictions of the LVE properties from the MW and molecular weight distribution (MWD) of linear polymers, was used to correlate the MWs of NRs to their LVE properties. It was found that the dual constraint model could predict the dynamic moduli of NRs masticated at high speeds (70 and 100 rpm), indicating that the rheological behavior of the masticated NRs at 70 and 100 rpm conformed to linear polymers. On the other hand, the predictions for the unmasticated NR and the NR masticated at a lower speed of 40 rpm (NR40 rpm) deviated from the experimental values, especially in the terminal zone. This deviation might be due to the presence of physical gel and microgel in NR, which might still exist at mastication temperatures below 100 °C.

**Keywords** Natural rubber · Mastication · Rheological parameter · Molecular weight · Dual constraint model

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## Introduction

Natural rubber (NR) has been used as a raw material for many products such as tires, threads, and seals. In rubber industries, mastication of NR before compounding with other chemicals and fillers is a common process because the viscosity of NR is usually very high. So far, characterization of the actual NR molecular weight (MW) has been a difficult task. The MW determination by size exclusion chromatography (SEC) required filtration of gel in NR by microfiltration to prevent blockage of the SEC column, where it was thought that this filtration step led to inaccurate measurement of NR MW. Kim et al. (2009) characterized MW of NR by using SEC equipped with multiangle light scattering. They found that the soluble portion of NR was the mixture of linear-chain NR and some nanoaggregates. Most of the earlier works on elimination of gel in NR were carried out in the solution state. Leblanc et al. (2010) reported that the gel fraction of NR in an organic solvent could decay over a very long time (weeks), indicating that complete dissolution is possible. However, they did not carry out further experiments to investigate the changes in MW of the soluble fraction over time. Therefore, it was still unclear whether the solubility of NR after a long time was due to dissolution kinetic of the high MW fraction or due to the breakdown of physical gel. Later on, it was readily accepted that gel was actually formed mainly by physical interaction of polar functional groups at the ends of NR chains. Sakdapipanich (2007) reported that gel in NR could be reduced by deproteinization and were completely destroyed by transesterification. They found that transesterification could completely eliminate macrogel, where the transesterified NR contained no branched structure. They also conducted experiments and found that long-chain branching in the purified NR was mainly derived from the association of phospholipids linked with terminal groups at the end of rubber chains via

hydrogen bonds (Amnuaypornsi et al. 2010; Tarachiwin et al. 2005). Following these works, Ehabe and Bonfils clarified that transesterification could almost completely converted the macrogel to soluble low to average MW sol, while the amount of microgel was not changed after transesterification (Ehabe and Bonfils 2011). As can be seen, tremendous efforts have been put into quantifying the MW and MWD of NR. All of them found that quantification of NR structure was not possible without several cumbersome pretreatments, which excluded some parts of or destroyed the original NR structure. Therefore, this paper proposes to investigate the changes in NR MW and molecular structure indirectly by using the rheological method. Here, various grades of NR were prepared by mastication at different mastication speeds to observe the changes in their rheological and molecular properties after mastication. The rheological properties of NR after mastication are of interest because mastication of NR has been commonly used in NR compounding. Knowing the changes in NR structure after mastication at different conditions could be advantageous in fine tuning its desirable final product properties.

Regarding the effects of mastication, Mullins and Watson (1959) proposed that the structure of NR after mastication could be broken down by two mechanisms, namely, the mechanical breakdown by shearing action and thermo-oxidative degradation. In the presence of a small amount of oxygen, these mechanisms lead to shorter rubber chains. On the other hand, the high-temperature thermal degradation in a controlled inert atmosphere (no oxygen) or in the presence of curing agents leads to the formation of crosslink networks. At low to moderate temperatures, which are the general conditions for rubber compounding, mechanical breakdown is the dominant phenomenon due to the high friction generated from high rubber viscosities. At higher temperatures, the lower rubber viscosity decreases the role of mechanical breakdown, while the thermal oxidation becomes increasingly dominant. For NR, the region between 100 and 130 °C is the region where chain scission is the least effective as the temperature is in transition from the mechanical to thermo-oxidative breakdown (Busse and Cunningham 1938, Dimier et al. 2004, Stern 1967, Valsamis et al. 1997).

In 2006, Ehabe et al. compared the MW of common unstabilized NR with the viscosity-stabilized NR, where the stabilization of viscosity was done by adding a chemical to prevent gel formation during storage. They found that the viscosity and MW of the unstabilized NR decreased substantially and approached those of the viscosity-stabilized grade after mastication at 100 rpm with the stock temperature rising to 160 °C. This implied that the higher MW of unstabilized NR was due to the formation of gel during storage (Ehabe et al. 2006).

In the past, rheological models have been investigated for explaining the flow behavior of polymers, elastomers, and polymer blends. It is, however, impossible to obtain

quantitative predictions for commercial randomly branched or gelled polymers since their rheological properties depend on several factors including the homogeneity of molecular architecture. Therefore, the highest potential for quantitative predictions is in linear polymers, where several theoretical models have been shown to provide good predictions by using the least number of fitting parameters (Pattamaprom et al. 2008, Léonardi et al. 2002, Likhtman and McLeish 2002, van Ruymbeke et al. 2002). So far, no work has correlated the effects of mastication on the structure of masticated NR by using the rheological point of view. Therefore, the changes in the rheological behavior of NR after mastication were investigated here by using this type of theoretical model to investigate the effect of breakdown mechanisms. The model used here was a linear viscoelastic (LVE) model, namely, “the dual constraint model” (Pattamaprom et al. 2000, 2008; Pattamaprom and Larson 2001), which is known to be quite accurate for linear organic polymers. If the model prediction is valid for NR, it could be used to predict viscosities and other rheological properties of the rubber from their MWs at any temperature. Similarly, the MW of NR could be obtained by measuring the rheological properties without need for the complicated SEC technique. This could be a very attractive advantage since the MW determination of NR has always been a difficult task due to the presence of physical gel and nanoaggregates, which have posed a significant challenge and risk of SEC column blocking. Here, the “dual constraint” model was evaluated for its validity in masticated NR, where the rheological experiments were carried out to obtain the plateau modulus and the LVE moduli of the unmasticated and masticated NRs.

### Theoretical description: the dual constraint model

The dual constraint model was originally developed by T.J. Van Dyke, R.G. Larson, D.W. Mead, and M. Doi and refined by Pattamaprom and Larson (2001), Pattamaprom et al. (2000). This model provides good predictions for monodisperse, bidisperse, and polydisperse linear polymers and star-branched polymers, including polyisoprene, over a broad range of molecular weights. The required parameters for this model are the plateau modulus ( $G_N^0$ ) and the relaxation time for an entanglement segment ( $\tau_e$ ), where these two parameters are independent of molecular architecture, molecular weight, or molecular weight distribution. The plateau modulus can be obtained from the polymer handbooks or obtained experimentally, whereas  $\tau_e$  can be calculated from the friction coefficient  $\zeta$  of Rouse theory or be allowed as the only one fitting parameter for a single type of polymer at one temperature. The governing equations for this model are shown below, where the most-updated full description of the model could be found in Pattamaprom et al. (2008).

The dual constraint model combines two forms of constraint release. The first is “double diffusion” which augments “double reptation” by inclusion of primitive path fluctuations as a mechanism of constraint release. The second form of constraint release is “dynamic dilution,” which was introduced by Ball and McLeish (1989) to describe the time-dependent loosening of the effective entanglement network, or widening of the tube. The upper limit of the combined constraint release rate from both mechanisms is controlled by Rouse-like motions of the tube containing the test chain; these motions are called “constraint-release Rouse” processes (Milner et al. 1998, Doi and Edwards 1986).

The diffusion equation for the tube survival probability  $p_i$  of chain type  $i$  including the constraint release is rewritten as

$$\frac{\partial p_i(s_i, t)}{\partial t} = \frac{D_i}{L_i^2} \frac{\partial^2 p_i(s_i, t)}{\partial s_i^2} - \frac{p_i(s_i, t)}{\tau_{\xi,i}(s_i)} \tag{1}$$

where  $p_i(s_i, t)$  is the survival probability of a tube segment occupied by a chain of type  $i$  as a function of time  $t$  and contour distance  $s_i$ , where  $s_i$  ranges from 0 at the center of a linear polymer chain to  $1/2$  at the end.  $D_i$ , the curvilinear diffusion coefficient, is given by  $\frac{L_i^2}{\tau_{d,i}\pi^2}$ , where  $L_i$  is the average contour length of the tube and  $\tau_{d,i}$  is the reptation time constant (Doi and Edwards 1986).  $\tau_{\xi,i}$  is the time constant for contour-length fluctuations in the presence of constraint release consisting of the early-time ( $\tau_{\text{early}}$ ) and late-time ( $\tau_{\text{late}}$ ) fluctuations.  $\tau_{\xi,i}$  is obtained from  $\tau_{\text{early}}$  and  $\tau_{\text{late}}$  using a crossover formula reported in our earlier work. (Note that in Pattamaprom et al. (2000), due to a typographical error, a square root is missing from the second line of the crossover formula in Eq. 4, where  $\tau_{\xi,i}^*$  should equal  $\sqrt{\tau_{\text{early},i} \cdot \tau_{\text{late},i}^*}$ ).  $\tau_{\text{early}}$  and  $\tau_{\text{late}}$  are related to the relaxation time of one entanglement segment,  $\tau_e$ , by the equations described in Table 1 of Pattamaprom et al. (2008).

The overall survival probability  $\phi_i(t)$  of a tube occupied by chain  $i$  can then be calculated from  $p_i(s_i, t)$  by

$$\phi_i(t) = \int_0^1 p_i(s_i, t) ds_i \tag{2}$$

and the average survival probability  $\phi(t)$  of all tubes is

$$\phi(t) = \sum w_i \phi_i(t) \tag{3}$$

Where  $w_i$  is the weight fraction of chains of type  $i$ .

The relaxation modulus  $G(t)$  from the contributions of reptation, contour-length fluctuations, and constraint release can be obtained from:

$$G(t) = G_N^0 \phi(t) \phi'(t) \tag{4}$$

where  $\phi'(t)$  is the average survival probability modified by accounting for the constraint-release Rouse mechanism proposed by Viovy et al. (1991).

A full description of  $\phi_i(t)$ , as well as a complete explanation of the model, can be found in Pattamaprom et al. (2008).

For this model, the model parameters are the plateau modulus  $G_N^0$  and the Rouse relaxation time of a single tube segment  $\tau_e$ , which are both independent of the polymer molecular weight. The input parameters, which reflect the effects of molecular weight, are the average MW ( $M_w$  or  $M_n$ ) and the MWD. These data are used to generate the weight fraction  $w_i$  of the polymer chains with the molecular weight  $M_i$ . The  $M_i$  is then used to calculate the number of tube segment ( $Z_i$ ), the reptation time ( $\tau_{d,i}$ ), the contour-length fluctuation time ( $\tau_{\xi,i}$ ), and the Rouse relaxation time ( $\tau_{R,i}$ ), respectively. The prediction of the model is the linear viscoelastic relaxation modulus  $G(t)$ , which can be converted by the Fourier transform method into the linear viscoelastic storage modulus  $G'(\omega)$ , loss modulus  $G''(\omega)$ , and the complex viscosity  $\eta^*(\omega)$ . The latter of which can be linked with the shear viscosity of natural rubber through the Cox-Merz rule.

## Experimental

### Materials

The grade of NR used in this research was Standard Thai Rubber 5L (STR5L) supplied by the Rubber Estate Organization of Thailand. No chemicals or fillers were added to the rubber during mastication.

### Sample preparation

NR (STR5L) was masticated in the Brabender Plasti-corder Lab-station internal mixer, which comprises two Banbury-type counter-rotors in a 55-cm<sup>3</sup> chamber. A fill factor of 0.8 was chosen to permit good homogenization in the mixer. The rubber was fed into the internal mixer at the chamber temperature of 50 °C. The mastication was carried out at constant speeds (40, 70, and 100 rpm) for a fixed time of 20 min. Simultaneously, the torque and temperature profiles were recorded. Subsequently, the rubber was kneaded in the two-roll mill to make a thin sheet and cut into disks of 25 mm in diameter for the rheological test.

### Gel and molecular weight characterizations

The characterization of NR included the determination of macrogel content, MW, and molecular weight distribution (MWD) before and after mastication. The gel content

experiment was carried out by dissolving small pieces of rubber in toluene (0.1 % w/v). The mixture was then kept in the dark at room temperature without shaking for 1 week. The gel fraction was separated from the solution and dried at 40 °C for 24 h. The percentage of gel in the original rubber piece was estimated as the macrogel content.

The weight averaged MW and MWD of NR were determined by SEC. The SEC analyses were carried out on a Waters 2414 refractive index detector equipped with a Styragel HR5E 7.8 × 300 mm column. The SEC columns were eluted using tetrahydrofuran with a flow rate of 1.0 mL/min at 40 °C and calibrated with polystyrene standards.

The viscosity average MW ( $M_v$ ) of NR samples was also measured by the intrinsic viscosity method. The NR solutions were prepared by dissolving small pieces of NR samples in toluene at concentration ranging from 0.1 to 1.6 g/dL. The solution was kept in the dark at room temperature without shaking for 1 week before the test. The viscosity of the NR solution was determined by using the Cannon–Fensky viscometer. The  $M_v$  was determined by using the Mark–Houwink–Sakurada relationship, as shown in equation (5):

$$M_v = \left( \frac{[\eta]}{K} \right)^{1/a} \quad (5)$$

where  $[\eta]$  is the intrinsic viscosity, and the constants  $K$  and  $a$  are  $17.4 \times 10^{-3}$  mL/g and 0.74, respectively, for NR in toluene at 35 °C (Kurata and Tsunashima 1999).

## Rheological measurements

The rheological properties of NR were measured by the Malvern-Kinexus Pro stress-controlled rheometer equipped with the 25-mm parallel-plate configuration with the plate gap distance of 1 mm. The linear dynamic oscillatory measurements were carried out over the frequency range of 0.001–150 Hz and over the temperature range of 5–125 °C in the stress-controlled mode. The amplitude of 1 % strain, which was found to be within the LVE region, was imposed on the samples.

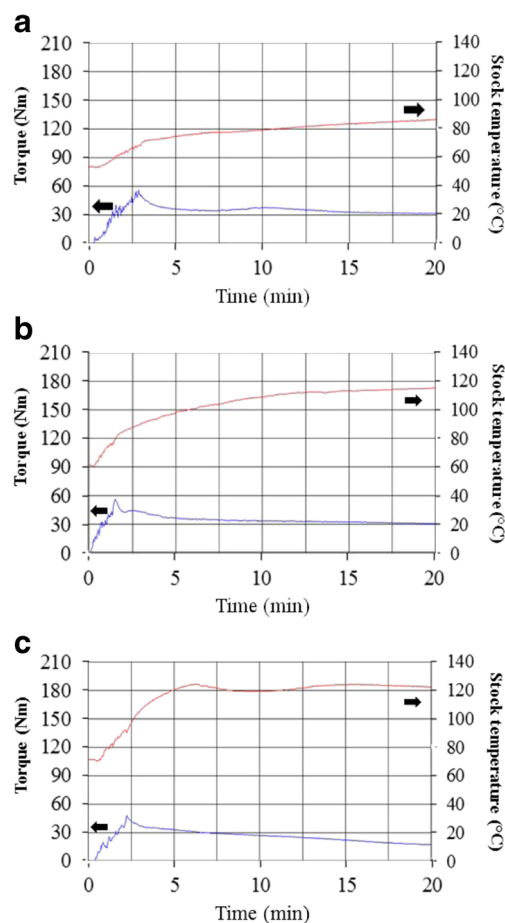
## Results and discussion

The first part of this research investigated the changes in several NR properties after mastication at different speeds. The second part evaluated the rheological predictions for unmasticated and masticated NRs by using the so-called dual constraint model.

## Changes in NR properties after mastication

Figure 1 indicates the torque and temperature profiles during mastication at different rotor speeds. At 40 rpm (NR40 rpm), the temperature range was well below 100 °C (between 55 and 85 °C), which was the range in which chain scission occurred mainly by mechanical shearing. In this case, the torque reached a stable level due to the balance between molecular breakdown and a recombination of chains. On the other hand, when masticated at 100 rpm (NR100 rpm), the temperature quickly rose beyond 100 °C and reached the final temperature of 120 °C within 5 min. In this temperature range, the chain scission occurred mainly by thermal oxidation (Busse and Cunningham 1938), while the torque profile continued to decrease without reaching a stable level. At 70 rpm (NR70rpm), the torque and temperature ranges were somewhere in between, where the temperature rose beyond 100 °C within 5 min.

The macrogel content of NR before mastication (UNR) was found to be as high as 40 % w/w. Nevertheless, after mastication for 20 min, no macrogel was detected at any of the rotor speeds in this study. The decrease in macrogel

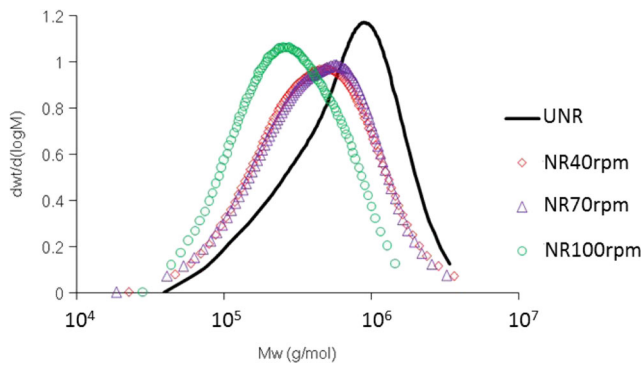


**Fig. 1** Torque and temperature profiles of natural rubber masticated at rotor speeds of **a** 40 rpm, **b** 70 rpm, and **c** 100 rpm

content during mastication was consistent with the work by Ehabe et al. and could be attributed to random polymer chain scission as well as the breakdown of physical gel naturally present in NR (Ehabe et al. 2006, Tangpakdee and Tanaka 1993, Shiibashi et al. 1989).

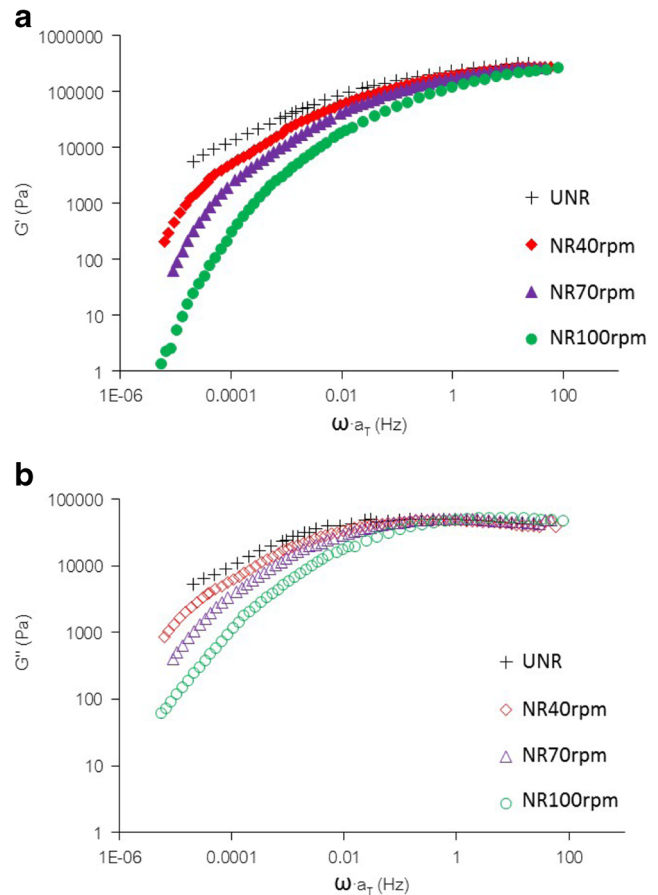
The MW and MWD of NR determined by SEC shown in Fig. 2 indicated that the MW of NR decreased with mastication speed. However, the SEC result indicated that the decrease in the MW when increasing the mastication speed from 40 to 70 rpm was minimal. This might be because at 70 rpm, the mastication temperature fell into the transition zone from mechanical to thermo-oxidative breakdown, where neither mechanism was at their dominant stage.

The rheological properties of four NR samples (UNR, NR40rpm, NR70rpm, and NR100rpm) were determined by the dynamic frequency sweep over the temperature range of 5–125 °C. The  $G'$  and  $G''$  curves were shifted experimentally to the master curves at the reference temperature of 25 °C by the time–temperature superposition method, as shown in Fig. 3, and the complex viscosities of these samples are shown in Fig. 4. As can be seen, the moduli and viscosity of the masticated NRs decreased with mastication speed. Interestingly, the rheological properties of NR40rpm and NR70rpm were very different, while their SEC traces in Fig. 2 were almost identical. This again indicated the problem in the SEC method, which could not account for the effect of gel. The solid lines in Fig. 4 are the best fit to the zero-shear regime by using the well-known Carreau–Yasuda model (Yasuda et al. 1981). Since the Carreau–Yasuda model is an entirely empirical model with five fitting parameters, the values of their parameters are trivial and could not be used to link with the molecular properties.



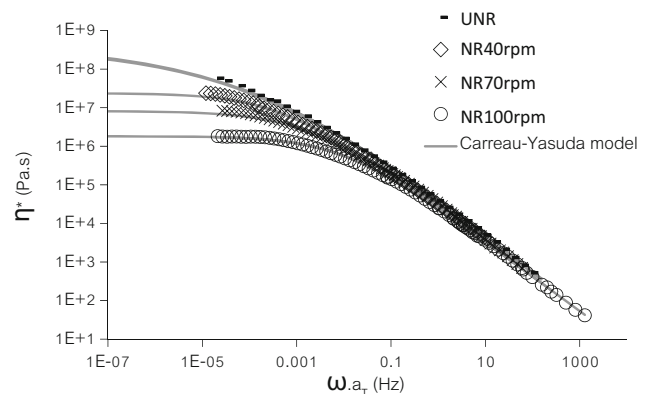
Sample	Rotor speed (rpm)	$M_w$ (g/mol)	$M_n$ (g/mol)	MWD
UNR	0 (unmasticated)	886229	410712	2.16
NR40rpm	40	644288	272291	2.37
NR70rpm	70	621635	261434	2.38
NR100rpm	100	368776	194658	1.89

**Fig. 2** The molecular weight distribution given by SEC of NR before and after being masticated at 40, 70, and 100 rpm

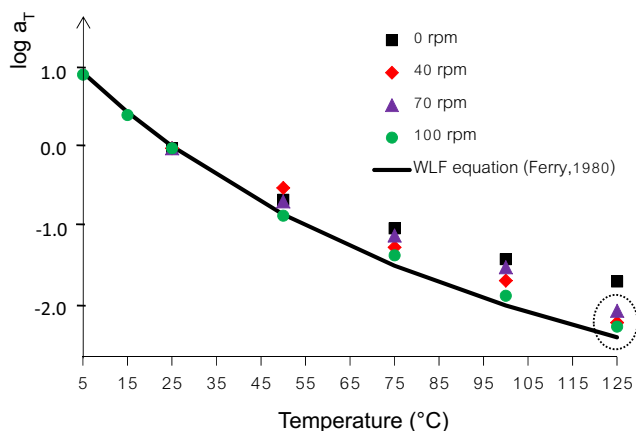


**Fig. 3** Master curves of the **a** storage moduli ( $G'$ ) and **b** loss moduli ( $G''$ ) of the unmastered and masticated natural rubber samples

In Fig. 5, the shift factors obtained experimentally for all samples were compared with those obtained from the Williams–Landel–Ferry (WLF) relationship ( $a_{T, WLF}$ ) by using the WLF parameters reported by Ferry (1980) for Hevea NR ( $T_{ref} = T_g + 50 = -23$  °C,  $C_1 = 8.86$ , and  $C_2 = 101.6$ ) (Ferry 1980), as shown in equation (6):



**Fig. 4** Master curves of the complex viscosities ( $\eta^*$ ) of the UNR and masticated NR samples fitted with the Carreau–Yasuda model (Yasuda et al. 1981)



**Fig. 5** Shift factors of the UNR and masticated NRs obtained experimentally compared with that calculated from the WLF equation in equation (6) at  $T_{ref}$  of 25 °C. The dotted circle indicates the convergence of  $a_T$  values for masticated NRs at high temperature

$$\log a_{T,WLF} = \frac{-8.86 (T - (-23))}{101.6 + (T - (-23))} \quad (6)$$

Note that since the experimental shift factors ( $a_T$ ) are based on the reference temperature ( $T_{ref}$ ) of 25 °C, the WLF shift factors in Fig. 5 were also converted from  $T_{ref}$  from -23 to 25 °C using equation (7), where the constant 2.84 is the value of  $\log a_T$ , WLF at 25 °C.

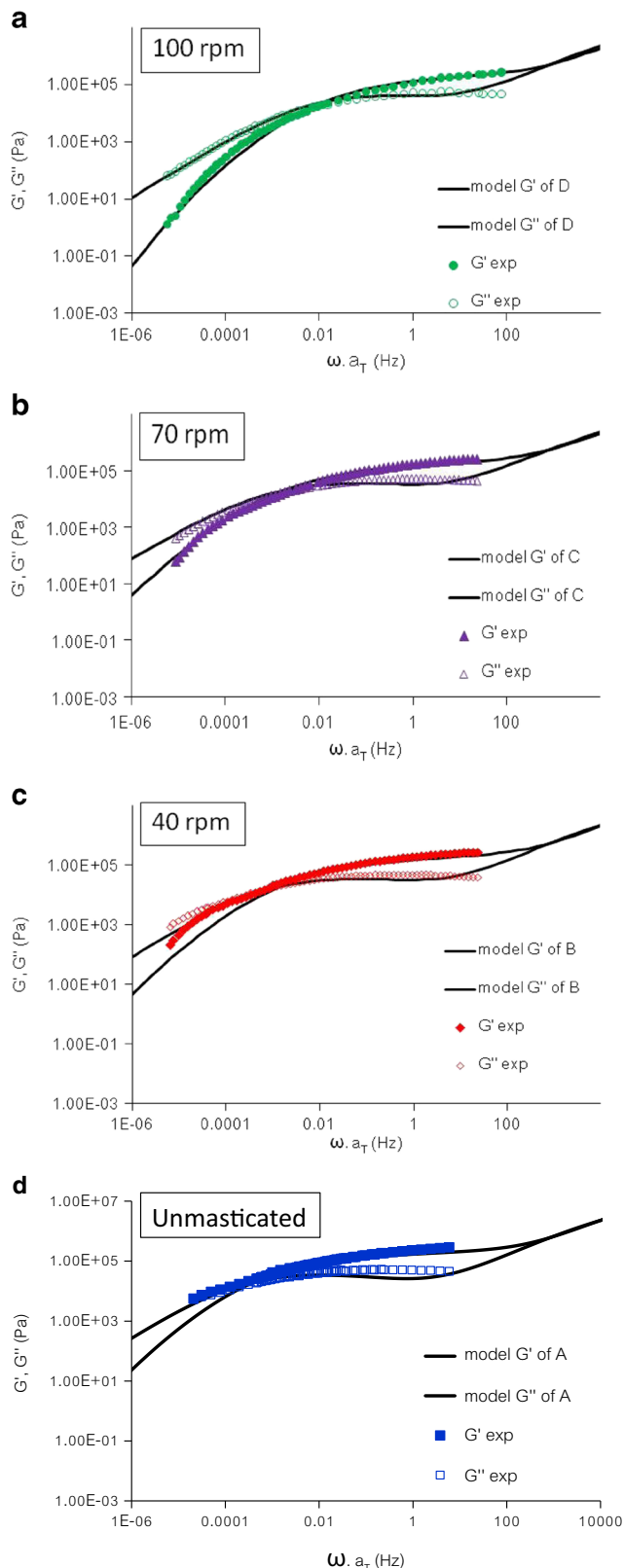
$$\log a_T = \log a_{T,WLF} + 2.84 \quad (7)$$

Figure 5 shows the experimental  $a_T$  for UNR and masticated NRs and compared with the  $a_T$  obtained from the tabulated WLF shift factor in Ferry (1980). Usually, the shift factor curves of polymers with the same molecular structure and architecture are so similar that a universal equation like the WLF shift factor with a specific set of constants for each polymer can be used to describe the dependence of  $a_T$  on temperature. But from Fig. 5, the  $a_T$  values of unmasticated NR were less sensitive to temperature compared with those of the masticated ones. This implied the potential difference in the molecular architecture of the masticated and unmasticated NRs. In addition, Fig. 5 indicated that the tabulated shift factor provided a good fit only for the NR100rpm, where the breakdown mechanism occurred mostly by the thermo-oxidative effect.

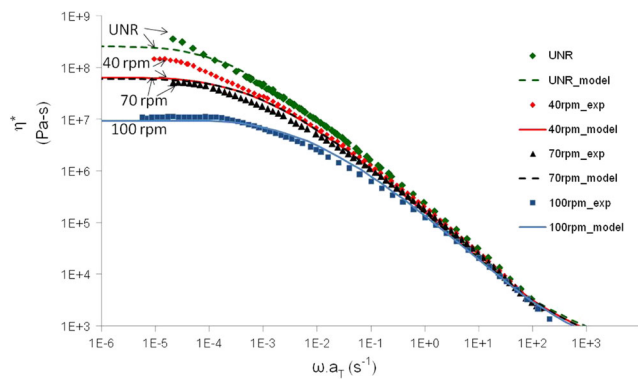
The plateau modulus ( $G_N^0$ ) was estimated from the plateau regime of Fig. 3(a) to be  $2.75 \times 10^5$  Pa. The MW between entanglements ( $M_e$ ) was calculated from the plateau modulus by using the equation proposed by Ferry (1980), as shown in equation (8):

$$G_N^0 = \frac{\rho RT}{M_e} \quad (8)$$

The calculated  $M_e$  (Ferry’s definition) in this case was 8382.9 g/mol.



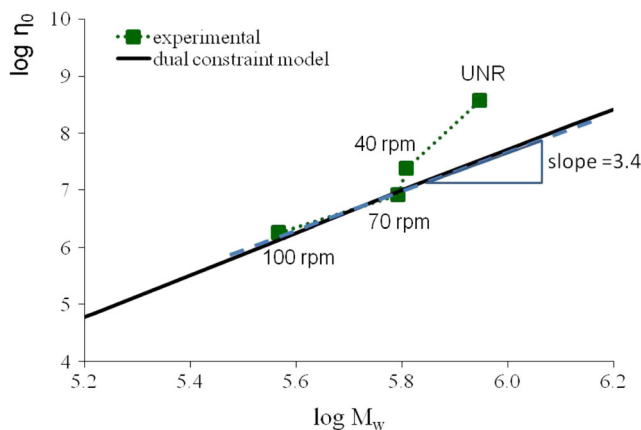
**Fig. 6** Comparison between the prediction of the dual constraint model and the experimental storage ( $G'$ ) and loss ( $G''$ ) moduli of the natural rubber masticated at **a** 100 rpm, **b** 70 rpm, **c** 40 rpm, and of **d** unmasticated natural rubber. The solid lines are the model predictions and the symbols are experimental values



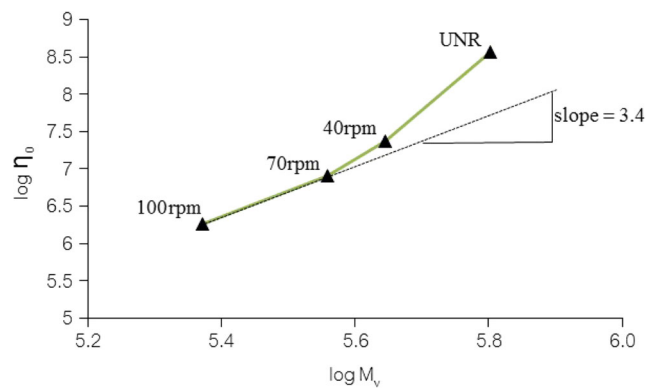
**Fig. 7** Comparison between the experimental complex viscosities (symbols) and the complex viscosities predicted by the dual constraint model (lines) of the UNR and NR masticated at 40 rpm, 70 rpm, and 100 rpm, respectively

**Prediction of NR’s rheological properties from their molecular weights by the dual constraint model**

As mentioned earlier, the Carreau–Yasuda empirical model could not be used to extract molecular information of polymers. On the other hand, the dual constraint model is a theoretical model that could well describe the LVE properties of linear organic polymers from their MW and MWD. For this model, there are only two model parameters, namely, the plateau modulus ( $G_N^\circ$ ) and the relaxation time of one entanglement segment ( $\tau_e$ ). Here,  $G_N^\circ$  of NR was obtained from the previous section to be  $2.75 \times 10^5$  Pa. The only fitting parameter for these predictions is  $\tau_e$ , which is independent of MW and is therefore kept constant for all samples. In this study, the best fit value of  $\tau_e$  for NR at 25 °C was 10 s. The  $\tau_e$  values at other temperatures could also be calculated by using the WLF shift factors. The predictions of  $G'$  and  $G''$  and the complex viscosity ( $\eta^*$ ) by the aforementioned dual constraint model for all NR samples were compared with the experimental values in Figs. 6 and 7, respectively. As can be seen, the dual constraint model could predict the rheological properties of NR100rpm and NR70rpm well,



**Fig. 8** Plot of weight average molecular weight vs. zero-shear viscosity. The solid line is the prediction of the dual constraint model, while the broken line indicates the slope of the 3.4 power law



**Fig. 9** Plot of viscosity average molecular weight vs. zero-shear viscosity. The dotted line indicates the slope of the 3.4 power law

while the predictions of NR40rpm and UNR deviated substantially, especially in the terminal regime. This result indicated that mastication at high speeds (high temperature), where the temperature during mastication was above 100 °C, could make NR behave more like linear polymers and implied the disappearance of macrogel and branches. This indicated that high temperature could more or less breakdown the association of phospholipid linkages at the NR chain ends. It is also consistent with the work reported by Ehabe et al. about the disappearance of macrogel, as well as the reduction of microgel content and MW, of NR after being masticated at high temperature (even though their mastication temperature was significantly higher (140–160 °C) (Ehabe et al. 2006). Their findings also agreed with what was found in our laboratory that the gel fractions of NR could be reduced in hot toluene.

In Fig. 8, the deviations of UNR and NR40rpm also manifested themselves in their deviation of the zero-shear viscosity ( $\eta_0$ )–MW relationship from the 3.4 power law index reported by Berry and Fox (1968), who experimentally observed the dependence of  $\eta_0$  on  $M_w^{3.4}$  for linear polymers. As can be seen, the prediction of  $\eta_0$  from the dual constraint model is also in close agreement with this power law. Due to the controversy about the inability of the SEC method to account for the contribution of gel, thus rendering inaccurate molecular information, the 3.4 power law was also checked against the viscosity average MW ( $M_v$ ) obtained from the intrinsic viscosity technique (Fig. 9). As can be seen, the deviation from the 3.4 power law still existed in UNR and NR40rpm but at a lower degree, indicating that the  $M_v$ , which allows inclusion of some physical gel, could better describe the molecular properties of NR than the MW obtained by the SEC technique. Nevertheless, the limitation of the intrinsic viscosity technique is its inability to provide the MWD information.

**Conclusion**

This research investigated the changes in the molecular and rheological properties of NR (STR 5L) when it was masticated

at different speeds. The friction from higher mastication speed generated higher mastication temperature, where the mastication temperatures for NR70rpm and NR100rpm were higher than 100 °C. It was found that the dual constraint model, which is considered one of the effective LVE models for linear organic polymers, could predict the LVE properties of NR70rpm and NR100rpm from their MW and MWD. On the other hand, the LVE properties of NR masticated at a lower temperature (NR40rpm) and UNR deviated from the dual constraint prediction, especially in the terminal regime, indicating that the structures of these NRs were not linear. This was confirmed by the deviation of their zero-shear viscosity–MW relationship from the 3.4 power law. Therefore, it can be concluded that the masticated rubber had a linear structure when the mastication temperature was higher than 100 °C, at which molecular degradation occurred mainly by thermo-oxidative mechanism. Consequently, the dual constraint model could be used to obtain the MWs from the LVE properties and vice versa.

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