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Study of raw rubber and dynamic properties of RRISL 203 genotype using rubber process analyzer

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Abstract

Quality raw materials are essential for a sustainable rubber product industry. RRISL has introduced RRISL 203 clones as a solution for demand in high-yielding, and disease-resistant clones with vigorous growth. The objective of the present study is to study the raw rubber and rheological properties to find the suitability to produce advanced rubber products. Un-fractioned-unbleached crepe rubber manufactured using latex from the clone was collected from three crepe rubber factories in three different areas in Sri Lanka. RRIC 121, which is the most popular clone in Sri Lanka was selected as the control. Studies carried out on the raw rubber properties of these rubbers revealed that RRISL 203 clone recorded the highest Plasticity number as well as the highest Mooney viscosity among clones available in Sri Lanka. Further, this clone possesses relatively higher Plasticity Retention Index, nitrogen, and gel content with a significantly higher Mooney relaxation rate which leads to high elasticity. A frequency sweep test carried out using RPA (Rubber Process Analyzer) revealed that RRISL 203 possesses linear polymer with a low degree of branching while having a high molecular weight and broader molecular weight distribution. The overall results revealed that rubber obtained from the new clone leads could be used to produce rubber products with high strength and elastic properties. RRISL 203 clone showed moderate raw rubber properties with the highest Mooney viscosity value. Hence, the associated mastication energy requirement would be higher than that of RRIC 121.

Key words: dynamic properties, elasticity, molecular weight, raw rubber properties, rubber genotype, viscosity

Introduction

Development of new clones is a major task in research and development activities related to the rubber industry to develop clones with various intended features such as vigorous growth (Kudaligama, 2010). Therefore, during the initial hybridization stage above factors are generally considered. RRISL 203 clone is such a clone introduced recently to the plantation sector by crossing of two promising clones, RRIC 100 and RRIC 101. This clone has a vigorous growth in both pre and post-tapping periods and has a significantly higher yield compared to other clones and resistance to some threatening diseases (Liyanage, 2016). The commercial average latex yield of this clone is around 2,500 $kgha^{-1}yr^{-1}$ and it has a potential yield of 3,000-3,500 kg ha^{-1} yr^{-1} as a high yielding clone. This clone has recorded relatively higher polyphenol content (Karunaratne *et al*., 2018). This is the reason for the formation of blackish colour layer in the coagulum. According to the Sakdapipanich, 2022 the polyphenol react with oxygen in the presence of polyphenol oxidase. When these quinines react with amino acids and proteins, colourants will form (Attanayake *et al*, 2015). It has been shown that the fractionation process of the latexm obtained from the RRISL 203 clone yields white colour crepe rubber compared to the widely used clones in Sri Lanka. Similar to colour, raw rubber, and dynamic properties are also of great importance during the conversion process of rubber into value-added advanced products.

As the rubber properties derived from latex from RRISL 203 were not ascertained during the clone development, the properties of dry rubber produced out of this clone are not available. Quality and property of natural rubber depends on the non rubber elements in the latex (Yip, 1990: Haque *et al*., 1995; Le Roux *et al*., 2000).Technological properties of natural rubber vary according to the time of shelf life and clonal origin (Le Roux *et al.*, 2000; Ferreira *et al.*, 2002; Moreno *et al.*, 2003). Physical and technological properties of rubber could be uniform within a clone, but clone wise differences do occur (Attanayake *et al*., 2014). Therefore, this study focused on the raw rubber and dynamic properties of fractioned unbleached crepe rubber of this genotype. Un-fractioned unbleached crepe rubber (UFUB) was selected for this study. UFUB has the simplest manufacturing process among the other possible types of crepe rubber. Other types of crepe rubber such as fractioned-bleached (FB), Fraction-Unbleached (FUB), Un-fraction bleached (UFB) crepe rubber are subjected to various chemical modifications by the addition of certain chemicals which can be influenced for the raw rubber and dynamic properties. Properties of Crepe rubber derived from RRIC 121 clone were also evaluated for the purpose of comparison.

Materials and Methods

Sample preparation

Un-fractioned and unbleached crepe rubber samples were prepared with unpreserved latex RRISL 203 clone and RRIC 121 clone by following standard crepe rubber manufacturing procedures, were used for the study. RRIC 121 clone which is the most abundant clone in Sri Lanka was used as the control genotype. Samples prepared by latex collected from three locations in Wet Zone and Intermediate Zone in Sri Lanka.

Determination of raw rubber properties

All raw rubber properties were tested according to ISO standard procedures. The initial plasticity value was tested according to the ISO 2007:2007 while the plasticity retention index (PRI) was tested according to the ISO 2930:2009) by using Wallace rapid plastimeter. Gel Content was tested according to the ISO/DIS17278:2012 standard. Mooney Viscosity was tested by the (EKT 2001) EKTRON TEK Mooney viscometer according to ISO 289-4:2003 standard. The Mooney stress relaxation test was done simultaneously with the Mooney viscosity measurement. ASTM D1646-07 was used to calculate the elasticity of natural rubber. Relaxation data was expressed in a log-log plot. Slope and the intercept of the graph (trend line of the graph) were used to quantify the stress relaxation co-efficient and rubber elasticity (Malac, 2009).

$M = k\,(t)^a$ ………………… Eq 1

Where, M = the torque value in Mooney units;

k = the torque value one second after the rotor has stopped;

a = an exponent that measures the rate of stress relaxation

t = time in seconds

Power low model was converted into log-log expression as follows,

$\text{Log } M = a\,(\log t) + \log k$ ……………. Eq 2

Relaxation data was expressed in a log-log plot. Slope and the intercept of the graph (trend line of the graph) were used to quantify the stress relaxation co-efficient and rubber elasticity.

Determination of dynamic properties RPA analysis

The rubber process analyzer (RPA) is a dynamic mechanical rheological tester and it is universally used for characterizing raw elastomers and unvulcanized compounds (Henry, 1992). Dynamic measurements of raw rubber were tested by D-MDR 3000 (Mon-Tech, Germany) Rubber Process analyzer (RPA) according to the ASTM D6204 standard at 100°C. This method describes a test method for determining the dynamic properties of raw rubber and uncured rubber compounds.

Frequency sweep is used to characterize the polymeric materials. The samples were cut from a pneumatic cutter and placed into a molding chamber. The frequency sweep was carried out at a strain of 99.9% and at 100°C while the frequency was increased from 0.5Hz - 2.0Hz. The following parameters were measured by the frequency sweep test. Storage modulus (G') and Loss modulus (G'') represents the elastic nature of the sample and the viscous nature of the sample respectively. Tan δ, which is known as the dissipation factor *i.e.* ratio between the loss modulus (G'') to storage modulus (G'), was also measured.

In rubber rheology, the strain sweep is used to characterize the raw polymeric material as well as rubber compounds after the mixing. Strain sweep can reflect the rubber compound behavior during the processing such as injection molding, extrusion, *etc*. ACS 1 rubber gum compound was prepared for two rubber clones according to the standard rubber formulation and a strain sweep test was carried out at a constant frequency of 1.67Hz. Stain value increased from 7-99.9% Storage modulus and Tan δ values were measured by the above test.

Results and Discussion

Raw rubber properties

Table 1. *Summary of raw rubber properties (with the coefficient of variation in parentheses)*

Property	RRIC 121	RRISL 203
Initial Plasticity Number (P^{o})	49.20 (3.94)	66.82 (9.30)
Plasticity Retention Index (PRI)	64.25 (6.44)	52.02 (9.92)
Mooney Viscosity [MU] ML(1+4) @100°C	87.70 (4.12)	110.61 (13.14)
Exponent a [log MU/log (s)]	-0.272	-0.224
Elastic energy retention exponent (a+1)	0.728	0.776
Stress Relaxation time (seconds)	18.56 (0.72)	26.18 (1.72)
Gel Content % (w/w)	10.54 (3.45)	34.62 (19.57)

Initial Wallace Plasticity number (P_o) is a measure of the plasticity of the rubber, which indirectly gives the estimation of the polymer molecular chain length (or molecular mass). In general, rubbers with high P_o values would possess a high molecular mass (Bonfils, 1997). The plasticity value of the RRISL 203 clone showed a significantly higher P◦ value when compared to the RRIC 121 clone (Table 1), therefore, we can expect a higher molar mass in RRISL 203 clone. This result is on par with the Mooney viscosity values yielded for clones studied. Mooney viscosity is a measure of the processability of raw natural rubber or compounded rubber. However, Mooney viscosity cannot be considered the direct indication of the molar mass of rubber (Malac, 2011). This is because Mooney viscosity is not sensitive enough to the average molecular mass of natural rubber as characterization at a speed lower than 2 rpm (Malac, 2011). This value could also increase due to the presence of non-rubbers at significant levels in the rubber. Raw rubber produced from RRISL 203 clone showed a comparatively higher Mooney viscosity value than the raw rubbers produced from most of the natural rubber clones present in Sri Lanka (Attanayake, 2014). This would increase the cost of compounding due to the additional energy and time required to reduce the high Mooney viscosity value to the desired level.

The plasticity Retention Index (PRI) measures the oxidation resistance of the rubber. PRI value indicates the resistance of the material toward thermal aging (Bateman, 1966). RRIC 121 clone showed a relatively higher PRI value than RRISL 203 clone. This suggests that latex from 203 clones has a lower content of antioxidants than that of 121 clone, even though the non-rubber content of the former is higher than the latter. According to Karunaratne (2018), RRISL 203 clone has relatively higher content of thiol during wintering period whilst no significant changes observed during high yielding period.

Stress relaxation is the measurement of the change of stress with time under constant strain. The rate of Mooney stress relaxation can correlate with molecular structure characteristics such as molecular weight distribution, chain branching, and gel content. It can also be used to give an indication of the polydispersity index (Brown, 1997). Stress relaxation co-efficient exhibit the elasticity of the material and deformation characteristics.

According to Figure 1, RRISL 203 clone showed significantly higher stress relaxation time when compared with the RRIC 121 clone. This might be due to the molecular entanglement of higher molecular weight in the above clone. This observation is further confirmed by the high plasticity value recorded for rubber manufactured from this particular clone. If we place relaxation data in a log-log plot, the uncured rubber elasticity is given by slope "a" (Malac, 2009). The rubber with higher elasticity has a slower relaxation and *vice-versa* (Mark, 1979). RRISL 203 clone exhibit a higher value for elastic energy retention exponent (Table 1) calculated according to Eq2. Higher values of exponent (a + 1) mean higher deformation energy retention in material and therefore higher elasticity of rubber. By measuring Mooney viscosity, it is very difficult to predict the viscoelastic behavior since it does not distinguish between the elastic and viscous components. Therefore, two polymers with the same complex viscosity could have totally different elastic and viscous components (Ehabe *et al*., 2005). Montes and white (1982) reported that *Hevea* rubber possesses the slowest relaxation amongst a range of polyisoprene and it can be attributed to the presence of gel or long-chain branching. The gel content of the RRISL 203 clone is significantly higher than that of the RRISL 121 clone. Sakdapipanich *et al*., 1999 reported that virgin trees tapped for the first time contained as much as 80% gel, and this amount reduced to 3% within 6 days of tapping, while molecular weight changed from 262 to 2,530 kg/mol.

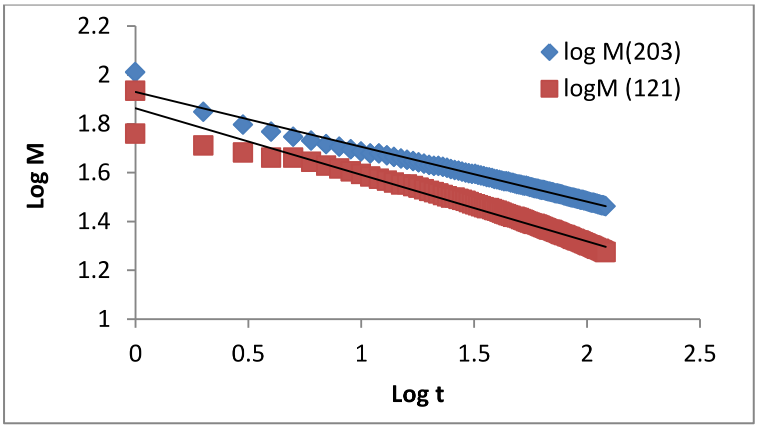

Fig. 1. Relaxation data on a log t (time) versus log M (Mooney value) values for RRIC 121 clone and RRISL 203 clones

Results of dynamic properties

Under an external force, molecular chain orientation is caused by internal friction. When the elastomer molecular weight is lower than a certain value, there is a crossover point between the curves of G' and G" which means that there is a balance in the state of internal friction and disorientation (Fig. 2). With an increase in molecular weight, the crossover point moves to a lower frequency because of restricted disorientation (Zhai, 2010). The lower frequency allows for sufficient time for molecular orientation. The higher molecular weight molecules, therefore, need more time for molecular orientation (Tianming Gao, 2015). The mechanical properties of a material depend on frequency. Isothermal frequency sweep provides information about the molecular weight distribution (crossover modulus) as well as average molecular weight (crossover frequency). Due to the higher molecular weight of RRISL 203, it is not possible to capture the crossover point as the crossover point is happening at a very low-frequency domain. However, a crossover point can be observed for RRIC 121 clone at the very low frequency range.

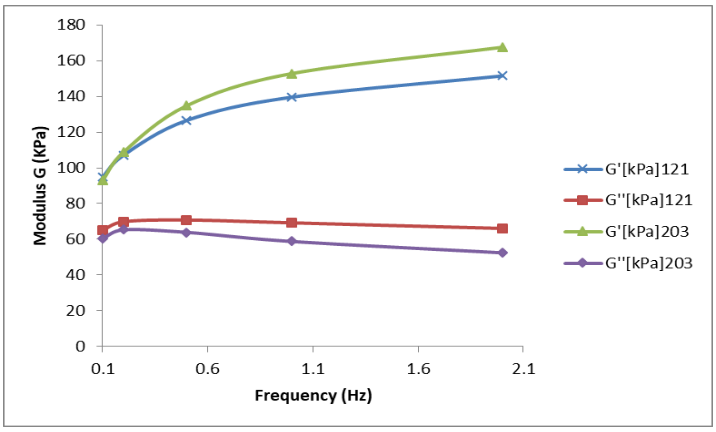

Fig. 2. Variation of storage modulus and loss modules under frequency sweep raw rubber

According to Figure 3, the RRISL 203 clone showed higher crossover modulus and crossover frequency than the RRIC 121 clone. Therefore, RRISL 203 showed lower average molecular weight (AMW) and wide molecular weight distribution (MWD). However, the raw rubber of the RRISL 203 clone showed broader MWD and higher AMW. Therefore, we can suggest that, in the process of rubber compounding, there must be significant chain breakdown to reduce MWD and AMW. Rubber compounds are extremely sensitive to processing operations such as milling. During the milling process, high molecular weight long-chain polymers may be more prone to breakdown than short-chain polymers.

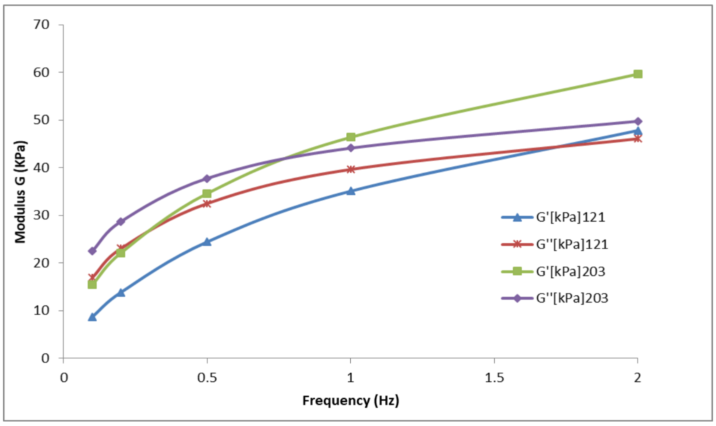

Fig. 3. Overlay plot of frequency sweep test results: Storage modulus (G‘) and Loss modulus (G‘‘) for ACS1 gum compound

Trend of storage modulus of RRISL 203 sample is relatively higher than RRIC 121 sample, which indicates that the RRISL 203 sample has a relatively higher molecular weight and thereby higher molecular entanglements than RRIC 121 sample (Fig. 4).

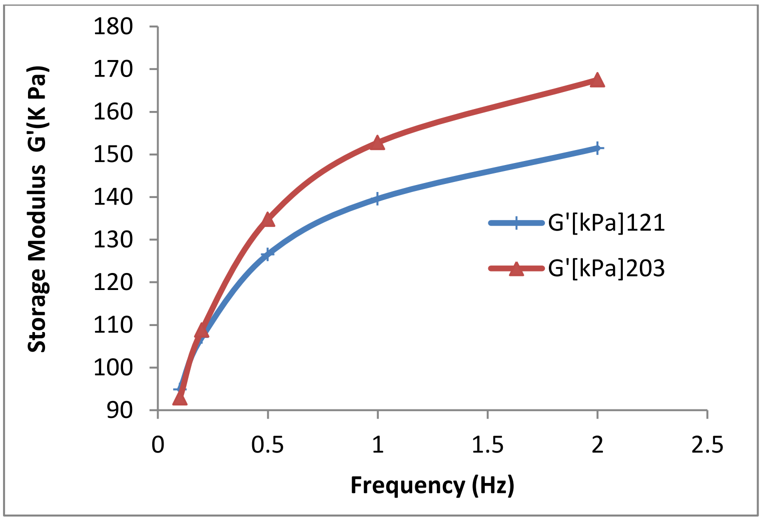

Fig. 4. Overlay plot of frequency sweep test results: overlay plot of storage modulus (G‘) only

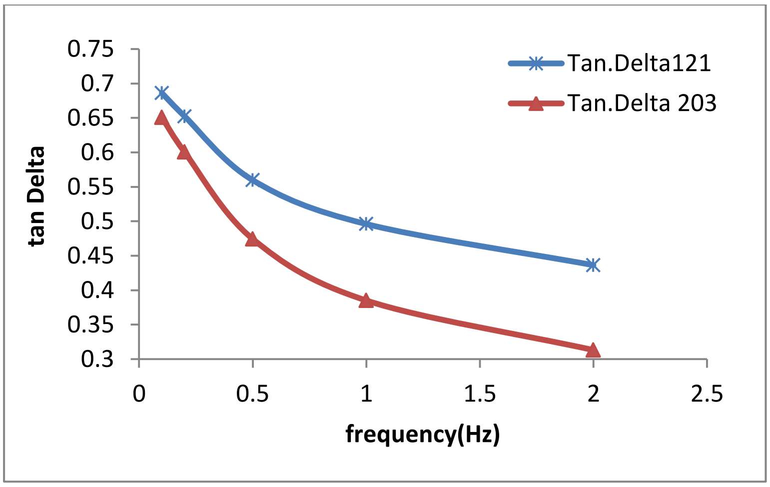

Fig. 5. Variation of Tan Delta values under frequency sweep for raw rubber

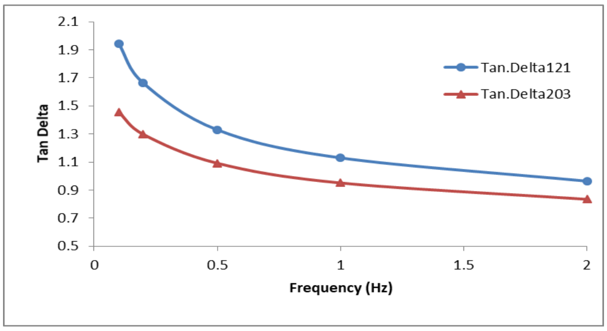

Fig. 6. Overlay plot of tan delta value comparison for ACS 1gum compound

Tan delta is a good indicator of the molecular weight and molecular weight distribution. According to the overlay plot of tan delta values (Fig. 6), the tan delta values of RRIC 121 is higher than R203. It is clearly shown that lower frequency tan delta values are slightly different. The above results showed that the lower molecular fraction of the RRISL 203 clone and RRIC 121 clones are slightly different However, higher frequency tan delta values are significantly different for the two clones studied. A large change in tan delta values indicates that the RRISL 203 clone is a linear polymer with low chain branching with respect to RRIC 121 clone.

Conclusion

RRISL 203 clone showed moderate raw rubber properties with the highest Mooney viscosity value. RRISL 203 possesses linear polymer with a low degree of branching while having a high molecular weight and broader molecular weight distribution. The overall results showed that RRISL 203 could be used for rubber products with high strength and elastic properties. However, the associated mastication energy requirement would be higher than that of RRIC 121.

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