J. Rubb. Res., **5(4)**, 199–208

PRI Ageing *and Some Related Properties of Constant Viscosity Natural Rubbers*

A.H. ENG [*,#], C.F. CHANG[*] AND S. KAWAHARA[**]

Constant viscosity natural rubber (NR) samples from different clones showed no correlation between copper content and Plasticity Retention Index (PRI) value. When the NR samples were stabilised with hydroxylamine, the degree of storage hardening was low but the PRI remained high. The gel content of the NR samples decreased significantly after the PRI test. The extent of reduction in gel content was much greater than that of the reduction in molecular weight of the NR samples. This was attributed to the denaturation of the proteins, which led to the disintegration of crosslinks, or higher rate of oxidation due to the presence of a high level of metal ions in the gel. The extent of molecular weight reduction was slightly lower than that of plasticity value. The Wallace plasticity could be correlated with the geometrical mean of $\overline{M}_n$ *and* $\overline{M}_w$, i.e., $(\overline{M}_n\overline{M}_w)^{1/2}$. *The correlations obtained from linear regression before and after PRI ageing were quite comparable probably because the NR samples were processed and aged under the same conditions. Activation energy of oxidation (AEO) determined by differential scanning calorimeter provided a more sensitive method of assessing the ageing resistance of NR samples than PRI. However, the correlation between PRI and AEO was insignificant.*

Key words: constant viscosity; copper content; hydroxylamine; molecular weight; Wallace plasticity; differential scanning calorimeter

Natural rubber (NR) molecules contain olefinic hydrocarbon which is prone to oxidation reactions. Plasticity Retention Index (PRI) is a method commonly used to assess the ageing resistance of commercial raw NR. It involves the determination of the Wallace plasticity of the NR before and after ageing at 140°C for 30 min in an air-circulating oven. The PRI value is expressed as:

$$\text{PRI} = (P_{30}/P_0) \times 100 \qquad \ldots 1$$

Where P_{30} is the plasticity after ageing and P_0 is the plasticity before ageing.

Although PRI ageing is a useful method of assessing the susceptibility of NR to thermal oxidation, it has several drawbacks. PRI is an indirect method of assessing the ageing resistance of NR, measuring the net change in

[*]Rubber Research Institute of Malaysia, Malaysian Rubber Board. P.O. Box 10150. 50908 Kuala Lumpur, Malaysia
[**]Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan
[#]Corresponding author; current address: Ansell Shah Alam Sdn Bhd., P.O Box 7188, 40706 Shah Alam. Selangor, Malaysia (e-mail: engah@ap ansell com)

physical property, *i.e.*, Wallace plasticity, arising from chain scission and crosslinking reactions during the test. The changes in physical properties, such as plasticity, are a net result of the variations in the molecular properties, such as molecular weight distribution and gel content. Measurement of such fundamental properties of NR could provide an insight into the changes in the physical properties observed during the ageing process. In addition, it has a drawback of being narrow in the scale because the Wallace plasticity has a maximum reading of 100 units. Therefore, it is difficult to further differentiate the ageing resistance of NR with PRI value close to 100.

A survey in the literature revealed that most studies on PRI were on commercial NR. The effects of processing conditions of latex, such as exposure to sunlight, excessive heating, purification, and soaking, on the PRI of NR were studied several decades ago[1]. Several reports on the kinetic study of oxidative scission in NR using Wallace plasticity measurements have been published[2–4]. An alternative method of measuring PRI ageing using differential scanning calorimeter (DSC) has also been reported recently[5]. Another paper investigated the contribution of storage hardening on the PRI test[6]. However, the correlation between PRI and other properties of clonal NR has not been collectively studied. Such knowledge is important for the understanding and improvement of the ageing resistance of NR as well as the method used for quantification. The objective of this paper is to investigate the relationship between PRI and some of the related properties of constant viscosity NR from different clones. The clonal variation would provide NR of different properties when the NR is processed under the same conditions. The effects of the PRI ageing on the molecular weight and gel content were then examined. An alternative method of evaluating the ageing resistance of the NR using DSC was compared with the PRI method.

EXPERIMENTAL

All the latex samples were collected from rubber trees planted in the RRIM Experimental Stations. The rubber trees were tapped on the 1/2S, d/2 system. The latices were stabilised with 0.08% ammonia, followed by the addition of 0.15 part per hundred rubber of hydroxylamine neutral sulphate before coagulation with formic acid at pH 5~5.2. The coagula were then crumbled, washed and dried at 100°C. Wallace plasticity, PRI, copper content and degree of storage hardening were determined using the standard test methods[7]. Gel content was determined by dissolving the rubber in toluene for one week in the dark and the gel isolated by filtration with a 200 mesh sieve.

The rubber samples for molecular weight analysis were allowed to dissolve in tetrahydrofuran (THF) at 0.1~0.15%w/v for 24 h in the dark. The samples were then filtered through a 0.45 μm filter. Gel Permeation Chromatography (GPC) measurements were carried out with a Waters GPC system, consisting of a Waters 2690 Separation Module and a Waters 410 Differential Refractometer. Three columns, packed with crosslinked polystyrene, with the exclusion limits of 2×10^8, 5×10^6, and 5×10^5, connected in series, were used for the GPC measurement. Commercial standard polystyrenes were employed for the calibration of the columns. The measurements were made at 40°C, and the flow rate of the mobile phase, THF, was 0.8 mL/min. The molecular weights of the rubber samples are converted into natural rubber molecular weights of equivalent coil size using the following equation[8]:

COPYRIGHT © MALAYSIAN RUBBER BOARD

$$\log M_{NR} = 0.185 + 0.95 \log M_{PS} \quad ... 1$$

where M_{NR} and M_{PS} are the molecular weights of NR and polystyrene, respectively. Measurement of activation energy of oxidation (AEO) of the rubber sample by DSC has been described previously[9]. Accordingly, 1 mg of rubber sample was placed in an aluminum sample pan and scanned with a Perkin-Elmer DSC 7 from 50°C to 450°C at the rates of 2°C, 4°C, 6°C, 8°C, 16°C, 32°C, and 64°C per min by using oxygen as the purging gas, flowing at a rate of 20 mL/min. The AEO was calculated according to the Kissinger's equation:

$$[d \log(r/T_p^2)/d\,(1/T_p)] = -E/(2.303\,R) \quad ... 2$$

where r is the heating rate, T_p the exothermic peak temperature, E the activation energy and R the gas constant. AEO could be calculated from the linear regression of a plot of log (r/T_p^2) *versus* $1/T_p$.

RESULTS AND DISCUSSION

PRI and Copper Content

PRI test involves the ageing of NR samples at a relatively high temperature, *i.e.*, 140°C. The thermal oxidative degradation of NR is a reaction catalysed by certain metal ions of which copper and manganese are the common potent ones[1]. The level of these metal ions may influence the PRI value of the NR. It is, therefore, important to examine the level of these metal ions in the NR samples. The results are shown in *Table 1*. The level of these metal ions was in the normal range as reported in the previous studies[8]. The samples did not show any significant variation in their manganese content. On the other hand, a variation in the copper content of the samples was observed. However, there is no significant correlation between copper content and the PRI value of the NR samples (P = 0.57, r = 0.15).

PRI and Storage Hardening

Constant viscosity NR are normally produced by stabilising the rubbers with hydroxylamine to minimise the formation of crosslinks during the storage of the rubbers, or the storage hardening phenomenon. The storage hardening can be accelerated by drying the rubbers at an elevated temperature, *e.g.*, 60°C, in the presence of a desiccant, such as phosphorous pentoxide.

Table 1 shows the degree of hardening (ΔP) of the viscosity-stabilised clonal rubbers after the accelerated test. All the samples, except one, showed the ΔP value below 8 units. Under the SMR Scheme, a rubber is considered viscosity-stabilised if the ΔP value does exceed 8 units. The slight hardening that occurred during the test was probably due to the incomplete reaction of the hydroxylamine with the abnormal groups on the NR molecules. Storage hardening has been shown to contribute to the PRI value of non-CV rubbers[6]. However, the correlation between ΔP and PRI values is not expected to be linear (P = 0.047, r = 0.50), because the ΔP measures mainly the hardness of the rubber that is due to crosslinking reaction whereas the PRI test, carried out at a higher temperature, measures the effects of both degradation and cross-linking reactions on the rubber hardness.

When NR was stabilised with hydroxylamine, the degree of storage hardening was low but the PRI remained high, *i.e.*, above the minimum value of 60 under the SMR-CV scheme, as indicated in *Table 1*. Hydroxylamine has been reported to be a scavenger of oxygenated free radicals and therefore it can reduce the oxida-

TABLE 1. PRI AND MANGANESE, COPPER, INITIAL PLASTICITY, DEGREE OF STORAGE HARDENING OF CONSTANT VISCOSITY NR SAMPLES

Sample	PRI	ΔP	Mn (p.p.m.)	Cu (p.p.m.)	P_o
RRIM 936	87	3.5	<1	2	26.5
RRIM 937	87	5.0	<1	3	30.0
RRIM 938	88	4.0	<1	7	28.0
RRIM 940	86	4.5	<1	3	29.5
PB 260	81	3.0	<1	4	26.0
RRIM 600[a]	80	3.0	<1	2	33.0
RRIM 600[a]	92	7.0	<1	3	24.0
RRIM 2001	93	9.5	<1	3	28.5
RRIM 2025	89	6.0	<1	2	41.0
RRIM 2008	92	4.0	<1	2	25.0
RRIM 2009	89	4.0	<1	4	32.0
RRIM 901	89	5.0	<1	3	47.0
RRIM 908	88	4.0	<1	2	41.0
RRIM 911	82	6.0	<1	2	46.0
RRIM 921	87	3.0	<1	2	30.0
RRIM 928	76	4.0	<1	2	51.0

[a]Trees planted in different areas

tive degradation of the CV rubbers during the PRI ageing test[10–12]. This explains the high PRI value observed in the viscosity-stabilised clonal rubbers.

The relationship between initial plasticity, P_o, and PRI has been reported in the earlier paper and therefore will not be repeated here [13].

Effects of PRI Ageing on Gel Content of NR

The oxidation could lead to the formation of crosslinks or chain scission of the molecule. These would change the gel content and PRI value of the rubber. The gel content of the CV rubbers before and after the PRI ageing test is given in *Table 1*. Of the 16 samples, 3 samples were found to contain gel before the PRI test, ranging from 7% – 24%. The gel content of these rubbers was found to decrease significantly after the PRI test. This could be due to the chain scission reactions of the rubber molecules in the gel to form smaller molecules, or the dissociation of crosslinks in the gel fraction had occurred. The extent of reduction in gel content was larger than that of reduction in the molecular weight of the rubbers, as described later. The gel fraction of natural rubber has been reported to contain higher protein and mineral contents than the sol fraction[14]. In addition, the crosslinks in the gel fraction have been shown to be mediated by the proteins because a significant reduction in the gel content is observed after deproteinisation[15]. Therefore, the high rate of gel reduction after PRI test could be due to the denaturation of the proteins which led to disintegration of crosslinks or higher rate of oxidation due to the presence of high level of metal ions in the mineral fraction of the gel. This is expected to

affect the molecular weight and molecular weight distribution of the NR.

Effects of PRI Ageing on Molecular Weight of NR

The changes in the molecular weight of the rubber during the PRI ageing were determined by GPC, and the results are shown in *Table 2*. Three molecular weights were used to monitor the changes, *i.e.* number average ($\overline{M}_n$), weight average ($\overline{M}_w$) , and peak molecular weights (M_p).The molecular weight retention index of the rubber was calculated using the similar method of PRI calculation. Therefore, $\overline{M}_n$RI, $\overline{M}_w$RI, and M_pRI represent the retention indices of the respective molecular weights. Most of the samples were found to have lower molecular weights after the ageing test, indicating that under the conditions employed, the net result was molecular degradation of the rubbers. The molecular weight retention indices were found to be in the ranges of 81–108, 83–109, 75–108 for $\overline{M}_n$RI, $\overline{M}_w$RI, and M_pRI, respectively. These are comparable to each other except for the lower range value of M_pRI, indicating a shift in the peak value to a lower molecular weight region, which was probably due to the dissolution of gel in the samples during the PRI ageing. The gel phase in NR has been shown to consist of low molecular weight NR molecules, linked up through lipids and proteins[16,17]. The dissociation of the crosslinks released the low molecular weight rubbers into the soluble fraction. This led to the observation of lower $\overline{M}_n$RI, and M_pRI values for the NR with high gel content.

The extent of molecular weight reduction was slightly lower than that of plasticity value. The difference is not surprising since the changes in the molecular weight of the rubbers are not expected to lead to the exact changes in the plasticity because the two values are not linearly correlated.

Although the measurement of molecular weight retention indices is a direct method of assessing the changes that occur during the PRI ageing, the presence of insoluble gel in the rubber, which is removed by filtration before analysis, limits the application of such technique in the ageing study of NR.

Plasticity and Molecular Weight of NR Before and After PRI Ageing

In his clonal study, Subramaniam[8] reported a linear correlation between log V_R (Mooney viscosity) and log $(\overline{M}_n\overline{M}_w)^{1/2}$ for eighteen clonal rubber samples based on the work of Kramer and Good[18] on styrene butadiene rubbers. A good linear correlation between V_R and Wallace plasticity has also been reported. Therefore, the Wallace plasticity can be correlated with the geometrical mean of $\overline{M}_n$ and $\overline{M}_w$, *i.e.*, $(\overline{M}_n\overline{M}_w)^{1/2}$, and the effects of PRI ageing on the correlation can be studied.

Figures 1 and *2* show the correlations between $(\overline{M}_n\overline{M}_w)^{1/2}$ and Wallace plasticity before and after PRI ageing, respectively. The plot for the data before PRI ageing yields $y = 1.22x - 6.15$ ($r = 0.95$, $P < 0.001$), compared to that of after PRI ageing which yields $y = 1.20x - 5.63$ ($r = 0.89$, $P < 0.001$). The two equations obtained from linear regression are quite comparable probably because the same NR samples were aged under the same conditions. These equations are quite different from those reported in a previous study[8], *i.e.*, plasticity = $KM^{0.98} + C$, where $M = (\overline{M}_n\overline{M}_w)^{1/2}$, K and C = constant, because the samples were treated under different conditions. On the other hand, the correlation between log

TABLE 2. CHANGES IN GEL CONTENT AND MOLECULAR WEIGHT OF NR SAMPLES AFTER PRI AGEING

Sample	Before PRI test				After PRI test								
	$\overline{M}_n \times 10^5$	$\overline{M}_w \times 10^6$	$M_p \times 10^6$	Gel (%)	$\overline{M}_n \times 10^5$	$\overline{M}_w \times 10^6$	$M_p \times 10^6$	Gel (%)	$\overline{M}_n$RI	$\overline{M}_w$RI	M_pRI	PRI	E (kJ/mol)
RRIM 936	2.71	1.11	1.78	0	2.53	1.01	1.73	0	93	91	98	87	234
RRIM 937	2.97	1.14	1.84	0	2.67	1.07	1.72	0	90	94	94	87	202
RRIM 938	2.64	1.07	1.73	0	2.69	1.06	1.48	0	102	99	101	88	195
RRIM 940	3.47	1.15	1.73	0	2.86	0.97	1.49	0	83	86	87	86	246
PB 260	2.65	1.04	1.73	0	2.57	1.00	1.62	0	97	96	94	81	253
RRIM 600[a]	3.14	1.28	2.52	7	2.79	1.20	2.00	0	89	94	80	80	266
RRIM 600[a]	2.60	1.08	1.90	0	2.47	1.09	2.05	0	95	101	108	92	265
RRIM 2001	3.51	1.17	1.76	0	2.96	1.09	1.70	0	84	93	97	93	309
RRIM 2025	4.35	1.22	1.74	0	4.06	1.27	1.78	0	93	104	102	89	359
RRIM 2008	2.57	1.01	1.73	0	2.79	1.10	1.82	0	108	109	105	92	216
RRIM 2009	3.42	1.36	2.42	0	3.13	1.20	1.92	0	91	88	80	89	204
RRIM 901	4.30	1.45	2.44	20	3.82	1.30	1.87	0	89	90	77	89	341
RRIM 908	3.52	1.39	2.41	0	3.40	1.27	1.93	0	97	91	81	88	228
RRIM 911	4.13	1.44	2.32	24	3.36	1.23	1.72	4	81	85	75	82	341
RRIM 921	2.74	1.27	2.32	0	2.79	1.05	1.82	0	102	83	79	87	204
RRIM 928	6.02	1.39	1.99	0	5.47	1.01	1.91	0	92	104	96	76	72
Range									81–108	83–109	75–108	76–93	72–359

$\overline{M}_n$: Number average molecular weight; $\overline{M}_w$: Weight average molecular weight; M_p: Peak molecular weight; Gel: toluene as solvent
E: Activation energy of oxidation
[a]Trees planted in different areas

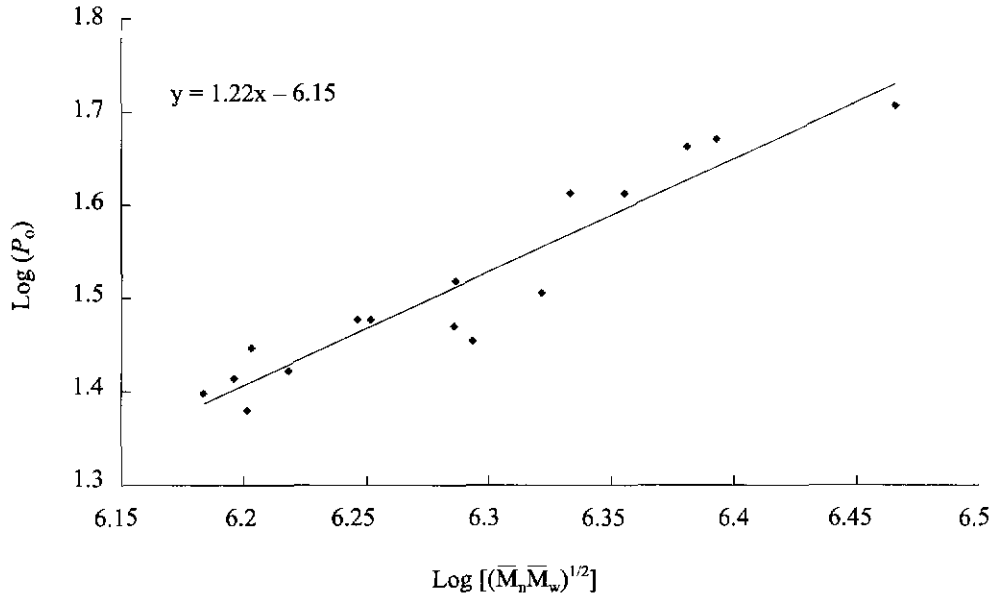

Figure 1. Relationship between plasticity and molecular weight of clonal NR before PRI ageing.

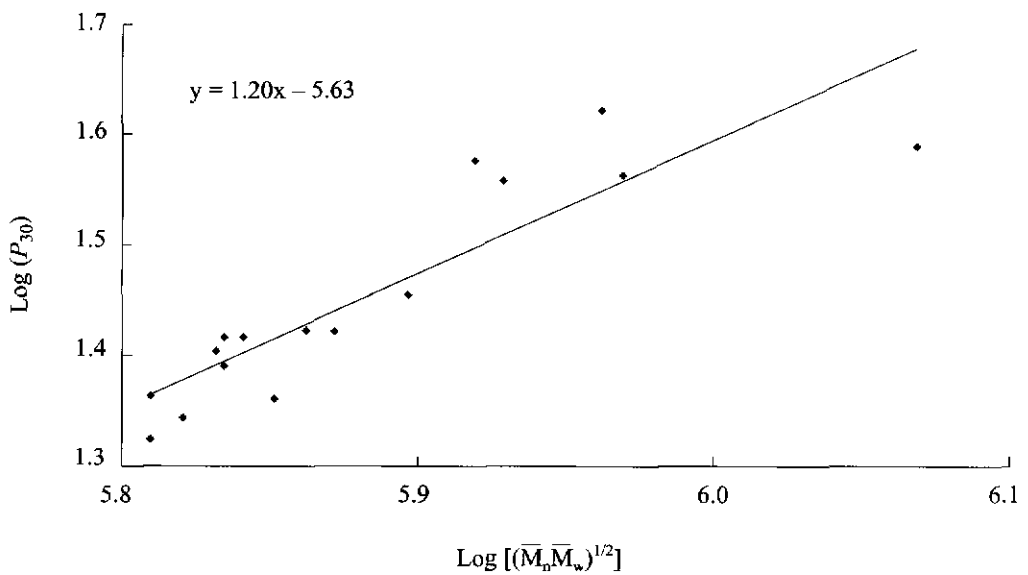

Figure 2. Relationship between plasticity and molecular weight of clonal NR after PRI ageing.

PRI and log $[\overline{M}_n\overline{M}_w(\text{aged})/\overline{M}_n\overline{M}_w(\text{unaged})]^{1/2}$ is insignificant (r = 0 21, P = 0 42) The correlation between log PRI and log M_nRI is also insignificant (r = 0 26, P = 0 32)

PRI and Activation Energy of Oxidation

Besides PRI, there are other thermal analytical methods that can be used to study rubber ageing, of which DSC is the most popular technique The technique normally involves the determination of enthalpy, onset temperature, isothermal induction time, activation energy of oxidation (AEO), and oxidation peak temperature[19] Bonfils *et al*[5] reported a linear correlation between PRI and the onset temperature from DSC measurements of NR samples with PRI values below 70 However, a poor correlation was found for the samples with PRI values above 70 Since the PRI values of the NR samples used in the present study were above 70, the onset temperature method was not used As an alternative, the AEO was measured using DSC and correlated with the PRI values Unlike the onset temperature, which is a single-point determination, AEO in the present study is derived from at least 6 scans, using different heating rates The results are shown in *Table 2* The range of AEO-value was found to be 72–359, which is much larger than that of PRI This shows that AEO is a more sensitive method than PRI in assessing the ageing resistance of NR samples The correlation between PRI and AEO was examined and found to be insignificant (r = 0 37, P = 0 16) For the logarithmic plot, the correlation was also insignificant (r = 0 50, P = 0 05) although a slight improvement was observed The lack of correlation is not surprising since the degradation mechanisms in both methods are expected to be different, due to the fact that they were carried out at different temperatures

CONCLUSION

Although constant viscosity natural rubber samples from different clones were found to contain different copper contents, no correlation between copper content and the PRI value of the NR samples was observed The PRI values of the NR samples remained high despite that the degree of storage hardening was low, probably due to the role of hydroxylamine as an antioxidant The gel content of the NR samples decreased at a faster rate than that of the molecular weights This is attributed to the denaturation of the proteins in the crosslink-point, leading to the dissociation of crosslinks, or higher rate of oxidation due to the presence of a high level of metal ions in the gel The correlation between Wallace plasticity and the geometrical mean of $\overline{M}_n$ and $\overline{M}_w$, *i e* $(\overline{M}_n\overline{M}_w)^{1/2}$ of the samples was found to be similar after PRI ageing probably due to the same processing and ageing conditions Determination of activation energy of oxidation by DSC is a more sensitive method than PRI in assessing the ageing resistance of NR samples The correlation between PRI and AEO was examined and found to be insignificant probably due to the difference in the conditions of ageing

ACKNOWLEDGEMENT

The authors wish to thank the Director General of the Malaysian Rubber Board for his permission to publish this paper, Ministry of Science, Technology, and Environment for funding this project under the IRPA (Intensification of Research Priority Areas) grant

Date of receipt September 2001
Date of acceptance August 2002

REFERENCE

1. BATEMAN, L. AND SEKHAR, B.C. (1966) Significance of PRI in Raw and Vulcanised Natural Rubber. *J. Rubb. Res. Inst. Malaya*, **19**, 133–140.

2. SAMBHI, M.S. (1982) Degradative Studies Related to the Plasticity Retention Index of the Standard Malaysian Rubber Scheme. I Kinetics of Degradation. *Rubb. Chem. Technol.*, **55**, 181–190.

3. SAMBHI, M.S. (1988) Degradative Studies Related to the Plasticity Retention Index of the Standard Malaysian rubber Scheme. II. Kinetics of Degradation *J nat. Rubb. Res.*, **3(2)**, 107–114.

4. GAN, L.H., NG, S.C. AND CHEE, K.K. (1991) Kinetic Study of Oxidative Scission in Natural Rubber. *Rubb. Chem. Technol.*, **65**, 1–4

5. BONFILS, F., LAIGNEAU, J.C., SYLLA, S. AND SAINTE BEUVE, J. (2001) DSC Valuation of PRI of Raw Natural Rubber. *J. Appl. Polym. Sci.*, **79**, 2354–2359.

6. MORRIS, M.D. (1991) Contribution of Storage hardening to Plasticity Retention Index Test for Natural Rubber. *J. nat. Rubb Res.*, **6(2)**, 96–104.

7. RUBBER RESEARCH INSTITUTE OF MALAYSIA (1992) RRIM Test Methods for Standard Malaysian Rubber. *SMR Bull. No. 7.*

8. SUBRAMANIAM, A. (1976) Molecular Weight and Other Properties of Natural Rubber: A Study of Clonal Variation. *Proc. Int. Rubb. Conf Kuala Lumpur. 1975*, **4**, 3–27.

9. ENG, A.H., SYAHIDAH, Y. AND LAI, P.F. (2000) Assessing Ageing Resistance of Chlorinated Natural Rubber Gloves by Thermoanalytical Technique. *J. Rubb. Res.*, **3(2)**, 63–69.

10. DWEIK, H.S. AND SCOTT. G. (1984) Mechanisms of Antioxidant Action: Aromatic Nitroxyl Radicals and Their Derived Hydroxylamines as Antifatigue Agents for Natural Rubber. *Rubb. Chem. Technol.*, **57**. 735–743.

11. SUHADOLNIK. J., RAVICHANDRAN, R., BORZATTA, V. AND VIGNALI. G. (1996) *US Patent No 5,552,464.*

12. POSPPISIL, J., NESPUREK, S., OSAWA, Z. AND KURODA, S. (1998) Optimisation of Polymer Stabilization though Proper Exploitation of Stabiliser Inherent Chemical Efficiency. *Proc. Addon World '98, London.* Paper 9.

13. ENG, A.H., OTHMAN, H., HASMA, H., RAMLI, O., MASAHULING, B., MUNIANDY, V. AND KAWAHARA, S. (2001) Some Properties of Natural Rubber from Latex-timber Clones. *J Rubb. Res.*, **4(3)**, 140–152.

14. GRECHANOVSKII, V.A., DMITRIEVA, I.P. AND ZAITSEV, N.B. (1987) Separation and Preliminary Characterization of Protein Component from Commercial Varieties of *Hevea* Rubber. *Int. Polym Sci. Technol.*, **14**, T/1–T/4.

15. ICHIKAWA, N., TANAKA, Y. AND ENG, A.H. (1993) Properties of Deproteinised Natural Rubber. *Proc. Int. Rubb. Technol. Conf. Kuala Lumpur, 1993*, 101–110

16. TANGPAKDEE, J. AND TANAKA, Y. (1997) Characterization of Sol and Gel in Natural Rubber. *Rubb. Chem. Technol.*, **70**, 707–713.

17. TANGPAKDEE, J. AND TANAKA, Y (1998) Branching in Natural Rubber. *J. Rubb. Res.*, **1(1)**, 14–21.

18. KRAMER, O. AND GOOD, W.R. (1972) Correlating Mooney Viscosity to Average

Molecular Weight. *J. Appl. Polym Sci.*, **16**, 2677–2684.

19. SIRCAR, A.K. (1997) Elastomers, *Thermal Characterization of Polymeric Materials* (*Turi, E.A. ed.*), Volume 1. Chapter 5, pp. 888–1378, Second edition. USA: Academic Press.