

Rheological and Processing Properties of Purified Natural Rubber

N. Rattanasom,^{1,2} K. Suchiva^{2,3}

¹*Institute of Science and Technology for Research and Development, Mahidol University, Salaya, Nakhon Pathom 73170, Thailand*

²*Centre for Rubber Research and Technology Unit, Mahidol University, Salaya, Nakhon Pathom 73170, Thailand*

³*Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand*

Received 23 October 2003; accepted 19 January 2005

DOI 10.1002/app.21968

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Studies were performed on the nature and magnitude of the variabilities in the rheological and processing properties of purified natural rubber (PNR). PNR samples were prepared from three clones of NR (RRIM 600, GT 1, and KRS 156). The corresponding whole NR (WNR) containing total nonrubber substances was also prepared for comparative purposes. All samples were stored for 3 months to elucidate the effect of storage on their rheological and processing properties. A novel study was also conducted to determine whether the commonly reported variabilities in the rheological properties had actual effects on the mixing. These were studied by means of an instrumented torque rheometer fitted with a small mixer head. The results showed that the vulcanization time of PNR was consistent and did not show clonal variation. PNR exhibited large

clonal variation in the viscosity at a low shear rate and storage hardening, similar to the ordinary NR. However, the variations in the viscosity of PNR became less evident as the shear rates increased toward 200 s^{-1} . The significant findings were that the observed variations in the rheological properties had no practical effect on the mixing time of PNR samples with carbon black. Moreover, the PNR samples required less energy for mixing than their WNR counterparts. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 456–465, 2005

Key words: purified natural rubber; clonal variation; non-rubber substances; rheological properties; processing properties

INTRODUCTION

Purified natural rubber (PNR) is NR from which most of the nonrubber constituents are removed by repeated centrifugation. PNR, being largely free of non-rubber substances (mainly proteins and lipids), should be particularly suitable as a starting material for the manufacturing of medical products such as catheters because nonrubber substances that cause allergies (e.g., proteins) are mostly removed. The mechanical and dynamic properties of PNR were studied previously.^{1,2} It was found that PNR exhibited superior crack growth resistance to NR. This article reports a study of the rheological and processing properties of PNR. Apart from making contributions to additional knowledge of the processing characteristics of PNR, the present study was undertaken to solve or alleviate the problems of the variability of NR.

NR, which is a tough and highly elastic material, is notorious for its inconsistent processing properties. The variability of NR is a disadvantage as an industrial raw material compared to synthetic rubbers, because the modern NR processing industry has become increasingly automated for improved productivity and product quality. Therefore, consistent raw materials input is necessary. The nonrubber constituents of NR have been reported to be at least partially responsible for the variability in the properties of NR. For instance, amino acids have been demonstrated to be capable of causing increases in the viscosity of NR during storage, thus making it difficult to control the viscosity of NR at a steady level.³ Nitrogenous compounds occurring naturally in fresh latex could act as natural activators for sulfur vulcanization.^{4,5} The rheological properties and cure behaviors have been shown to be influenced by clonal variations and the methods of preparation of NR.⁶ Therefore, it was of interest to investigate whether PNR, which was essentially free of nonrubber constituents, would exhibit more consistent rheological and process properties compared with whole NR (WNR) or normal NR. A novel study was also performed to determine whether the commonly reported variability in the rheological properties had actual effects on its mixing behavior.

Correspondence to: K. Suchiva (krisdasc@mtec.or.th).

Contract grant sponsor: National Metal and Materials Technology Center, National Science and Technology Development Agency.

TABLE I
Compound Formulation

Ingredient	Amount (phr)
Rubber	100
ZnO	6.0
Stearic acid	0.5
Sulfur	3.5
CBS	0.5

CBS, *n*-cyclohexylbenzothiazole-2-sulfenamide.

EXPERIMENTAL

Preparation of WNR and PNR samples

Fresh NR latex of three clones, including RRIM 600, GT 1, and KRS 156, was collected from cups 2–3 h after tapping. The latex of each clone was separated into two portions for preparation of PNR and WNR samples. For preparation of PNR samples, the fresh NR latex was centrifuged at 10,000 rpm for 60 min using sodium dodecyl sulfate as a dispersant. Centrifugation was carried out 4 times at 25°C using an ultracentrifuge machine (Sorval 3600S). After the fourth centrifugation, the rubber cream was cast into thin films. The dried rubbers were then stored in polyethylene bags in the dark at room temperature for further use. P600, PGT1, and P156 designate PNR samples prepared from RRIM 600, GT 1, and KRS 156 lattices, respectively. WNR was prepared by casting fresh NR latex of various clones into thin films and leaving them to dry at room temperature (ca. 30°C) for 24 h. The WNR sheets were then removed and further dried in the oven at 50°C for 24 h. The dried WNR was then kept under the same conditions as PNR. W600, WGT1, and W156 designate WNR samples prepared from RRIM 600, GT 1, and KRS 156 lattices, respectively. Finally, the nitrogen content, which is an indication of the amount of proteins present in the NR samples, was determined by the semimicro Kjeldahl method.

Determination of cure time

All NR samples were compounded according to the formulation in Table I. The cure time of each compound was determined by using an oscillating disk rheometer (Monsanto 100S) at 155°C and a 3° arc, in accordance with ASTM D 2084-88. The optimum cure time was taken as the time at which the rheometer torque reached 90% of maximum.

Measurements of rheological properties

The Mooney viscosities of various NR samples were determined at 100°C with a Mooney viscometer (Monsanto 1500), in accordance with ASTM D 1646-99. A large rotor was used. The preheating time and reading

time were 1 and 4 min, respectively. Thus, the Mooney viscosity values were reported as ML (1 + 4 at 100°C) Mooney unit.

The initial Wallace plasticity (P_0) values of various NR samples were determined by using a Wallace rapid plastimeter, in accordance with ASTM D 926-98. The median of three specimens was taken as the P_0 value.

The apparent shear viscosities of the samples were determined at shear rates of 20, 50, 100, and 200 s⁻¹ by using a Monsanto processability tester. The test was carried out at 120°C. A die diameter of 2 mm (length/diameter ratio = 16 : 1) was used. About 12 g of the rubber sample was cut into small pieces, put into the barrel, and preheated for 10 min before the extrusion measurement. This period was required for complete fusion and uniform heating of the sample. The relaxed die swells of the extrudate were also measured at shear rates of 50 and 100 s⁻¹.

To elucidate the effect of storage, the samples were stored in black polyethylene bags and kept in a dark cabinet for 3 months.

Measurement of gel content

About 2 g of the sample was immersed in 200 mL of toluene for 7 days. The amounts of the dissolved and undissolved parts were determined by filtration using a 60-mesh aluminum screen. The gel content was taken as the percentage of the undissolved part after being completely dried at 50°C. The error in the percent gel content was computed to be about ±0.02% for all samples.

Determination of molecular weight (MW) and MW distribution (MWD)

The MW and MWD of the samples were determined by using gel permeation chromatography. Four columns (10⁴, 10⁵, and 10⁶ Å and CPD linear ultrastyrage, Waters) were used in series. The samples were prepared as 0.1% (w/v) solutions in tetrahydrofuran.

Measurement of mixing behaviors

The mixing behaviors of the rubber samples were determined at 50°C using the 79-mL minimixer of an instrumented torque rheometer (Haake Rheocord 90) with a rotor speed of 65 rpm. Forty grams of the rubber sample in strip form was put into the mixing chamber and masticated for 1.5 min. Then, 40 phr of carbon black (N 330) was added and the mixing curve was recorded. A black incorporation time (BIT) was defined as the time interval between the addition of carbon black and a second peak in the mixing curve.⁷ The mixing time was determined from the point where the main slope of the mixing curve meets the

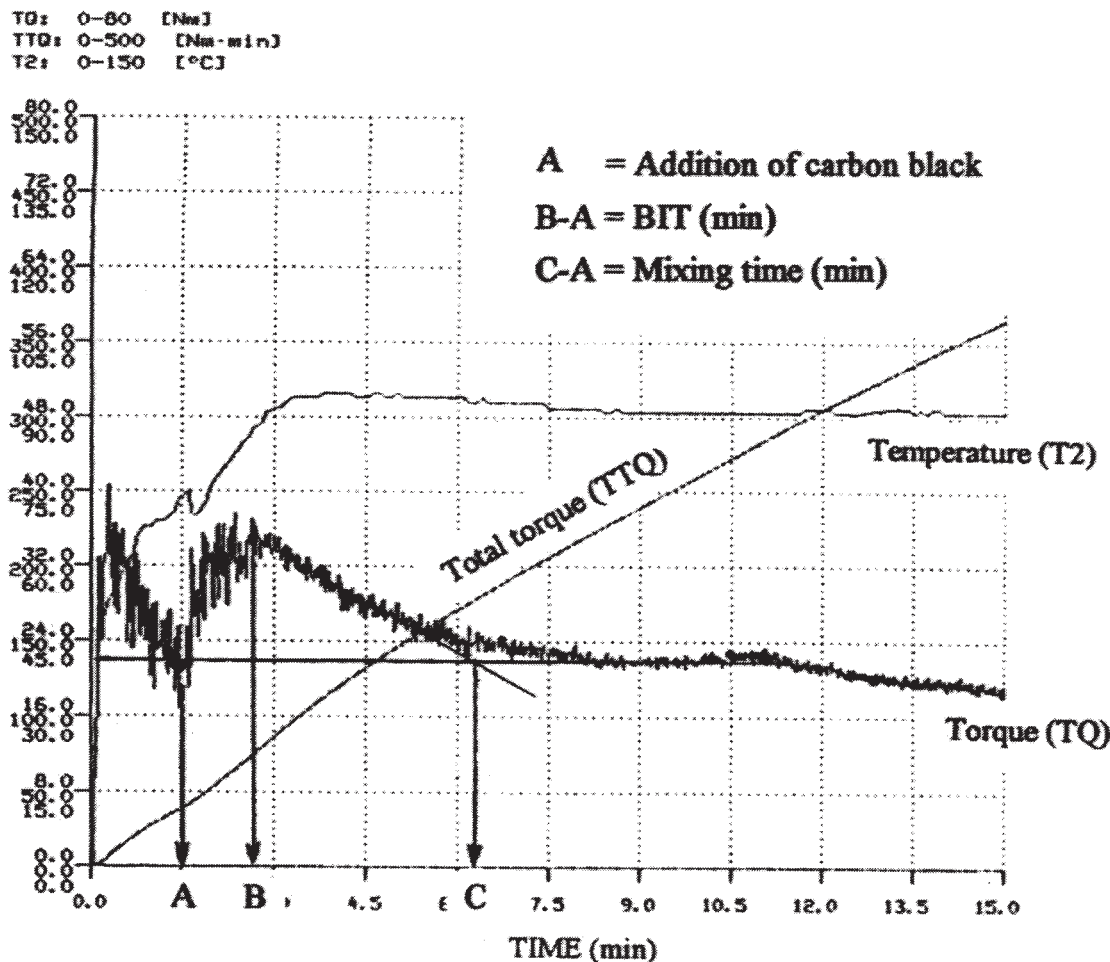


Figure 1 Characterization of the mixing curve.

extrapolated baseline as shown in Figure 1. The total mixing torque is the total torque value at mixing time.

RESULTS AND DISCUSSION

Vulcanization behavior of PNR

Table II shows the vulcanization time of PNR prepared from three clones of NR (RRIM 600, GT 1, and KRS156, designated as P600, PGT1, and P156, respectively). The corresponding properties of WNR are also

TABLE II
Cure Time and Nitrogen Content of PNR and WNR

Property	PNR			WNR		
	P600	PGT1	P156	W600	WGT1	W156
Cure time (min)	6.9	6.8	6.5	4.5	4.7	3.9
Nitrogen content (wt % rubber)	0.03	0.03	0.04	0.52	0.45	0.61

given for comparison, together with the nitrogen contents of all the rubber samples under study. Table II shows that the cure times of PNR were significantly longer than those of the normal NR, represented here by WNR. Their cure times were also quite consistent, independent of the clone from which they were prepared. The same could be said of WNR, where only small clonal variations of the cure times were observed. It has been reported that nitrogenous substances, which occur naturally in NR, act as activators for sulfur vulcanization.^{4,5} Thus, when they were removed from the NR, as in PNR, the rubber exhibited a slower cure. In addition, if the nitrogen contents in the NR are well controlled, for example, by removing all of it (the case of PNR) or leaving it intact (the case of WNR), the cure behaviors of NR would be expected to be invariable.

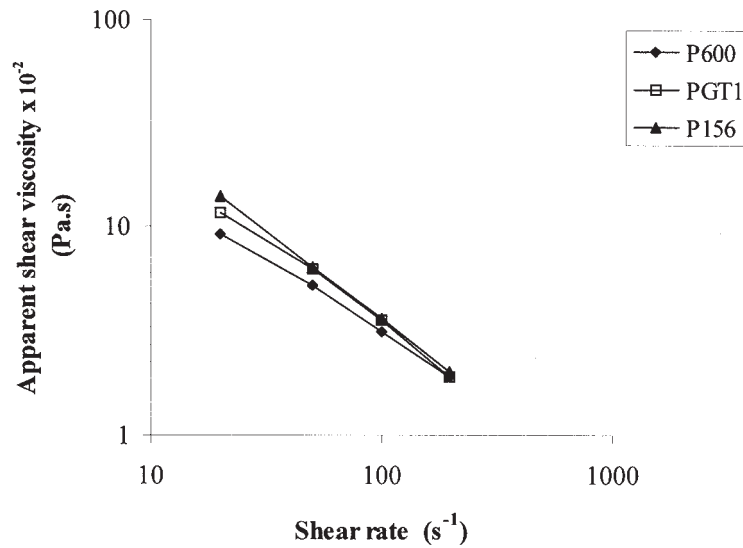
Rheological properties of PNR

Various measurements of the viscosity (P_0 , Mooney viscosity, and apparent shear viscosity) were made. These measurements represent the flow behavior of

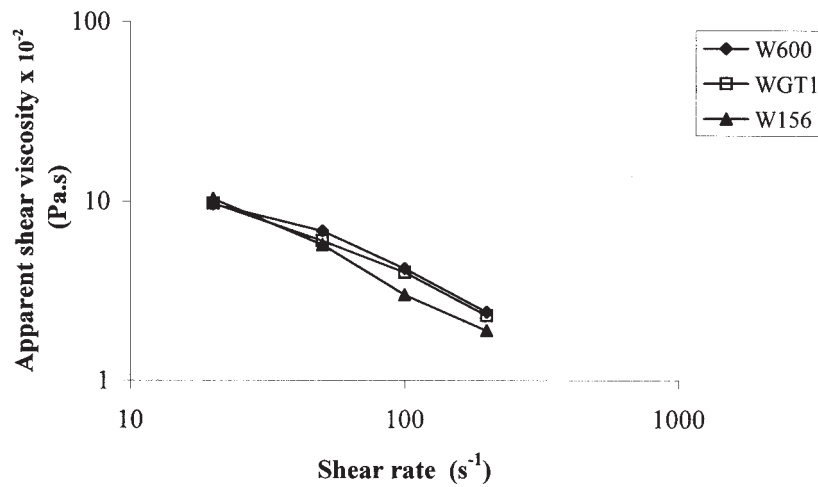
TABLE III
Initial Wallace Plasticity (P_0) and Mooney Viscosity of PNR and WNR

Property	PNR			WNR		
	P600	PGT1	P156	W600	WGT1	W156
P_0	50	66	60	58	64	52
Mooney viscosity	70	91	83	86	92	82
Gel content (wt %)	0.03	0.03	0.05	0.06	0.05	0.58

PNR at different shear rates from 0.1 (Wallace plasticity) to 1 (Mooney viscosity) and 20–200 s^{-1} (shear viscosity by capillary rheometer). Thus, the range of rheological properties that were studied should give information on the mixing and extrusion behaviors of PNR. The results of the measurements are displayed in Table III for the P_0 and Mooney viscosity and in Figure 2 for the shear viscosity. The rheological properties of WNR are also given for comparative purposes. Results show that PNR exhibited clonal variation in the viscosity at a low deformation rate (P_0 and



(a)



(b)

Figure 2 The shear viscosities of (a) PNR and (b) WNR as measured by a capillary rheometer.

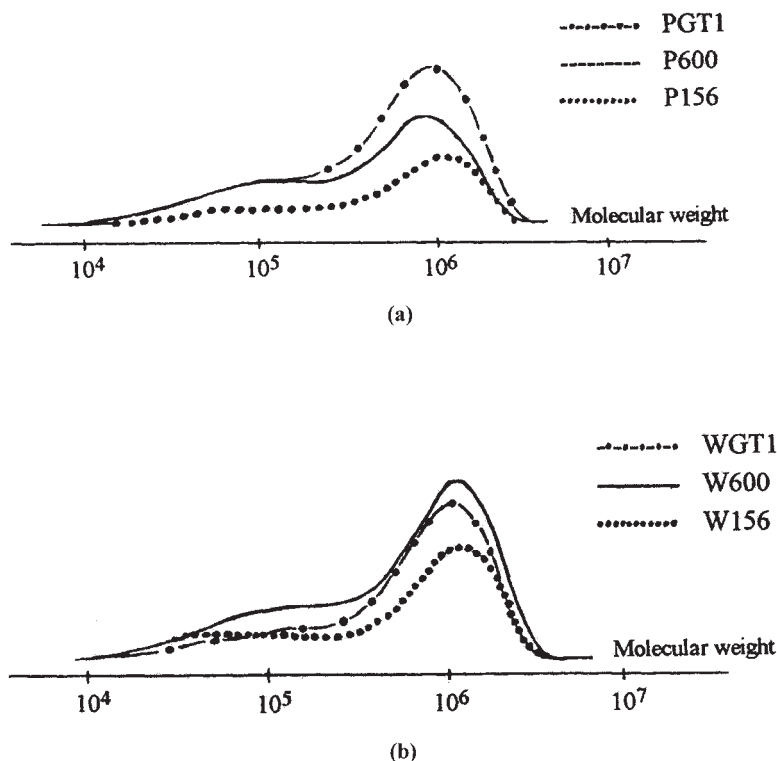


Figure 3 The MW and MWD of (a) PNR and (b) WNR as measured by gel permeation chromatography.

Mooney viscosity), similar to WNR or the normal NR where clonal variations are well known.⁶ Because the nonrubber constituents were mostly removed from the PNR, the observed clonal variation could not be accounted for by the nonrubber content of NR. Therefore, the differences in the P_0 and Mooney viscosity of PNR and WNR should arise from the structural parameters of the rubbers. This may be the gel content, MW, MWD, or molecular structure of NR.

Table III also shows the gel contents of the NR samples. The MW and MWD were also measured, the results of which are given in Figure 3. From the results of the present measurements, it was surprising that the gel contents of both PNR and WNR were very low (0.03–0.58 wt %). Much higher gel contents (30–40 wt %) are usually reported for NR.^{8,9} However, because the gel contents of PNR and WNR in the present study were both low and invariable, it is unlikely that gel is the cause of the high viscosity of NR or that it is responsible for the observed clonal variation. Figure 3 provides evidence that the MW and MWD should not be responsible factors for the variation in the viscosity of PNR or WNR of different clonal types. It was apparent that different clones of NR exhibited similar MWD curves and close values of the peak MW (number-average MW). Thus, the results of the present study showed that the variation in the viscosity of PNR and WNR could not be accounted for by the gel content, MW, or MWD of the rubbers. Other structural

parameters (e.g., the molecular structure of NR) are more likely to be the responsible factors.

Recently, Tanaka and Tangpakdee have proposed that the molecular structure of NR consists of long-chain branching.^{10,11} Two types of branches have been proposed: one is due to the association with proteins and the other involves ionic interactions between the terminal phospholipid groups. The formation of these branches is still not understood, but it has been demonstrated that they can be removed separately by enzymatic deproteinization and transesterification.¹⁰ The branched structures of NR could be the major factor that influences the observed rheological properties of PNR and WNR. Further work is required to elucidate the structures and rheological properties of NR.

Figure 2 displays the viscosities of PNR at higher shear rates between 20 and 200 s^{-1} that were studied using a capillary rheometer. It reveals that the shear viscosities of PNR and WNR decreased with increasing shear rate. This was to be expected because polymers are known to exhibit non-Newtonian flow. PNR showed large clonal variations of the shear viscosity at a low shear rate (20 s^{-1}) but the variations became less evident as the shear rates increased toward 200 s^{-1} . The data in Figure 2 also reveal that WNR exhibited larger variations in viscosity with the clonal type than PNR when the shear rate was $>50 s^{-1}$.

TABLE IV
Die Swell of PNR and WNR

Property	Shear rate (s ⁻¹)	PNR			WNR		
		P600	PGT1	P156	W600	WGT1	W156
Die swell (%)	50	50	37	60	74	64	70
	100	67	61	71	100	80	90

In addition to the shear viscosity, the capillary rheometer used in the present study (Monsanto processability tester) can also be used to measure the extrusion die swell. Thus, the die swells of PNR and WNR were measured. These measurements were of interest because they give indications of the elasticity of the rubbers. Rubber that has high elasticity exhibits a large die swell upon being extruded and will be difficult to incorporate a filler such as carbon black. The results of the present study are shown in Table IV. Based on the above reasoning, it can be seen from Table IV that PNRs were less elastic than WNRs because their die swell values were significantly smaller than those of WNRs at both shear rates. It is still unclear why PNR should exhibit smaller elasticity than WNR, but this is likely to be linked to the molecular structure and interactions with nonrubber substances. Further study is required to verify this point.

Storage hardening

One of the major disadvantages of NR, compared to synthetic rubber, is that it undergoes viscosity increases during storage.¹² This phenomenon, known as storage hardening, contributes to the problem of invariability in the properties of NR. The mechanism of storage hardening is still not completely understood, but reactions of carbonyl-containing groups on the NR molecules and amines on the

proteins has been proposed to be responsible.^{13,14} Technology does exist to prevent storage hardening from occurring.¹⁵

We were curious to find out whether PNR exhibited storage hardening because proteins, or most other nonrubber compounds, have largely been removed from PNR. Thus, the NR samples were stored at room temperature for 3 months and the viscosity changes were followed. The results are presented in Table V. It can be seen that PNR underwent storage hardening to the same extent as WNR. This was rather surprising because storage hardening is believed to be caused by crosslinking involving carbonyl groups on NR molecules and amino groups of proteins present in NR. The nitrogen contents for PNR were very low (0.03–0.04 wt %), so that they should be relatively free of proteins. Therefore, the condensation reactions leading to crosslinking and increases of the viscosity should not occur to a significant extent. In fact, this was supported by the results of the measurement of the gel contents shown in Table V. Note that the gel content for PNR did not increase after storage. However, WNR showed slight increases of the gel content. Results of the present study thus suggested that the storage hardening or viscosity increase in PNR was not caused by chemical crosslinking or at least it was not the major cause.

Figure 4 shows the shear viscosities of stored PNR and WNR as a function of the shear rate up to 200 s⁻¹. It can be seen that the relatively large increases in the viscosity of PNR following storage did not affect its mixing behavior because the shear viscosities of the initial and stored PNR of all clones converged to almost the same value at shear rates relevant to the mixing process (i.e., 100–200 s⁻¹). In contrast, storage-hardened WNR would affect their mixing with filler and other chemicals more than would PNR, because greater variations of the shear viscosity were observed at shear rates between 100 and 200 s⁻¹.

TABLE V
Storage Hardening of PNR and WNR

Property	PNR			WNR		
	P600	PGT1	P156	W600	WGT1	W156
<i>P</i> ₀						
Initial	50	66	60	58	64	52
After storage	54	69	68	65	66	58
Extent of increase	4	3	8	7	2	6
Mooney viscosity						
Initial	70	91	83	86	92	82
After storage	91	107	94	102	103	93
Extent of increase	21	16	11	16	11	11
Gel content (wt %)						
Initial	0.03	0.03	0.05	0.05	0.06	0.58
After storage	0.03	0.02	0.06	2.42	0.47	10.5

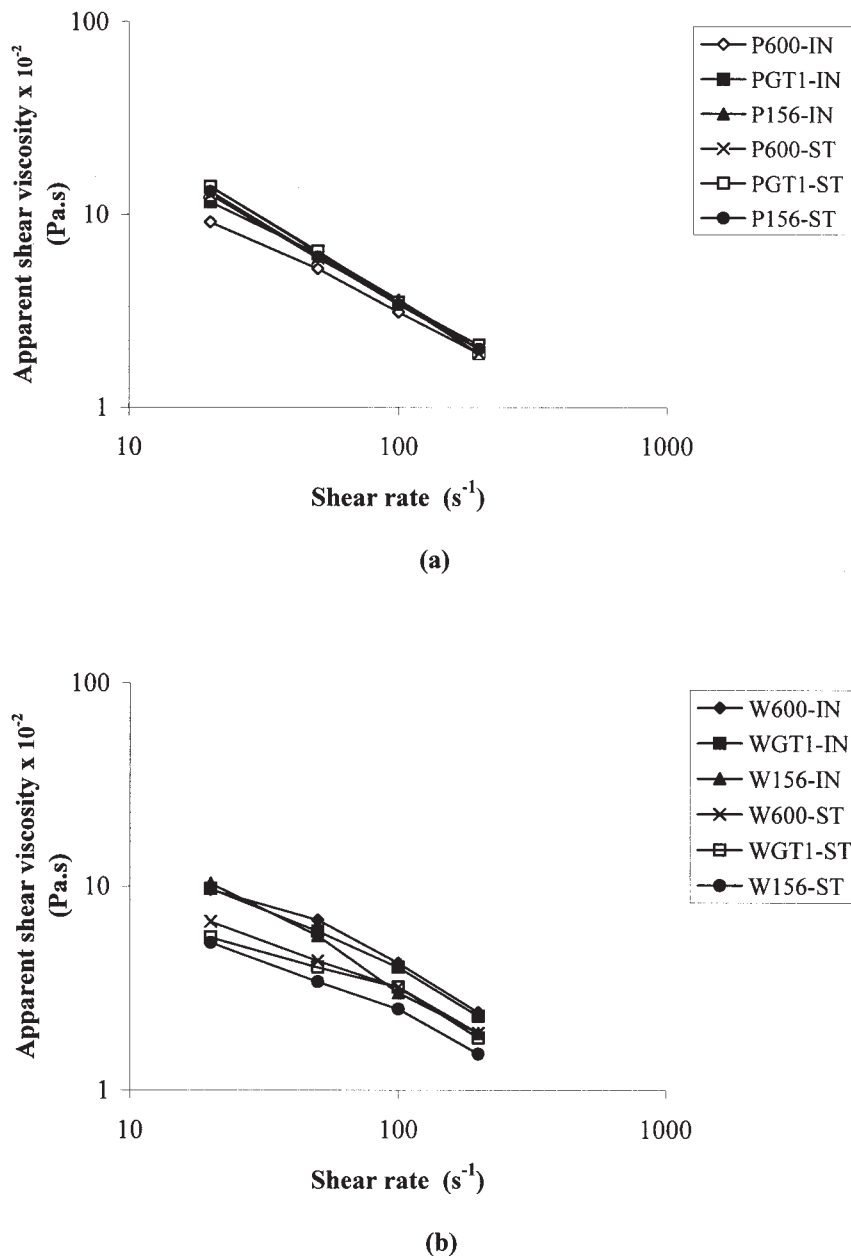


Figure 4 The shear viscosities of the initial (IN) and storage-hardened (ST) NR at shear rates between 20 and 200 s⁻¹ for (a) PNR and (b) WNR.

Mixing behaviors

The mixing behaviors of all WNR and PNR samples with carbon black before and after storage were studied. The two types of NR exhibited two different mixing behaviors, independent of the clonal types. Typical mixing curves of PNR and WNR samples are shown in Figures 5 and 6, respectively. All PNR samples exhibited maxima in the mixing curves, designated as BIT, similar to other synthetic rubbers (e.g., butadiene rubber, styrene-butadiene rubber).⁷ The explanation is that the initial rise in mixing torque after the addition of carbon black to the rubber is caused by

the incorporation of carbon black into the rubber. In this region, the rate of incorporation is thought to be higher than the rate of dispersion. The progressive decrease in mixing torque after BIT is due to dispersion of carbon black and possibly plasticization of the rubber. Here, the rate of dispersion is greater than the rate of incorporation.⁷ By contrast, WNR showed no BIT on the mixing curves. The mixing torques of WNR showed rapid increases when carbon black was added and gradually decreased to a constant level. Therefore, the BIT could not be measured. Moreover, the mixing torques of the WNR samples showed large fluctua-

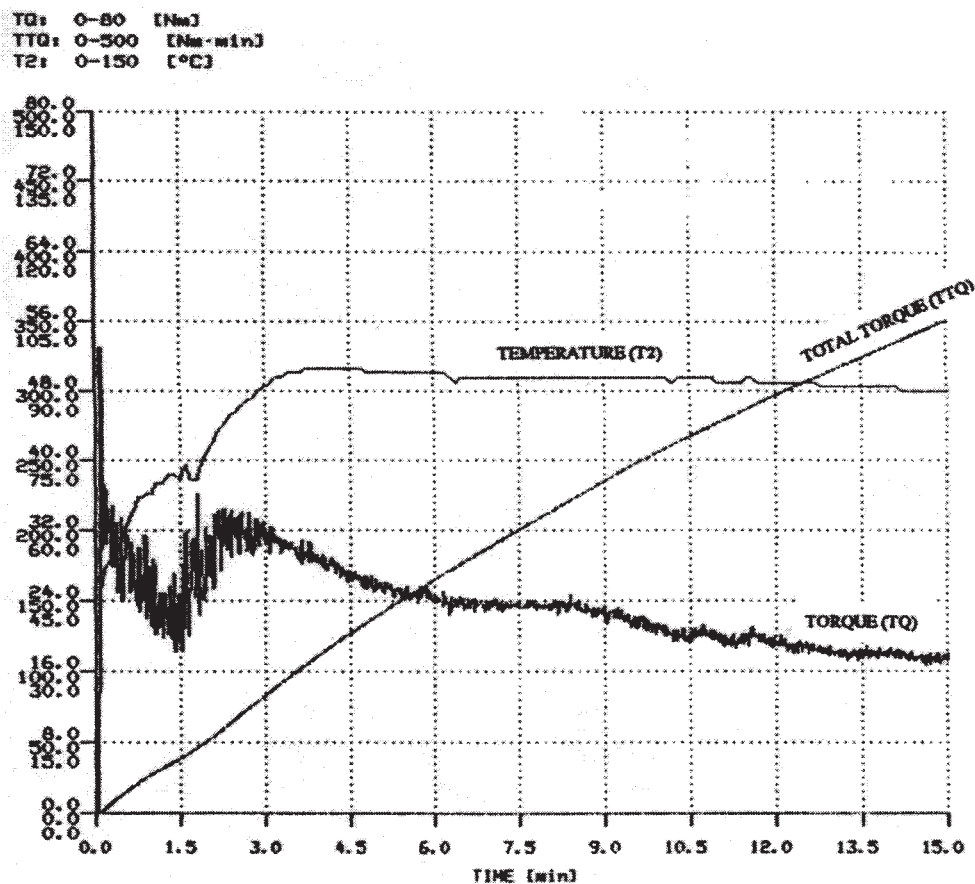


Figure 5 The typical mixing curve of PNR.

tions compared to those of PNR samples. This may infer greater difficulty of mixing with carbon black for WNR samples because of their high elasticity. The higher elastic behavior of WNR samples, compared to PNR samples, could be seen from the die swell values in Table IV. It is clear that WNR samples exhibited greater elasticity, as indicated by the higher die swell, than PNR samples at a certain shear rate. When the rubber is more elastic than plastic, and with small flow, incorporation of filler becomes difficult because it tends to cause bouncing of the filler. Therefore, wetting of the filler will be more difficult and, with little flow of the rubber, large-scale incorporation of the filler cannot be expected to take place. Thus, the absence of an initial gradual increase in the mixing torque after the addition of carbon black in WNR samples might indicate no large-scale incorporation of carbon black into this type of sample at the beginning of mixing.

The mixing properties of PNR and WNR are summarized in Table VI. It can be seen that the BIT of all PNRs before and after storage were comparable and were in the range of 0.7–1.2 min, despite the fact that their Mooney viscosities were widely different (see Tables III, V). The mixing times of PNR, both before

and after storage, were also relatively independent of the Mooney viscosity. The mixing times of storage-hardened PNRs were actually even smaller than that of the initial PNR. The observed mixing properties of PNR were initially surprising because hard rubber (high Mooney viscosity) is expected to be more difficult to mix with filler, hence, more variations in BIT and mixing time. However, if the shear viscosity at the shear rate relevant to mixing ($100\text{--}200\text{ s}^{-1}$) is considered, it was understandable why the mixing properties were as shown, because the shear viscosities of PNR at shear rates of $100\text{--}200\text{ s}^{-1}$ were observed to assume approximately the same values, as previously reported in Figures 2 and 4. The mixing times of WNR were also observed to be rather insensitive to the Mooney viscosity, although their mixing times were slightly longer than those of PNR. The results indicated that it was a little more difficult to mix WNR with filler than to mix PNR with filler, and the higher elastic content of WNR should be the factor responsible. The total mixing torques of all PNRs and WNRs, which are measures of the energy required for mixing, were also not directly related to the Mooney viscosity values. For example, PGT1 with a Mooney viscosity of 91 required the same total torque for mixing as P156,

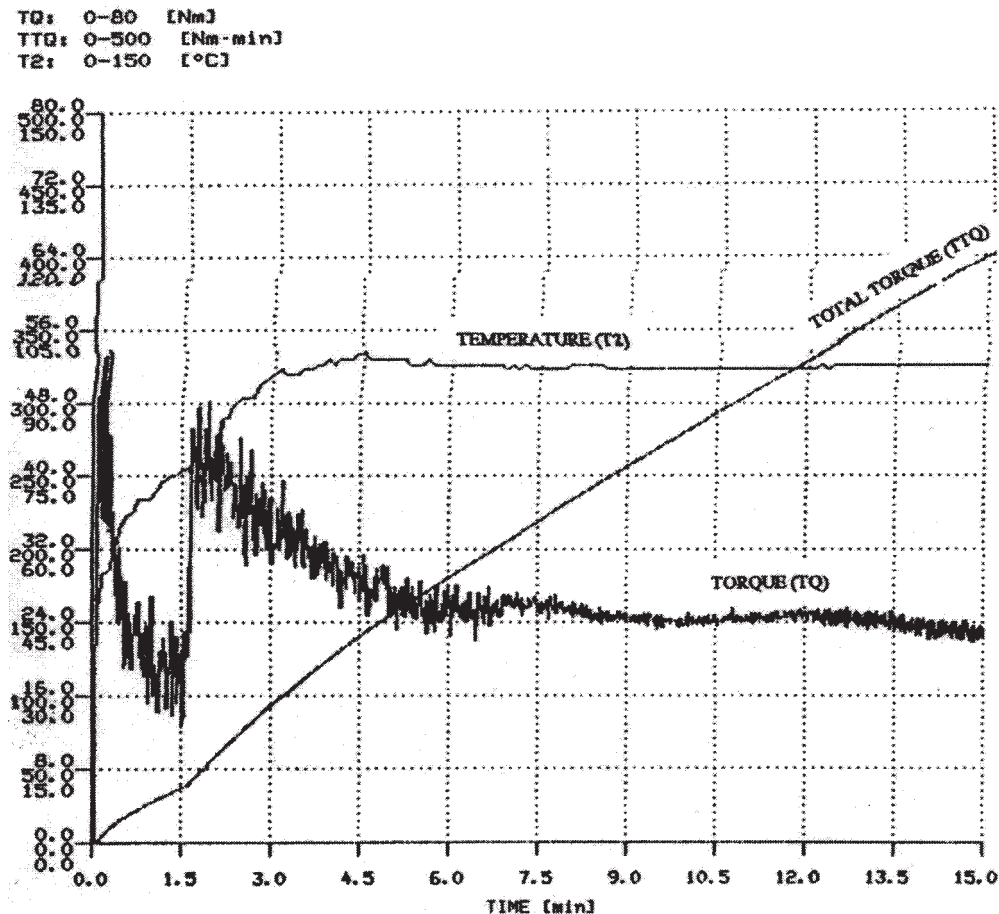


Figure 6 The typical mixing curve of WNR.

the Mooney viscosity of which was only 83, or storage-hardened PGT1 (Mooney viscosity of 107) required a smaller mixing energy or total torque than the corresponding P156, which had a Mooney viscosity of only 94.

CONCLUSIONS

PNR underwent sulfur vulcanization at rates slower than did normal NR (WNR). The vulcanization time

was consistent and did not show clonal variation. However, PNR still exhibited a large variation in the Mooney viscosity and P_0 , similar to the normal NR. The variation could not be accounted for by the non-rubber content, the amount of gel, MW, or MWD. The molecular structure of NR should be the major responsible factor. Further study is required in order to verify this hypothesis. The variation in the viscosity of PNR was insignificant at higher shear rates, particularly those relevant to the mixing process ($100-200 \text{ s}^{-1}$).

TABLE VI
Mixing Properties of PNR and WNR

Sample	BIT (min)		Mixing time (min)		Total mixing torque (Nm min)	
	Before storage	After storage	Before storage	After storage	Before storage	After storage
PNR						
P600	1.1	0.9	4.7	4.3	136	120
PGT1	0.9	1.0	4.8	4.3	150	131
P156	1.2	1.0	4.9	4.4	150	135
WNR						
W600	—	—	5.4	4.9	154	138
WGT1	—	—	5.2	5.2	159	157
W156	—	—	6.0	5.0	161	140

This was confirmed in the mixing study that was carried out. The mixing time and mixing torque of PNR with carbon black were found to be rather independent of the Mooney viscosity of the rubber. The same applies to the mixing properties of WNR. Another significant finding was that PNR still exhibited storage hardening, the behavior previously observed to be specific to the normal NR and believed to involve interactions with proteins in NR. Thus, the display of storage hardening by PNR was rather surprising unless the existing explanation of storage hardening in NR is incorrect. However, the increase in the viscosity of PNR during storage appeared to have no deleterious effect on its mixing properties, for reasons similar to that explained above.

The authors gratefully acknowledge the staffs of the Rubber Research Center in Songkhla, Yala Experiment Station, and the Rubber Research Institute, Department of Agriculture and Cooperatives, Thailand, for providing NR latex and other facilities. Sincere appreciation is extended to the National Metal and Materials Technology Center, National Sci-

ence and Technology Development Agency, for financial support.

References

1. Suchiva, K.; Kowitteerawut, T.; Srichantamit, L. *J Appl Polym Sci* 2000, 78, 1495.
2. Rattanasom, N.; Chaikumpollert, O. *J Appl Polym Sci* 2003, 90, 1793.
3. Boucher, M.; Carlier, G. *Rev Gen Caoutch* 1964, 41, 1297.
4. Metherall, C. *Plast Rubber Mater Appl* 1980, 15.
5. Altman, R. F. A. *Ind Eng Chem* 1948, 40, 241.
6. Subramaniam, A. *RRIM Technol Bull* 1980, 4, 1.
7. Coran, A. Y.; Cotton, J. B. *Rubber Chem Technol* 1992, 65, 973.
8. Wiriyasatit, S. M.S. Thesis, Mahidol University, 1990.
9. Tangpakdee, J.; Tanaka, Y. *Rubber Chem Technol* 1997, 70, 707.
10. Tanaka, Y. In *The 9th International Seminar on Elastomers*; Kyoto, Japan, 2003; p 41.
11. Tanaka, Y.; Tangpakdee, J. *J Nat Rubber Res* 1998, 1, 52.
12. David, B. R. *J Nat Rubber Res* 1986, 1, 202.
13. Yip, E. *J Nat Rubber Res* 1990, 5, 52.
14. Sekhar, B. C. In *Proceedings of the Natural Rubber Research Conference*; Kuala Lumpur, 1960; p 512.
15. Sekhar, B. C. *J Polym Sci* 1960, 48, 133.