Crystallization Behavior and Strength of Natural Rubber: Skim Rubber, Deproteinized Natural Rubber, and Pale Crepe

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ABSTRACT: Crystallization behavior of natural rubber prepared by different procedures, such as skim rubber, deproteinized natural rubber (DPNR), and pale crepe, was investigated by dilatometry at −25°C. DPNR was fractionated into four fractions by molecular weight. The high molecular weight fractions contained about 1.7 linked fatty acids per rubber molecule, while low molecular weight fraction showed an increase in quantity. The overall crystallization rate of the rubber decreased as the molecular weight decreased. Skim rubbers, purified by extraction with acetone, crystallized rapidly compared to acetone-extracted pale crepe, despite that the molecular weight of skim rubbers was about one-half of pale crepe. The quantity of linked fatty acid per rubber molecule of skim rubbers was less than 0.5, while that of pale crepe was 1.6. The difference in the rate of crystallization was presumed to be associated with the level of fatty acids linked to rubber molecule at the terminal and branch points present in pale crepe. The green strength of skim rubbers was significantly lower than those of untreated pale crepe and DPNR, but was comparable to transesterified DPNR, which contains no gel fraction and no linked fatty acids. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1510–1516, 2000

Key words: crystallization behavior; natural rubber; skim rubber; deproteinized natural rubber; pale crepe; dilatometry

INTRODUCTION

Natural rubber (NR), obtained from *Hevea brasiliensis,* shows outstanding strength[1,2] and tack[1] in the unvulcanized state and high tensile strength,[3] and crack growth resistance[4,5] in the vulcanized state. This is explained to be due to its rapid crystallizability on straining.[6] Factors influencing the crystallization behavior of NR have been investigated so far and reported in the previous works have originated from its high *cis*-1,4 isoprene unit content,[7] a long average sequence length of *cis*-1,4 units,[8] the presence of free fatty acids as a mixture,[9] and so on. However, the rate of crystallization of synthetic *cis*-1,4 polyisoprene (IR) was significantly lower than that of NR, even

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though stearic acid was added into it.[10] The difference in the rate of crystallization between NR and IR was presumed to be due to the unknown terminal group of NR.

In our previous study,[11] the fundamental structure of NR has been presumed to consist of an ω-terminal, two *trans*-1,4 isoprene units, about 5000 *cis*-1,4 isoprene units, and an α-terminal that is linked to phospholipid containing fatty acid ester group, aligned in that order. The ω-terminal was expected to be the dimethylalyl group modified with proteins, which was attracted together through the formation of hydrogen bonding, while the α-terminal was comprised of phospholipids forming chemical crosslinks.[11] Tensile strength and green strength of NR were found to be significantly reduced after transesterification, due to the decomposition of the chemical crosslinks of phospholipids linked with fatty acid groups,[12] but was not changed by deproteinization with a proteolytic enzyme and surfactant.[13]

The crystallization behavior of NR at -25°C was found in our previous studies[12,18] to be promoted primarily by fatty acids, but not by proteins. The rate of crystallization decreased after removing free fatty acids, which were present as a mixture, by means of acetone extraction,[9] while it was partly recovered by removal of residual fatty acids linked to rubber molecule after transesterification.[12] The crystallization of acetone-extracted rubber linked with fatty acids at the terminal was promoted by adding 1% (w/w) methyl linoleate, which is plasticizer for NR.[14] However, the crystallization of transesterified NR was suppressed by the addition of methyl linoleate as in the case of IR[15] due to the lack of fatty acids linked to the rubber.[14,16] These findings demonstrate that both of the outstanding strength and high crystallizability of NR were originated from the linked fatty acids.

In the present study, the effect of the level of linked fatty acids on the crystallization behavior and green strength of the rubber was investigated using skim rubbers, pale crepe, and deproteinized NR (DPNR). Small rubber particles, less than 0.2 μm in diameter, in fresh latex cannot be separated as cream phase by centrifugation and remained in the serum fraction. Skim rubber, recovered by acid coagulation of small rubber particles in the serum fraction, contained very small amounts of linked fatty acids. The DPNR contained fatty acid as in the case of ordinary NR. The level of fatty acid and its effect on crystallization was analyzed for four fractions of different molecular weights.

EXPERIMENTAL

Materials

Natural rubber samples used in this study were skim rubber-A (skim-A) and skim rubber-B (skim-B) provided by Rayong Bangkok Rubber, commercially available pale crepe, and fresh field latex isolated from RRIM 600. The skim-A was coagulated from small rubber particles in the serum fraction, whereas skim-B was coagulated from small and medium rubber particles, obtained from the serum of recentrifuged high-ammonia latex. The skim rubbers in 1% (v/w) toluene solution were centrifuged at about $10{,}000 \times g$ to remove nonrubber components followed by precipitation with methanol.

Enzymatic deproteinization was carried out by incubation of the fresh field latex diluted to 30% dry rubber contents (DRC) with 0.04 w/v % proteolytic enzyme (Novo Alcalase 2.0T) and 1 w/v % sodium dodecyl sulfate for 12 h at 38°C followed by centrifugation.[17] The cream fraction was redispersed in 1 w/v % SDS to make 30% DRC latex and was washed twice by centrifugation to prepare DPNR latex. DPNR was recovered by centrifugation followed by coagulation with methanol or acetone, and was dried under reduced pressure for at least one week.

Fractionation of DPNR was made in the usual way by adding methanol into the dilute toluene solution.

The rubbers were extracted with acetone in a Soxhlet apparatus for 24 h under nitrogen atmosphere and dried under reduced pressure for 3 days.

Transesterification of NR was carried out in toluene solution by the reaction with fresh sodium methoxide at room temperature for 2.5 h followed by precipitation with methanol–toluene.[12] Mixtures of the rubber and methyl linoleate in a ratio of 99 to 1 by weight were prepared by freeze drying of about 1.5 wt % benzene solution.

Measurements

Fourier transform infrared (FTIR) measurements were carried out with a JASCO 5300 FTIR spectrometer. The quantity of fatty acid ester groups present in the rubbers was determined based on the calibration curve prepared by using a mixture

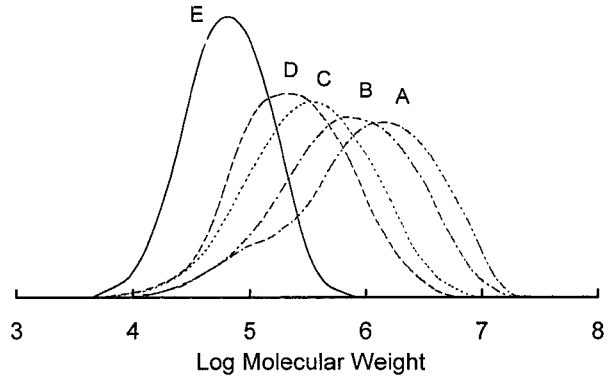

Figure 1 Molecular weight distribution of fractionated DPNR. (A) Fraction 1, (B) fraction 2, (C) fraction 3, (D) fraction 4, and (E) fraction 5.

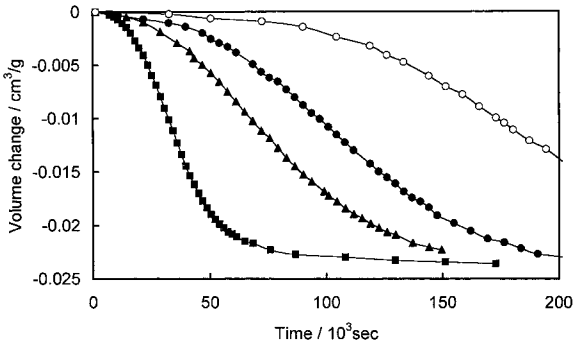

Figure 2 Crystallization behavior of fractionated DPNR. (■) Fraction 1, (▲) fraction 2, (●) fraction 4, and (○) fraction 5.

of methyl stearate and synthetic *cis*-1,4 polyisoprene, Kuraray IR10.

The measurement of isothermal crystallization behavior was made by dilatometry.[14,15] The dilatometer was placed in a cooling bath to achieve an isothermal setting at −25°C after annealing at 80°C for 30 min. The relative volumes were recorded for 5 s at 3 min intervals.

Average molecular weight and molecular weight distribution were measured by gel permeation chromatography (GPC) using a TOSOH LS-8000 with refractive index and low-angle-laser-light-scattering detectors. The eluent used was THF with a flow rate of 0.5 mL/min at 35°C.

The measurements of number average molecular weight $\overline{M_n}$ was made by a Wescan 231 Membrane Osmometer at 35 ± 0.1°C in filtrated toluene solution.

RESULTS AND DISCUSSION

Fractionated DPNR

Figure 1 shows the molecular weight distribution of fractionated DPNR. The distribution of the five fractions was unimodal and symmetrical. The polydispersity $\overline{M_w}/\overline{M_n}$ determined by GPC, was tabulated in Table I together with number average molecular weight $\overline{M_n}$ determined by membrane osmometry, and ester content. $\overline{M_n}$ decreased from fraction 1 to 5. The ester content was almost constant except for the low molecular weight fraction. The ester group was attributed to fatty acids linked to the rubber molecule at the terminal, the content of which would be proportional to the number of terminal group of the rubber. The quantity of linked fatty acid per rubber molecule was estimated from the ester content and $\overline{M_n}$ value, as shown in Table I. The quantity of linked fatty acids per rubber molecule was about 1.7 for fractions 1, 2, and 3, while low molecular weight fraction showed an increase in quantity.

Figure 2 shows isothermal crystallization behavior at −25°C for the fractionated DPNR. It is obvious that the overall crystallization rate of the fraction 1 is largest and decreases in turn as $\overline{M_n}$ decreases. In general, the rate of crystallization of a polymer increases as $\overline{M_n}$ decreases. This has been explained to be due to active translational

Table I Number Average Molecular Weight, Polydispersity, Gel Content, and Ester Content of Fractionated DPNR

			Ester Content	
Fraction No.	$\overline{M_n}$,osmo (10^5)	$(\overline{M_w}/\overline{M_n})$GPC	(mmol/kg-rubber)	(mol/mol-rubber)
1	5.21	3.28	3.3	1.7
2	4.42	2.76	3.6	1.6
3	2.60	2.46	5.0	1.3
4	2.09	2.29	13.9	2.9
5	0.81	1.61	61.0	4.9

Table II Ester Content, Nitrogen Content, and Gel Content of Skim-A, Skim-B, and Pale Crepe

Specimen	Ester Content (mmol/kg-rubber)	Nitrogen Content (%)	Gel Content (%)
Skim-A	7.5	1.72	—[d]
Skim-A-AE[a]	1.4	1.16	—[d]
Skim-B	3.6	1.88	—[d]
Skim-B-AE[b]	2.8	0.23	—[d]
Pale crepe	14.5	0.45	35
Pale crepe-AE[c]	6.2	0.45	—[d]

[a] Acetone-extracted skim-A.
[b] Acetone-extracted skim-B.
[c] Acetone-extracted pale crepe.
[d] Trace.

movements for low molecular weight polymers. In the present study, the overall crystallization rate decreased as $\overline{M_n}$ decreased. This may be attributed to impurities attached to the rubber molecule, which suppresses the crystallization of the rubber. The content of impurities should be proportional to the ester content shown in Table I.

Skim Rubber and Pale Crepe

Table II shows the ester content and nitrogen content of skim-A, skim-B, and pale crepe. The content of linked fatty acids in acetone-extracted skim rubbers was low in spite of the low molecular weight, by less than one-third in pale crepe. This may come from the difference in the preparation method of the samples and also from biosynthesis path way of natural rubber. In our previous work,[19] the small rubber particles, which were minor components of whole latex particles, were found to be composed of linear molecules with a living terminal group for chain elongation, while most of the large rubber particles were branched molecules with ester linkages. This is evidently consistent with the result that the fatty acid ester content of acetone-extracted rubbers was small for skim rubber coagulated from small rubber particles, but large for natural rubber from concentrated latex such as DPNR. For the untreated rubbers, the fatty acid ester content was larger than that of acetone-extracted rubbers, as shown in Table II. This demonstrates the presence of a significant amount of mixed fatty acid esters.

The nitrogen content of skim-A and skim-B considerably decreased after acetone extraction, while that of pale crepe did not change. Since skim-A and skim-B were prepared by acid coagulation of small rubber particles in serum fraction after centrifugation, they might include a significant amount of nonrubber components in the serum fraction, including water-soluble polar components. These were removed by centrifugation of toluene solution followed by precipitation of the toluene solution into methanol and by acetone extraction. On the other hand, pale crepe contained only small amounts of polar components, because it was coagulated directly from latex followed by washing with water. The skim rubbers used in this work did not contain gel fraction, because it was already removed by centrifugation, whereas pale crepe contained 35% gel fractions. The branch points of gel fraction for pale crepe were presumed to be comprised of phospholipids linked to fatty acids and protein.[11]

The molecular weight and molecular weight distribution of the acetone-extracted rubbers and

Table III Molecular Weight and Polydispersity of Skim-A, Skim-B, and Pale Crepe

Specimen	$\overline{M_{n,\mathrm{osmo}}}$ (10^5)	$\overline{M_n}$ (10^5)	$\overline{M_w}$ (10^5)	$\overline{M_w}/\overline{M_n}$
Skim-A-AE[a]	1.33	1.05	3.37	3.21
Skim-A-TE[b]		1.02	3.42	3.35
Skim-B-AE[c]	1.94	1.49	13.3	8.91
Skim-B-TE[d]		1.77	10.1	5.69
Pale crepe-AE[e]	2.90	2.69	18.3	6.81
Pale crepe-TE[f]		1.02	9.61	9.42

[a] Acetone-extracted skim-A.
[b] Transesterified skim-A.
[c] Acetone-extracted skim-B.
[d] Transesterified skim-B.
[e] Acetone-extracted pale crepe.
[f] Transesterified pale crepe.

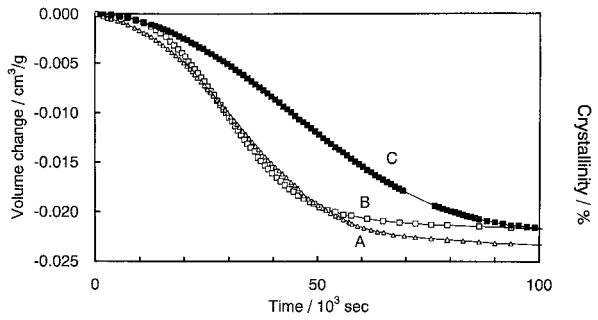

Figure 3 Crystallization behavior of acetone-extracted rubbers. (△) Skim-A-AE, (□) skim-B-AE, and (■) pale crepe-AE.

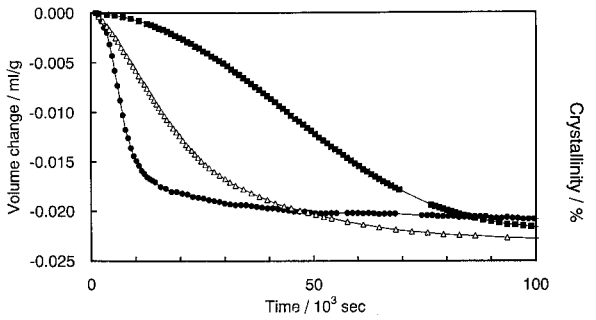

Figure 5 Crystallization behavior of pale crepe. (●) Untreated, (■) acetone-extracted and (△) acetone-extracted pale crepe + 1 wt % methyl linoleate.

transesterified rubbers are shown in Table III. The average molecular weight of skim-A and skim-B did not change after transesterification. On the other hand, the average molecular weight of transesterified pale crepe was one-half of that of acetone-extracted pale crepe. This demonstrates that the skim-A and skim-B should be linear molecules, whereas pale crepe is branched molecules as reported in our previous paper.[11]

Figure 3 shows isothermal crystallization behavior at −25°C for acetone-extracted rubbers such as skim-A-AE, skim-B-AE, and pale crepe-AE. The overall crystallization rate of pale crepe-AE was smaller than that of skim-A-AE and skim-B-AE. This is explained as due to the influence of branch points present in pale crepe-AE. The overall crystallization rates of transesterified rubbers, such as skim-A-TE, skim-B-TE, and pale crepe-TE, are shown in Figure 4. The overall crystallization rate of pale crepe-AE increased significantly after transesterification, while that of skim rubbers did not change. This may show the influence of terminal groups on the crystallization behavior of the rubbers. Since the quantity of linked fatty acids per rubber molecule for pale crepe was about 1.6 and pale crepe had branch points, the structure of its terminal group must be modified after transesterification. This may result in the change in the overall crystallization rate. However, for the skim rubbers, the quantity of linked fatty acids per rubber molecule was significantly low—that is, 0.19 for skim-A-AE and 0.54 for skim-B-AE. This suggests that the crystallization of skim rubbers was not promoted by the small amount of linked fatty acids.

In our previous paper,[14–16] we showed the presence of a synergistic effect of linked fatty acids and mixed fatty acids on the crystallization of natural rubber. It demonstrated the importance of mixed fatty acids in natural rubber. In the present work, methyl linoleate, being a plasticizer for *cis*-1,4 polyisoprene, was added to the skim rubbers and pale crepe. Figure 5 shows the isothermal crystallization behavior of pale crepe, pale crepe-AE, and pale crepe-AE mixed with 1 wt % methyl linoleate. The overall crystallization rate of pale crepe-AE increased significantly by adding 1 wt % methyl linoleate, which was a similar level to the overall

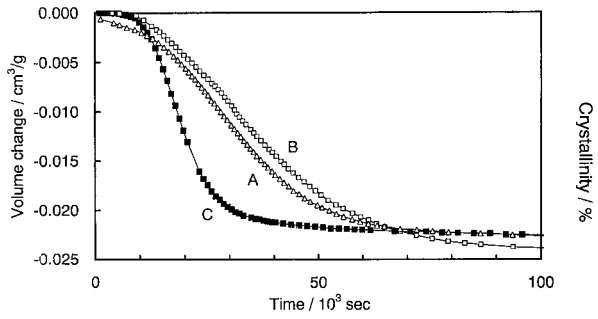

Figure 4 Crystallization behavior of transesterified rubbers. (△) Skim-A-TE, (□) skim-B-TE, and (■) pale crepe-TE.

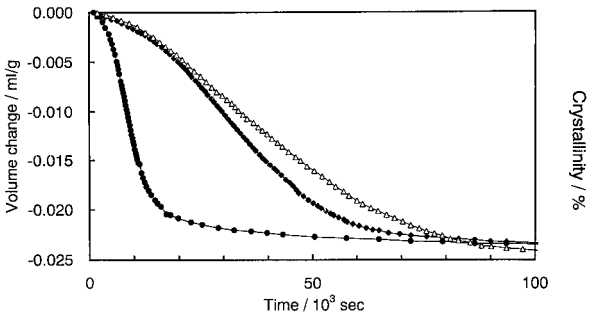

Figure 6 Crystallization behavior of skim-A. (●) Untreated, (■) acetone-extracted, and (△) acetone-extracted skim-A + 1 wt % methyl linoleate.

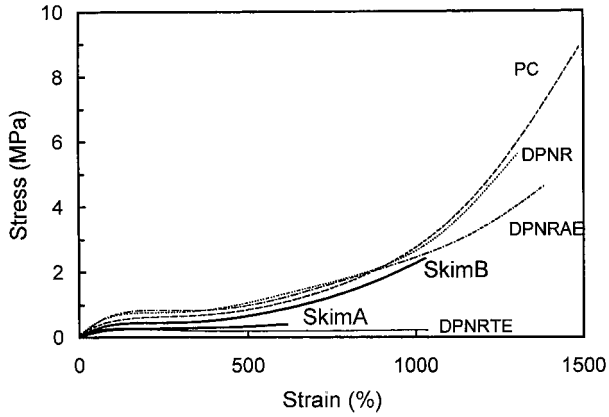

Figure 7 Stress–strain curve of unvulcanized rubbers.

crystallization rate of untreated pale crepe. On the other hand, Figure 6 shows the isothermal crystallization behavior of skim-A-AE and skim-B-AE mixed with 1 wt % methyl linoleate. Before adding 1 wt % methyl linoleate, the overall crystallization rate of skim-A-AE was quite similar to that of skim-B-AE, as shown in Figure 3. However, by the addition of 1 wt % methyl linoleate, the overall crystallization rate of skim-A-AE decreased, whereas that of skim-B-AE increased. Since the $\overline{M}_n$ value of skim-A-AE was similar to that of skim-B-AE, the difference in the overall crystallization rate may be attributed to the quantity of linked fatty acid per rubber molecule, i.e., 0.19 for skim-A-AE and 0.54 for skim-B-AE. The quantity of linked fatty acid per rubber molecule for skim-A-AE may be too small to promote the crystallization behavior of the rubber. Thus, the minimum level of linked fatty acids was determined to be at least 0.5 per rubber molecule.

Green Strength

Figure 7 shows the stress–strain curves of the unvulcanized rubbers such as skim-A, skim-B, pale crepe, DPNR, DPNR-AE, and DPNR-TE. The stress vs strain for pale crepe and untreated DPNR increased significantly at about 300% elongation. As reported previously,[1] this increase in stress is attributed to the crystallization of the rubber on straining. The stress at break, i.e., green strength, for pale crepe and untreated DPNR was the largest among the samples. On the other hand, the green strength decreased slightly after acetone extraction and was significantly reduced after transesterification. The green strength of transesterified DPNR was comparable with that of synthetic *cis*-1,4 polyisoprene. This may be due to the removal of mixed fatty acids and linked fatty acids in addition to the decomposition of chemical branch points formed by phospholipids.

Skim-A did not show the increase in stress as strain increased above 100% elongation. On the other hand, stress for skim-B increased slightly with increasing strain. The green strength of skim-A was quite similar to that of DPNR-TE, while the green strength of skim-B was larger than DPNR-TE by about 11 times. Skim-A and skim-B did not contain gel fraction, and the molecular weight of skim-A was almost similar to that of skim-B. This apparent difference in the green strength was attributed to the quantity of linked fatty acids per rubber molecule, i.e., 0.19 for skim-A and 0.54 for skim-B.

CONCLUSION

The overall crystallization rate of fractionated DPNR was reduced as the molecular weight decreased, due to the branch points and impurities that suppressed the crystallization of the rubber. The overall crystallization rate of skim rubbers did not change in spite of removal of linked fatty acids after transesterification. The difference in crystallization behavior between skim-A and skim-B was associated with the quantity of linked fatty acids per rubber molecule, i.e., 0.19 for skim-A and 0.54 for skim-B. The green strength of skim-A was similar to that of DPNR-TE as well as synthetic *cis*-1,4 polyisoprene. In contrast, the green strength of skim-B was larger than that of DPNR-TE by about 11 times, showing the effect of linked fatty acid on the green strength. The minimum quantity of linked fatty acid to give the increase in the strength was presumed to be about 0.5 per rubber molecule.

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