

Effect of Gel on Crystallization Behavior of Natural Rubber After Accelerated Storage Hardening Test

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ABSTRACT: Crystallization of natural rubber (NR) and purified NR after storage hardening of the rubbers under dried condition with phosphorus pentoxide was investigated by dilatometry and polarized light microscopy. The purified NR was prepared by removing proteins and fatty acid ester groups from fresh NR (FNR) through deproteination and transesterification, respectively. The rubbers were characterized in regard as gel content, ester content and crosslink density. Nucleation (I) and growth rates (V) of the gel fraction estimated from the number of spherulites and their sizes observed in the course of isothermal crystallization depended on supercooling ($\Delta T = T_m^0 - T$). T_m^0 is equilibrium melting temperature and T is absolute temperature. Slope of linear line in a plot of logarithmic

V versus $1/T\Delta T$ for NR was independent of time for storage hardening, suggesting that the lateral surface free energy and diffusion were little function of branching and crosslinking. The rate of crystallization of FNR significantly decreased when the crosslink density increased. Since the overall crystallization is functions of chain mobility and surface free energy, the slower crystallization of well crosslinked FNR may be attributed to the less chain mobility and small value of $\Delta\sigma$ due to the formation of crosslinked and branched entities. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 455–461, 2007

Key words: natural rubber; storage hardening; crystallization

INTRODUCTION

Three-dimensional (3D) network formed during storage hardening has been widely recognized to play an important role in mechanical properties of natural rubber (NR), i.e., high tensile strength, high tear strength, good elasticity, and so forth. The network may be formed, as the rubber molecules react with each other to yield chemical linkages between the molecules. In the previous works,^{1–3} the chemical linkages have been reported to be formed by reactions between some nonrubber components such as proteins and phospholipids and/or abnormal groups such as epoxy and formyl groups that existed in the rubber. However, no conclusive explanation has

been provided on the basis of structural evidence on the formation of the network, although extensive research works were made on storage hardening of the rubber.

A fundamental structure of NR was proposed to have two kinds of terminal groups: i.e., the initiating-end linking to proteins and the terminating-end linking to phospholipids consisting of phosphoric ester and two molecules of long-chain fatty acid esters,⁴ as shown in Figure 1(a). According to the structure of NR, one of the terminal groups is able to form branching points through intermolecular hydrogen bond with the proteins and the other may produce ionic linkages of the phospholipids with divalent metal ions or association of phosphate groups to form branching points,^{5–8} as shown in Figure 1(b). Since the proteins and the phospholipids at the terminals may interact with water, which may decompose the branching points, it is important to remove water from the rubber with a drying agent, such as phosphorus pentoxide. When water is removed from the rubber, the proteins and phospholipids at the terminals of rubber chains may come into contact with each other. Since both functional

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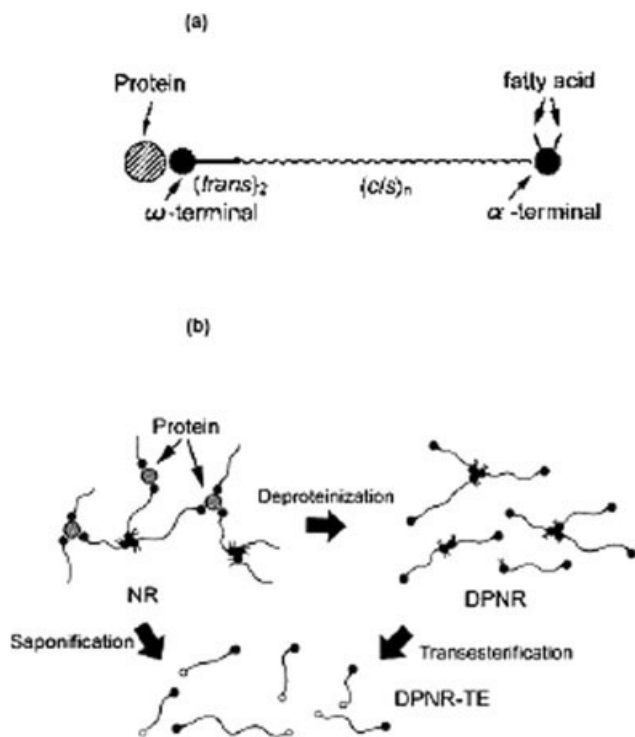


Figure 1 Presumed structure of natural rubber (a) α -terminal group, (b) after deproteinization, transesterification, and saponification.

groups of NR may be active for a reaction, the 3D networks may be formed during storage because of the reactions between the functional groups of NR chains, as shown in Figure 2.

The formation of gel or 3D network can be investigated by measuring crystallization of NR, since the crystallization is well-known to be a function of the crosslink density and long-chain fatty acid ester content.^{9–11} The crystallization of NR is investigated by both dilatometry to measure the overall crystallization process and polarized light microscopy (PLM) to observe nucleation and growth of NR crystal. In the previous work,¹¹ the rate of crystallization of NR at 248 K was reported to decrease significantly after removal of the free fatty acid groups or lipids with acetone extraction and it was recovered by transesterification. The crystallization of the acetone-extracted rubber was promoted by adding 1% w/w methyl linoleate.¹¹ However, the crystallization of transesterified NR was suppressed by the addition of methyl linoleate as in the case of synthetic *cis*-1,4 polyisoprene¹⁰ due to the lack of fatty acids linked to the rubber.^{10,12} This finding demonstrated that high crystallizability of NR is derived from the ability of the linked fatty acids to promote crystallization. As described above, the branching in NR was assumed to derive from the association of phospholipids or fatty acid groups in rubber molecules. The presence of gel phase originating from fatty acids or phospho-

lipids in NR may affect the crystallization. In the present study, the effect of gel on crystallization behavior of NR after storage hardening was clarified.

EXPERIMENTAL

NR latex used in this work was fresh field latex obtained from RRIM 600 clone. Fresh NR (FNR) film was prepared by casting freshly tapped NR latex onto a glass plate followed by drying it under reduced pressure. Deproteinized NR (DPNR) was prepared from fresh latex by incubation with proteolytic enzyme and surfactant followed by washing (centrifugation). Transesterification of DPNR was carried out in 1% w/v toluene solution of the rubber with freshly prepared sodium methoxide at room temperature for 2.5 h under N_2 atmosphere. The resulting solution was precipitated with methanol and dried under reduced pressure.

The accelerated storage hardening test of FNR film was carried out in desiccators preheated at 333 K for 30 min. Then, phosphorus pentoxide (P_2O_5) was placed in the preheated desiccators and the film was dried for 0 h (FNR-0), 9 h (FNR-9), 24 h (FNR-24), and 48 h (FNR-48), respectively.

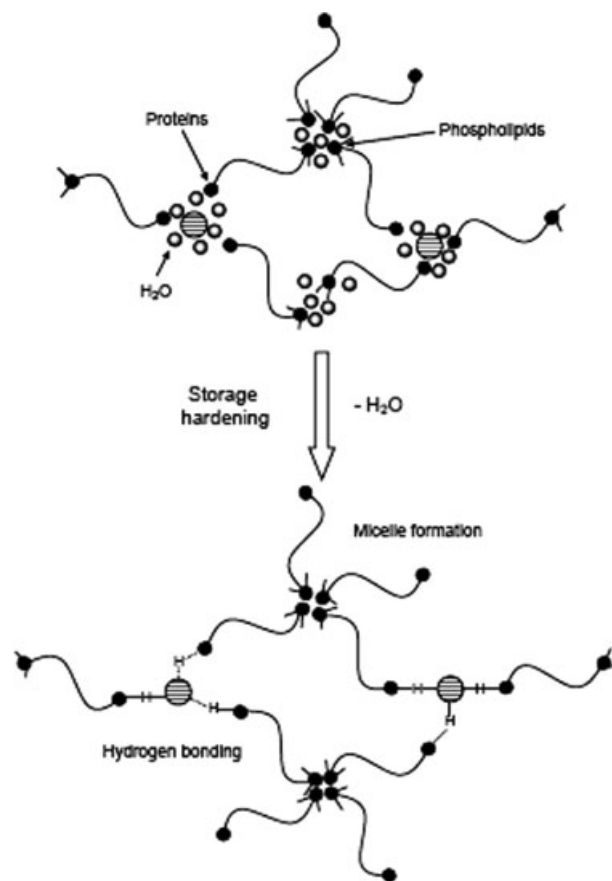


Figure 2 Proposed structure of gel of natural rubber after storage hardening.

TABLE I
Gel Content, Crosslink Density, Glass Transition Temperature and Ester Content of FNR and DPTE-NR After Accelerated Storage Hardening Test

Sample	Storage time (h)	Gel content (% w/w)	T_g (K)	Crosslink density (10^{-6})	Ester content (mmol/kg)
DPTE-NR	–	0	212.4	–	~0
FNR-0	0	10.3	212.4	1.15	29
FNR-9	9	40.0	213.3	11.3	24
FNR-24	24	52.6	213.3	13.4	21
FNR-48	48	84.4	213.5	14.1	16

MEASUREMENTS

Insoluble fraction of FNR after accelerated storage hardening was isolated from the rubber by swelling method. Small pieces of the dried rubbers were dissolved in toluene (0.1% w/v) and kept in the dark at room temperature for a week without stirring. The insoluble fraction in toluene solution was separated from soluble fraction by centrifugation at 10,000 rpm for 30 min. The insoluble and soluble fractions were collected as gel and sol fractions, respectively, and they were dried under reduced pressure at 323 K for a week. Gel content was determined by swelling method as the usual way.¹³

The quantity of fatty acid ester groups was determined by FT-IR, using a calibration curve obtained from a mixture of synthetic *cis*-1,4-polyisoprene, and methyl stearate.¹⁴

Crosslink density of FNR after storage hardening was estimated from a swelling ratio of the gel fraction, according to the method of Flory-Rehner equilibrium swelling equation.¹⁵

Isothermal crystallization was measured by dilatometry. The dilatometer was placed in a cooling bath at 248 K with a temperature control at ± 0.1 K. The volume change of the samples during crystallization was detected by video camera for 5 s at 3 min intervals.

Measurement of glass transition temperature (T_g) was performed for rubber samples by differential scanning calorimetry (DSC) using a Seiko Instrument DSC 220. The rubber sample was cut into small pieces (~ 1 mm³) and encapsulated in a standard aluminum pan without mechanical stress. The DSC measurements were made at heating rate of 10 K/min, after cooling the crystallized sample to 153 K. The accuracy was ensured to be within ± 0.01 K in term of standard Platinum calibration.

Crystallization of the gel fraction of FNR was investigated by polarized light microscopy (PLM), using a Nikon Eclipse E600 POL. The sample was sandwiched between two cover glasses, and then placed on a cooling stage (Linkam LK 600KM) with temperature control within 0.1 K. The sample was heated at 323 K to melt the preexisting crystal before crystallization. The melted rubber was isothermally

crystallized at various crystallization temperatures, T_c s, between 252 and 258 K. The number of spherulites was counted in a definite volume, while the size of the spherulites was measured as the longest ellipsoidal diameter.

RESULTS AND DISCUSSION

Accelerated storage hardening test of NR

Progressive hardening of NR was carried out by storing FNR over P₂O₅ for 0, 9, 24, and 48 h at 333 K. The gel content, ester content, crosslink density, and T_g for FNR and DPTE-NR after storage over P₂O₅ at 60°C are shown in Table I. The gel content and crosslink density represent the level of crosslink or branching entities. The gel content of FNR dramatically increased from 10.3 to 84.4% w/w after preserving it for 48 h. The crosslink density of FNR was greatly increased about 10 times after storage for 9 h and it increased to 14.1×10^{-6} mol/mL within 48 h. In contrast, DPTE-NR has no gel fraction due to the decomposition of the branching points and the removal of natural antioxidants after transesterification. The gel content and crosslink density of FNR increased after storage under dry condition, suggesting the formation of gel fraction, which would contain the fatty acid ester groups at the branching points, as described in our previous article.¹⁶

T_g of FNR was almost similar to that of DPTE-NR, that is about 212.4 K. The T_g of gel fraction of FNR increased in a few degree after storage hardening. This may be attributed to the formation of gel or branching points, which constrain the microbrownian movement of the rubber chains. The fatty acid ester contents of FNR before and after storage are also shown in Table I, in which mixed and linked fatty acids in NR were reported to play an important role in the crystallization of NR.^{10,11} The total ester contents in rubber samples after storage hardening were almost the same values. This suggests that the amount of the fatty acid ester groups of FNR after storage was not the function of crosslink density and gel content.

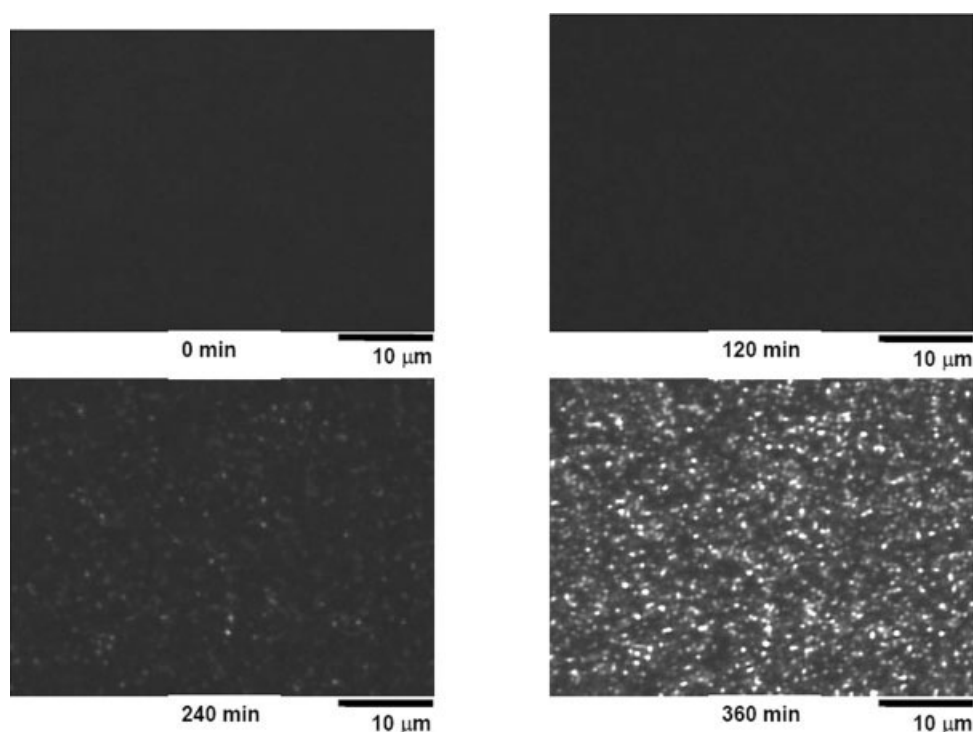


Figure 3 Polarized light micrographs for FNR-9 crystallized at 258 K.

Crystallization of gel fraction of FNR after storage hardening

The crystallization of the gel fractions of FNR after storage hardening was investigated by PLM. Typical polarized light micrographs for the gel fraction of FNR-9 at 258 K are shown in Figure 3. Small spherulites appeared after 180 min during isothermal crystallization at 258 K, and its size increased as the crystallization time, t , prolonged. Typical changes in the number of spherulites per unit volume, v , and its size, a , for the gel fraction of FNR-9 versus time are shown in Figures 4 and 5, respectively. The value of v increased gradually and then linearly in the steady

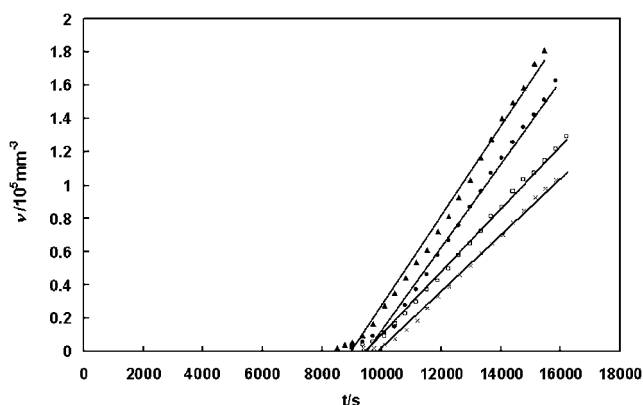


Figure 4 Number of crystal per unit volume for FNR-9 at crystallization temperatures of (\times) 252 K, (\square) 254 K, (\bullet) 256 K, and (\blacktriangle) 258 K, respectively.

nucleation period. On the other hand, the value of a increased linearly, as shown in Figure 5. Thus, the nucleation rate, I , was estimated as the slope of v versus time and growth rate, V , was determined from the plot of a versus time.

The melting temperature, T_m , of the gel fraction of FNR after storage for various times was measured as indicated in Table II. At the same isothermal crystallization temperature, T_c , all gel fractions of FNR gave the same T_m . Thus, the equilibrium melting temperature, T_m^0 , of the gel fraction of FNR was estimated in terms of the Gibbs-Thomson expression to be 308.9 K, which was similar to a value of T_m^0 , i.e., 308.7 K reported by Dalal et al.¹⁷ The fold free

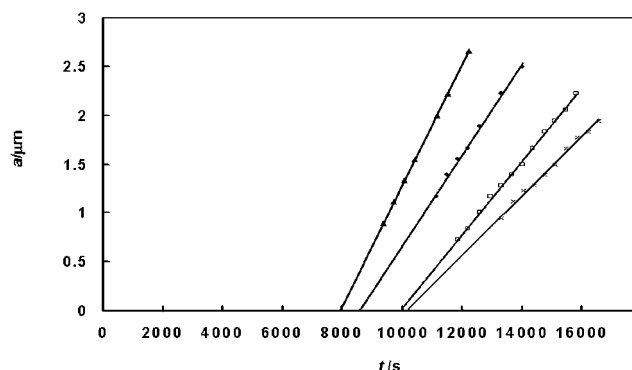


Figure 5 Size of crystal (a) for FNR-9 at crystallization temperatures of (\times) 252 K, (\square) 254 K, (\bullet) 256 K, and (\blacktriangle) 258 K, respectively.

TABLE II
Melting Temperature for Gel Fraction of FNR-0, FNR-9, and FNR-48

Sample	$T_c(K)^a$	$T_m(K)$
FNR-0	258	276
	256	275
	254	274
	252	273
FNR-9	258	276
	256	275
	254	274
	252	273
FNR-48	258	276
	256	275
	254	274
	252	273

^a Crystallization temperature of rubber.

energy (σ_e) was estimated from the slope of line drawn in Gibbs-Thomson plot to be 0.024 J/m^2 . This suggests that thermodynamic parameters such as T_m^0 and σ_e are independent of gel content for all gel fractions of FNR.

Figure 6 shows a plot of logarithmic V versus $1/T\Delta T$, for the gel fractions of FNR-0, FNR-9 and FNR-48, where T is absolute temperature, ΔT the supercooling temperature, that is, $\Delta T = T_m^0 - T$. The logarithmic V was inversely proportional to $T\Delta T$, and it decreased as crosslink density increased. According to a nucleation theory, V is expressed as follows:¹⁸

$$\ln V = \ln V_0 - (K_V/T\Delta T) \quad (1)$$

$$K_V = 4\sigma\sigma_e T_m^0 / 3K\Delta h_f \quad (2)$$

where σ is the lateral surface free energy, K the Boltzmann constant, three due to three dimensional growth for spherulite and Δh_f the enthalpy of fusion. In the present work, the reported values of Δh_f ¹⁹ and

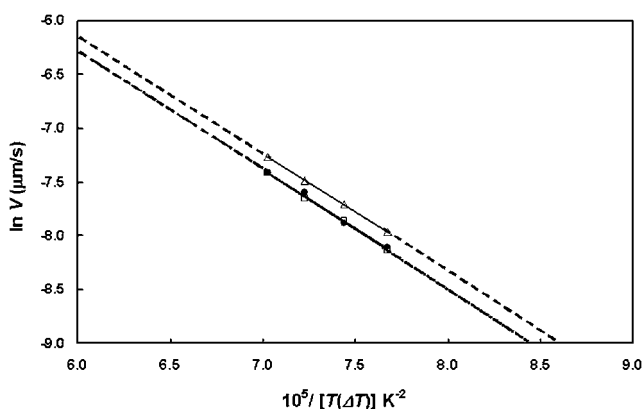


Figure 6 Semilogarithmic plots of growth rate versus $1/T\Delta T$ for (Δ) FNR-0, (\bullet) FNR-9, and (\square) FNR-48, respectively.

σ_e ¹⁷ are applied; that is, $\Delta h_f = 6.4 \times 10^7 \text{ J/m}^3$ and $\sigma_e = 0.024 \text{ J/m}^2$, respectively. Equations (1) and (2) suggest that the slope of the line in the plot of $\ln V$ versus $1/T\Delta T$ is a surface free energy term and the intersection of the line is related to a diffusion coefficient. Since the slope of the line was the same for the gel fractions of FNR-0, FNR-9, and FNR-48, as shown in Figure 6, the value of σ was estimated to be 0.015 J m^{-2} . This is in good agreement with a reported value of σ ¹⁷ equal to 0.014 J/m^2 . The same slope may imply that the σ_e and σ may be independent of the crosslink density. In contrast, the V_0 depended on the crosslink density; the smaller the crosslink density, the larger was the value of the V_0 . Since V_0 is proportional to a diffusivity of the rubber to form crystal, the decrease in V_0 may express the reduction of the chain mobility due to the formation of crosslinks or branches. This demonstrates that the formation of crosslinks or branches during storage hardening suppressed the crystallization of FNR. Almost similar slope and intersection for FNR-9 and FNR-48 may be due to the small difference in crosslink density of these two samples.

A semilogarithmic plot of I versus $1/T\Delta T^2$, for the gel fractions of FNR-0, FNR-9, and FNR-48 is shown in Figure 7. The logarithmic I was inversely proportional to $T\Delta T^2$, and the slope depended on the crosslink density of the rubber. Thus, the following expression¹⁸ was applied to the temperature dependence of the logarithmic I .

$$\ln I = \ln I_0 - (K_V/T\Delta T^2) \quad (3)$$

$$K_1 = 16\sigma\sigma_e(\Delta\sigma)T_m^0 / k\Delta h_f^2 \quad (4)$$

where $\Delta\sigma = \sigma + \sigma_{0N} - \sigma_N$, σ_{0N} is the interfacial free energy between the rubber crystal and nucleating agent, and σ_N is the interfacial free energy between rubber melt and nucleating agent, respectively. Using the values of $\sigma = 0.015 \text{ J/m}^2$ and $\sigma_e = 0.0244$

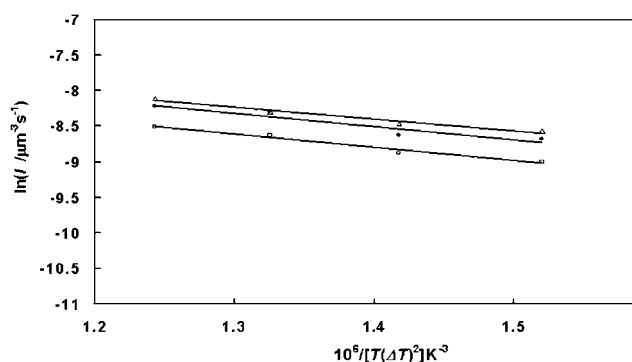


Figure 7 Semilogarithmic plots of nucleation rate versus $1/T\Delta T^2$ for (Δ) FNR-0, (\bullet) FNR-9, and (\square) FNR-48, respectively.

TABLE III
 σ , $\Delta\sigma$, and $\Delta\sigma/\sigma$ for Gel Fraction of FNR After Accelerated Storage Hardening Test

Sample	$\sigma(10^{-2}/\text{J m}^{-2})$	$\Delta\sigma(10^{-4}/\text{J m}^{-2})$	$\Delta\sigma/\sigma(10^{-2})$
FNR-0	1.5	5.8	3.8
FNR-9	1.5	6.6	4.3
FNR-48	1.5	8.9	5.8

J/m^{-2} , as mention above, the $\Delta\sigma$ value was estimated according to eqs. (3) and (4). The estimated values of $\Delta\sigma$ and $\Delta\sigma/\sigma$ for gel fractions of FNR after storage hardening are tabulated in Table III, together with the value of σ . The value of $\Delta\sigma$ was less than 2σ , suggesting that heterogeneous nucleation would occur for the gel fractions. Furthermore, the index of nucleating effect, $\Delta\sigma/\sigma$, increased as the crosslink density increased, and the value of $\Delta\sigma/\sigma$ for FNR-48 was higher than those for FNR-0 and FNR-9. This finding suggests that FNR-0 contain more effective nucleating agents than FNR-9 and FNR-48. As the results of V_0 and $\Delta\sigma/\sigma$, the overall crystallization of FNR-0 may be expected to be faster than those of FNR-9 and FNR-48.

To prove the faster crystallization, overall crystallization of FNR-0, FNR-9, and FNR-48 was investigated by dilatometry. Figure 8 shows isothermal crystallization at 248 K for the gel fractions of FNR after storage hardening for various sampling times. The overall crystallization of gel fractions of FNR was suppressed with increasing the storage time, as it can be seen for the gel fractions of FNR-0, FNR-24, and FNR-48. It is clear that high crosslink density for FNR-48 results in slower crystallization than FNR-0. Since the overall crystallization is functions of chain mobility and surface free energy, the slower crystallization of FNR-48 may be attributed to the less chain mobility and larger $\Delta\sigma$ value, due to the formation of crosslinked and branched entities.

According to the proposed mechanism of storage hardening of FNR, as shown in Figure 2, the proteins and phospholipids at the chain-end of the rub-

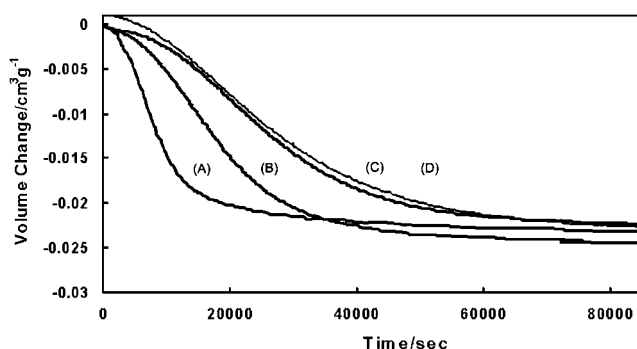


Figure 8 The overall crystallization of gel fraction of FNR after storage hardening at 248 K by dilatometry: (A) FNR-0, (B) FNR-9, (C) FNR-24, and (D) FNR-48.

ber molecule may interact with water under ambient condition; hence, the branching points can not be formed for the rubber in the presence of water. When water is removed from the rubber with a drying agent such as phosphorus pentoxide, the proteins and the phospholipids at the chain-end of the rubber may come into contact with each other. The contact may result in reactions to form crosslinking or branching entities during storage hardening. Based upon the mechanism, the chain mobility and nucleating effect are reduced during storage hardening. In the present work, we found the less chain mobility and larger $\Delta\sigma$ value for FNR-48 due to storage hardening. These are consistent with the postulation expected in Figure 8. Thus, one of the reactions occurring during storage hardening come from the aggregation of phospholipids present at the chain-end of the rubber, which may form the crosslinked and branched entities.

CONCLUSIONS

The isothermal crystallization at 248 K of NR after accelerated storage hardening and purified NR was investigated by dilatometry. The gel fractions of NR after various storage times gave the decrease in overall crystallization rate as the function of crosslink density and gel content. The crystallization of NR obtained after various storage times was investigated by polarized light microscopy and dilatometry. The number of spherulites increased gradually and then linearly in the steady nucleation period. The number and size of the spherulites increased linearly with increasing the crystallization time, in the steady state, after an induction time. The fold surface free energy and side surface free energy were independent of the crosslink density. The index of nucleating effect, $\Delta\sigma/\sigma$, increased as crosslink density increased, and the value of $\Delta\sigma/\sigma$ for FNR-48 was higher than those for FNR-0 and FNR-9. This finding suggests that FNR-0 contained more effective nucleating agent rather than FNR-9 and FNR-48. As the result of V_0 and $\Delta\sigma/\sigma$, the crystallization of FNR-0 may be faster than those of FNR-9 and FNR-48. The rate of crystallization of FNR significantly decreased when the crosslink density increased. Since the overall crystallization is the functions of chain mobility and surface free energy, the slower crystallization of FNR-48 may be attributed to the less chain mobility and small value of $\Delta\sigma$ due to the formation of crosslinked and branched entities.

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