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Characterization of fatty acids linked to natural rubber—role of linked fatty acids on crystallization of the rubber

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Abstract

Natural rubber isolated from *Hevea brasiliensis* contains two types of long chain fatty acids: fatty acids linked to rubber chain at the chain-terminal and those present as a mixture. The composition and role of these fatty acids were characterized by ^{1}H NMR spectroscopy, gas chromatography and differential scanning calorimetry. The linked fatty acids were composed of saturated and unsaturated C_{10}–C_{22} fatty acids, the composition of which was similar to that of mixed fatty acids. As models of natural rubber, fatty acid groups, such as decanoyl (C_{10}), myristoyl (C_{14}) and stearoyl (C_{18}), were esterified to synthetic *cis*-1,4-polyisoprene (IR) selectively at 3,4 isomeric units, by hydroboration followed by esterification with acyl chloride. The acceleration effect of linked fatty acids on the crystallization behavior was analyzed for these models and natural rubber. The IR linked with myristoyl group showed the most rapid crystallization at −25°C among the samples prepared, as it was mixed with palmitic acid. This was explained to be due to the nucleating effect of saturated fatty acid and plasticizing effect of unsaturated fatty acid for the polymer. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; *cis*-1,4-Polyisoprene; Crystallization behavior

1. Introduction

Crystallization behavior characteristic of natural rubber (NR) is one of the most important subjects to be elucidated, because the rapid crystallization on straining provides a good performance in mechanical properties such as excellent tack and green strength in unvulcanized states [1,2] and outstanding tear strength and tensile strength in vulcanized states [3,4]. The rapid crystallization of NR has been recognized, so far, to be due to certain non-rubber constituents present in the rubber, which were presumed to be mainly protein and lipids. Removing free fatty acids that are present as a mixture reduced the rate of crystallization of NR significantly, whereas the rate was recovered to the original level by mixing with 1 wt% stearic acid [5]. The effect of protein on the crystallization behavior was reported to be negligible, compared to the mixed fatty acids [6–8].

Guayule rubber (GR) and synthetic *cis*-1,4-polyisoprene (IR) prepared with a Zieglar type catalyst were presumed to show a similar potential in the crystallizability and mechanical properties to NR, based on structural similarity. Contrary to the expectation, the rate of crystallization of IR and GR was significantly smaller than that of NR [9,10], even when 1 wt% stearic acid was added to it. The mechanical strength of GR and IR was considered to be not enough for the practical use at high strain rate compared to NR [11,12]. This was explained to be due to the unknown terminal group of NR [13].

In our previous studies [13], we showed that the rubber hydrocarbon of NR is composed of ω-terminal, two *trans*-1,4 isoprene units, a long (more than 1000) sequence of *cis*-1,4 isoprene units and α-terminal, aligned in this order. The ω-terminal linking to protein was suggested to form physical crosslinks, whereas the α-terminal linking to phospholipids to form chemical crosslinks with long chain fatty acid ester groups. Protein present in NR was removed by deproteinization with proteolitic enzyme and surfactant, and phospholipids was decomposed by transesterification with CH_3ONa to form linear rubber molecules [14]. By comparing the crystallization behavior of NR to those of deproteinized NR, acetone-extracted NR and transesterified NR, the rapid crystallization was attributed to the synergistic effect

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Table 1
Conditions for gas chromatographic measurement

Column temp.	250°C, 40 min → 10°C/min → 300°C, 15 min; total 60 min
Injection temp.	270°C
Detection temp.	300°C
Column	Capillary column, 30 m
Solvent	Hexane

of mixed fatty acids and linked fatty acid ester groups present at a terminal unit of the rubber molecule [14–17].

NR was reported to contain various fatty acids as a mixture [18–20]; saturated fatty acids such as decanoic acid, myristic acid, palmitic acid and stearic acid, and unsaturated fatty acids such as palmitleic acid, oleic acid, linoleic acid and linoleinic acid. These fatty acids are also expected to link to the rubber molecule as phospholipids, because the mixed fatty acids are reported to be derived by hydrolysis of phospholipid during storage [21]. In this paper, we characterize the fatty acids linked to the rubber molecule by ^{1}H NMR spectroscopy and gas chromatography. As models of NR, we prepare a series of IRs linking with fatty acid ester group selectively at the 3,4 isomeric unit. The effect of linked fatty acids on the crystallization behavior is investigated by observing the crystallization behavior of these modified IRs.

2. Experimental

2.1. Materials

Rubber samples used in this study were commercial high ammonia NR latex (HANR) and Kuraprene IR10 (Kuraray Co. Ltd., Japan) consisting of 98.8% *cis*-1,4 isoprene, 1.0% *trans*-1,4, and 0.2% 3,4. HANR latex was purified by enzymatic deproteinization which was carried out by incubation of the latex diluted to 30% dry rubber content (DRC) with 0.04% (w/v) proteolytic enzyme (Novo, Alcalase 2.0T) and 1% (w/v) sodium dodecyl sulfate (SDS) for 12 h at 38°C followed by centrifugation. The cream fraction was redispersed in 1% (w/v) SDS to make 30% DRC latex and was washed twice by centrifugation to prepare deproteinized natural rubber (DPNR) latex. DPNR was recovered by centrifugation followed by coagulation with methanol or acetone and dried under reduced pressure for at least one week.

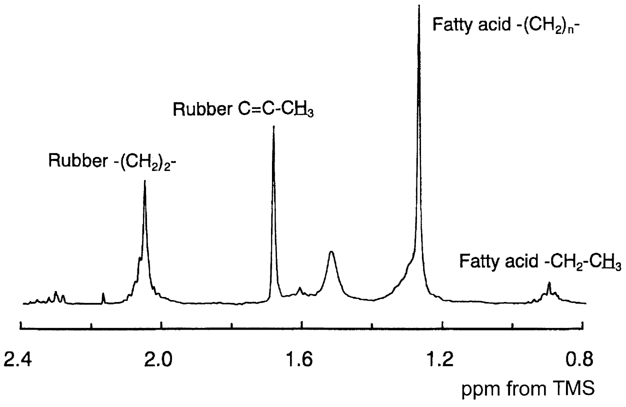

Fig. 1. ^{1}H NMR spectrum of soluble fraction in toluene–methanol separated from rubber fraction after transesterification of DPNR–AE.

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

Transesterification of acetone-extracted DPNR was carried out in toluene solution by reacting it with fresh sodium methoxide at room temperature for 2.5 h followed by precipitation in excess methanol. The toluene–methanol solution was recovered after separation of rubber fraction and neutralized by HCl. The fraction containing linked fatty acids was subjected to the analysis of component.

The content of fatty acids was determined by the AOAC method [22], in which heptadecanoic acid (C_{17}) was added to the solution as an internal standard. The fatty acids were esterified with 5 ml of $BF_3 \cdot 2CH_3OH$ and 3 ml of diethyl ether at 80°C for 5 min, and the residual BF_3 present in the solution after the reaction was deactivated by adding 2 ml of water at room temperature. Fatty acid esters were extracted with diethyl ether followed by washing with water. Hexane solution of fatty acids was prepared for gas chromatography.

Kuraprene IR10 was purified in the usual way. Mixtures of IR and saturated fatty acids (C_{10}, C_{12}, C_{14}, C_{16}, C_{18} and C_{20}) were prepared by freeze-drying of the benzene solution containing IR and fatty acids, and were dried at about 50°C under reduced pressure for 2 days.

The hydroboration of IR was made with 9-borabicycro[3.3.1]nonane (9-BBN) in dried THF solution under N_2 at 10°C, followed by the addition of ethanol, 6 N NaOH and 30% H_2O_2 at 0°C. The reaction mixture was heated at 40°C for 1 h. The hydroxylated IR in dried THF was reacted with stearoyl chloride in the presence of 4-dimethylaminopyridine by heating at 50°C for 3 h. The resulting esterified IR was purified by precipitation in the usual way. The other esterified IR was synthesized by using each acyl chloride of fatty acids in the same way.

2.2. Measurements

The ^{1}H NMR measurement of the toluene–methanol soluble fraction, after drying in vacuo, was made by a JEOL EX-400 at 50°C with 500 scans at a pulse repetition time of 7 s for 45° pulse. The characterization of linked fatty acid was carried out by gas chromatography (Hitachi G-5000A) under the condition shown in Table 1.

The quantity of linked ester groups in the esterified IR was determined by FT-IR (JASCO FT-IR5300) using a calibration curve obtained from mixtures of IR and methyl stearate.

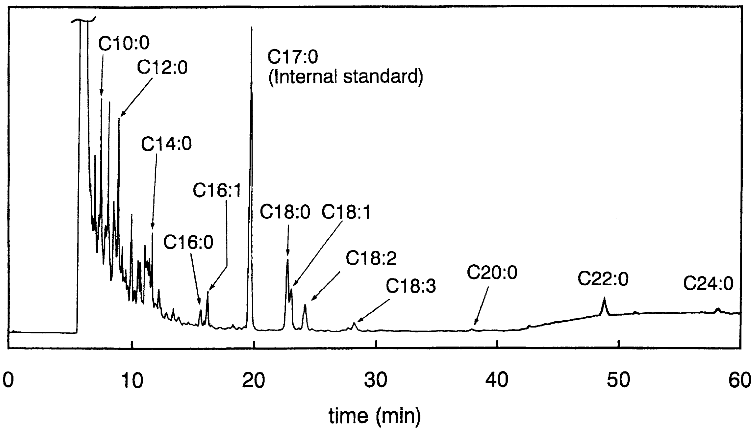

Fig. 2. Gas chromatogram of fatty acid ester groups linked to DPNR–AE.

The isothermal crystallization behavior of the rubber samples at −25°C was measured by differential scanning calorimetry using a Seiko Instruments DSC 220.

3. Results and discussion

3.1. Characterization of fatty acids present in NR

The toluene–methanol soluble fraction containing linked fatty acids was isolated from DPNR after acetone extraction. Fig. 1 shows the aliphatic region of ^1H NMR spectrum for the toluene–methanol soluble fraction. Signals at 0.88, 1.27 and 2.38 ppm were assigned to the protons in methyl, long sequence methylene, and methylene attached to carboxyl group in fatty acid ester groups, respectively. Here, residual low molecular weight fraction of NR showed signals at 1.6 and 2.0 ppm, corresponding to the methyl and methylene protons of isoprene units, respectively. To isolate fatty acids, the solution was saponified followed by esterification with $BF_3 \cdot 2CH_3OH$ in diethyl ether. The resulting fatty acid esters were characterized by gas chromatography. As shown in Fig. 2, sharp peaks appeared separately in the chromatogram. These peaks were identified by using standard fatty acids as given in Table 2, together with mixed fatty acids recovered by acetone-extract of deproteinized NR. The composition of linked fatty acids was similar to that of mixed fatty acids, i.e. the major fatty acids are stearic acid, linoleic and linoleinic acids for both, although the ratio is not the same.

Table 2
Composition of linked fatty acid and mixed fatty acid

Fatty acid (carbon:double bond)	Linked fatty acid (mmol/kg)	Mixed fatty acid (mmol/kg)
$C_{10:0}$	0.11	0.03
$C_{12:0}$	0.32	0.04
$C_{14:0}$	0.05	0.01
$C_{14:1}$	0.19	0.05
$C_{16:0}$	0.36	0.10
$C_{16:1}$	0.54	0.72
$C_{18:0}$	1.05	4.53
$C_{18:1}$	0.71	1.74
$C_{18:2}$	0.39	1.37
$C_{18:3}$	0.50	3.39
$C_{20:0}$	0.15	0.25
$C_{22:0}$	0.56	0.08

We reported that saturated fatty acids played a role of the nucleating agent for crystallization of NR, while unsaturated fatty acids were a plasticizer [23]. The saturated fatty acid such as stearic acid was miscible with the other saturated fatty acid, but immiscible with unsaturated fatty acid. NR is a multi-component system consisting of various fatty acids and a rubber hydrocarbon bonding to fatty acid ester groups. This feature makes it difficult to investigate directly the role of each fatty acid on the crystallization behavior of the rubber.

3.2. Effect of linked fatty acid ester groups

We have prepared model polymers for NR by hydoroboration of IR followed by esterification with acyl chloride, in which IR was esterified with various fatty acid ester groups selectively at 3,4 isomeric units [16,17]. The crystallization of IR was significantly suppressed by introducing hydroxyl group at 3,4 units of IR. However, the crystallization rate recovered to the original level by esterifing OH group with acyl group (IR-C_2) and further increased by esterifing with stearoyl group (IR-C_{18}). The difference in the rate of crystallization between IR-C_2 and IR-C_{18} was attributed to a nucleating effect concerned with a carbon sequence of linked fatty acid ester groups [16].

In the present work, the molar ratio of linked fatty acid ester groups to IR was held to be constant, in order to compare the effect of the chain length of fatty acid on the crystallization behavior of the rubber. Table 3 shows the content of fatty acid ester groups determined by FT-IR measurement, where subscript figures represent the number of carbon atoms, i.e. C_{10} for decanoyl group, C_{14} for

Table 3
Content of linked fatty acid ester groups in IR-C_{10}, IR-C_{14} and IR-C_{18}, determined by FT-IR measurement

Specimen	Ester content (mmol kg)
IR-C_{10}	17.1
IR-C_{14}	16.1
IR-C_{18}	17.8

myristoyl group and C_{18} for stearoyl group. The value of ester content was approximately 17 mmol/kg-rubber for IR-C_{10}, IR-C_{14} and IR-C_{18}. This implies that the number of fatty acids per a rubber chain was about 4, based upon the number average molecular weight of 2.2×10^5, as reported in our previous paper [17].

Table 4 shows the rate of crystallization for the IR esterified with C_{10} to C_{18}, abbreviated as IR-C_{10} to IR-C_{18}. No significant difference in the rate of crystallization was observed for IR-C_{10}, IR-C_{12}, IR-C_{14} and IR-C_{16}. Only IR-C_{18} showed an dramatic increase in the rate of crystallization compared to untreated IR.

Fig. 3 shows crystallization behavior of IR-C_{10}, IR-C_{14} and IR-C_{18} mixed with 4.0×10^{-2} mol/kg decanoic acid at isothermal crystallization temperature of −25°C. The overall crystallization rate of IR-C_{10}, IR-C_{14} and IR-C_{18} mixed with decanoic acid was apparently similar to that of IR, showing no effect of mixed fatty acid on the crystallization. In contrast, when 4.0×10^{-2} mol/kg myristic acid was mixed with the rubbers, the overall crystallization rate was significantly increased. The effect of various fatty acids on the crystallization behavior was compared quantitatively by using the half life of crystallization, $t_{1/2}$, that was defined as an inflection point of volume change versus time. The rate of crystallization of the mixtures, estimated to be the reciprocal $t_{1/2}$, is tabulated in Table 5 together with that for neat IR, IR-C_{10}, IR-C_{14} and IR-C_{18}. The rate of crystallization in Table 5 indicates that combination of linked fatty acids and mixed fatty acid brings about a significant effect on the rate. For instance, the rate of crystallization of IR-C_{10} and IR-C_{14} increased when 4.0×10^{-2} mol/kg decanoic acid (C_{10}) was mixed to them, whereas that of IR-C_{18} decreased. On the other hand, when 4.0×10^{-2} mol/kg myristic acid was mixed with IR, IR-C_{10}, IR-C_{14} and IR-C_{18}, all of the rubbers showed an increase in the rate of crystallization.

Table 4
Rate of crystallization at −25°C estimated from $t_{1/2}$ for IR having linked fatty acid ester groups

Specimen	Rate of crystallization/10^{-6} s^{-1}
IR	9.3
IR-C_2	8.8
IR-C_{10}	7.5
IR-C_{12}	8.0
IR-C_{14}	8.3
IR-C_{16}	8.0
IR-C_{18}	17.3

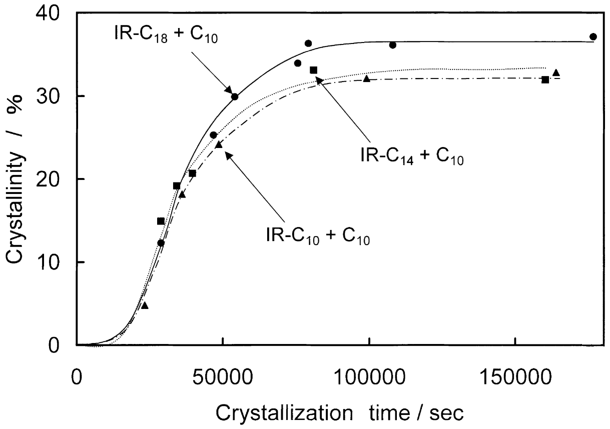

Fig. 3. Crystallization behavior at −25°C for (▲) decanoyl (C10) esterified IR mixed with decanoic acid (C10), (■) myristoyl (C14) esterified IR mixed with decanoic acid (C10) and (●) stearoyl (C18) esterified IR mixed with decanoic acid (C10).

In our previous paper [24], we showed that the effect of mixed fatty acid on the crystallization behavior of IR was related to an onset temperature of crystallization, T_c, of the fatty acid in IR during cooling after melting at 100°C. The crystallization of IR was promoted by mixing with fatty acids when the T_c was higher than the isothermal crystallization temperature of IR, but it did not change when the T_c was lower than that. This was also found for the saturated fatty acid mixtures, in which saturated fatty acids were miscible with dissimilar saturated fatty acids. In the present work, T_c was determined for the mixture of IR, IR-C_{10}, IR-C_{14} and IR-C_{18} with various saturated fatty acids as shown in Table 6. The T_c for the mixtures with decanoic acid was lower than the isothermal crystallization temperature of IR, compared to the other mixtures. The relationship between the rate of crystallization of these rubber mixtures versus T_c of fatty acids is shown in Fig. 4. The rate of crystallization for IR, IR-C_{10}, IR-C_{14} and IR-C_{18} mixed with fatty acids was significantly dependent upon T_c, as in the case of IR mixed with saturated fatty acids. This implies that the crystallization of IR is promoted, when the saturated fatty acids form crystalline phase in the IR matrix.

It is well known that primary nucleation of polymer crystal is influenced by impurity, which is referred to as

Table 5
Rate of crystallization at −25°C for IR, IR-C_{10}, IR-C_{14}, IR-C_{16} and IR-C_{18}

Mixed fatty acid	Rate of crystallization (10^{-6} s^{-1})			
	IR	IR-C_{10}	IR-C_{14}	IR-C_{18}
C_{10}	8.1	11.5	10.5	9.1
C_{12}	14.2	16.6	14.2	8.4
C_{14}	27.7	27.5	33.7	29.2
C_{16}	22.8	27.2	34.7	29.9
C_{18}	19.3	19.8	21.4	22.2
C_{20}	12.8	15.0	15.9	19.6
Non	9.3	7.5	8.3	17.3

Table 6
Segregation temperature T_c of mixed fatty acid in IR, IR-C_{10}, IR-C_{14}, IR-C_{16} and IR-C_{18}

Mixed fatty acid	T_c (°C)			
	IR	IR-C_{10}	IR-C_{14}	IR-C_{18}
C_{10}	−67.9	−46.7	−46.7	−39.1
C_{12}	−25.4	−21.2	−23.1	−24.0
C_{14}	−12.8	−17.0	−16.3	−14.7
C_{16}	8.5	5.4	4.4	2.1
C_{18}	24.4	21.5	21.8	17.6
C_{20}	38.3	33.8	33.6	34.5

Table 7
Avrami constant of the samples

Specimen	Avrami constant	Rate of crystallization (10^{-6} s^{-1})
IR-C_{10} + C_{10}	1.53	11.5
IR-C_{10} + C_{12}	1.64	16.6
IR-C_{10} + C_{14}	2.98	27.5
IR-C_{10} + C_{16}	2.30	27.2
IR-C_{10} + C_{18}	2.22	19.8
IR-C_{14} + C_{10}	1.80	10.5
IR-C_{14} + C_{14}	2.22	33.7
IR-C_{18} + C_{14}	2.23	29.2
IR-C_{18} + C_{18}	3.03	22.2

heterogeneous nucleation, in contrast to homogeneous nucleation of pure polymer. The crystallization behavior of IR, IR-C_{10}, IR-C_{14} and IR-C_{18} mixed with various fatty acids may proceed from the heterogeneous nucleation in spite of the difference in the rate of crystallization. To confirm a universal nature of the crystallization, the Avrami constant was estimated for the rubbers in terms of the following expression [25]:

$$-\Delta V/V_0 = 1 - \exp(-\mathrm{k}t^n) \qquad (1)$$

Here, V_0 is the initial volume of a sample measured before crystallization, ΔV the volume change during crystallization, k the constant, t the crystallization time and n the Avrami constant which represents 4 for homogeneous three-dimensional nucleation and 3 for heterogeneous three-dimensional nucleation. The estimated value of n is shown in Table 7. These n values were divided into two classes; n smaller than 2 and n larger than 2, which was distinguishable from about 4 for IR. For the former samples with n smaller than 2, the rate of crystallization was similar to IR. This is because all of fatty acids, present in IR-C_{10} + C_{10}, IR-C_{10} + C_{12} and IR-C_{14} + C_{10}, are melted at the crystallization temperature of the rubber of −25°C. In contrast, for the latter samples with n larger than 2, the rate of crystallization was significantly larger than that for IR, providing that the crystallization may occur in a way of heterogeneous nucleation. The heterogeneous nucleation may be influenced by diffusion process of the polymer chain, since some of the n values were close to 2.5 [26]. These results demonstrate that the saturated fatty acids act in the rubber as a nucleating agent when they form crystal domains.

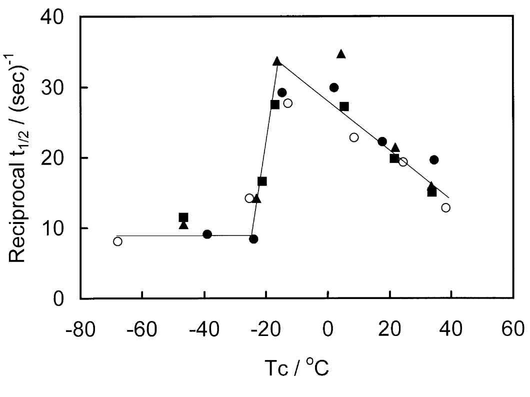

Fig. 4. Rate of crystallization at −25°C of various esterified IRs mixed with fatty acids, ○: IR, ●: IR-C10, ▲: IR-C14, and ■: IR-C18.

The effect of mixed, unsaturated fatty acids on the crystallization behavior of IR-C_{10}, IR-C_{14} and IR-C_{18} was also investigated at −25°C, as shown in Fig. 5. The overall crystallization rate of IR-C_{18} increased after mixing with 4.0×10^{-2} mol/kg methyl linoleate, but those of IR-C_{10} and IR-C_{14} did not change as in the case of IR. This would be explained in relation to the higher T_c of stearoyl group (C_{18}) linked to the rubber molecule than the isothermal crystallization temperature (−25°C) of the rubber, at which the C_{18} group may form crystal domains, while decanoyl group (C_{10}) and myristoyl group (C_{14}) will melt at this temperature due to their lower T_cs. Since methyl linoleate is a plasticizer for IR, the chain mobility of the rubber molecules should be enhanced by mixing with it. These two effects, i.e. the nucleating effect of C_{18} group and the plasticizing effect of methyl linoleate, will result in the rapid crystallization of IR. This demonstrates the validity of our assumption about the synergistic effect of linked fatty acid and mixed fatty acid on the crystallization

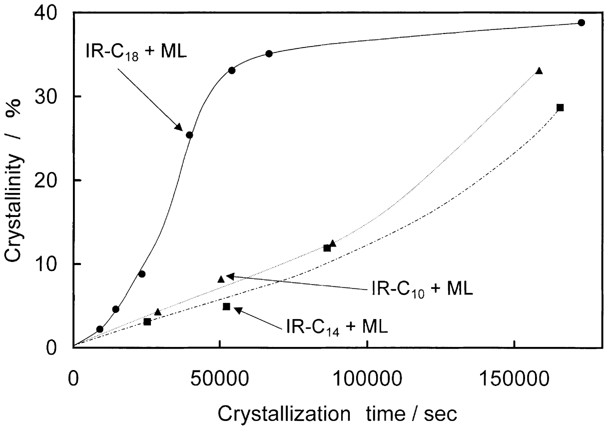

Fig. 5. Crystallization behavior at −25°C of (▲) decanoyl esterified IR mixed with methyl linoleate, (■) myristoyl (C10) esterified IR mixed with methyl linoleate and (●) stearoyl (C18) esterified IR mixed with methyl linoleate.

behavior of NR [15]. The synergistic effect should be attributed to both the nucleating effect of saturated fatty acid and the activated chain mobility of the rubber.

4. Conclusions

The composition of fatty acid ester groups linked to NR molecule at the terminal was identified to be saturated fatty acids such as stearic acid, and unsaturated fatty acids such as oleic acid, linoleic acid and linoleinic acid. The linked saturated fatty acid ester groups played an important role in the crystallization behavior of NR as a nucleating agent. This was confirmed by preparing model IRs esterified with fatty acids at 3,4 isomeric units of IR. The rate of crystallization for IR-C_{10}, IR-C_{14} and IR-C_{18} was significantly dependent upon T_c of saturated fatty acids, as in the case of IR mixed with saturated fatty acids. The most rapid crystallization of the polymer was achieved, when IR was attached to stearoyl group followed by mixing with methyl linoleate. The factors influencing on the crystallization behavior of NR are simplified to be the nucleating effect in terms of T_c and the plasticizing effect.

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