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Role of stearic acid in the strain-induced crystallization of crosslinked natural rubber and synthetic *cis*-1,4-polyisoprene

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Abstract

Strain-induced crystallization of crosslinked natural rubber (NR) and its synthetic analogue, *cis*-1,4-polyisoprene (IR), both mixed with various amounts of stearic acid (SA), were investigated by time-resolved X-ray diffraction using a powerful synchrotron radiation source and simultaneous mechanical (tensile) measurement. No acceleration or retardation was observed on NR in spite of the increase of SA amount. Even the SA-free IR crystallized upon stretching, and the overall crystallization behavior of IR shifted to the larger strain ratio with increasing SA content. No difference due to the SA was detected in the deformation of crystal lattice by stress for both NR and IR. These results suggested that the extended network chains are effective for the initiation of crystallization upon stretching, while the role of SA is trivial. These behaviors are much different from their crystallization at low temperature by standing, where SA acts as a nucleating agent.

Keywords: Network chain; Supercooling; Melting temperature

1. Introduction

Natural rubber (NR) is a biomass obtained from latex of *Hevea brasiliensis*. This biomass is processed into indispensable elastomeric materials for our modern life, e.g., as pneumatic tires for automobiles of heavy-duty use and for aircrafts [1,2]. Without NR, these vehicles would not be able to bring out their present performances. What is more, surgical gloves and condoms are also manufactured from NR latex, both are essential for prevention of infection. This versatility of NR in both industrial and hygienic applications is ascribable to its toughness based on the outstanding tensile properties and excellent crack growth resistance, which are assumed to be due to the ability to crystallize upon stretching [1–13].

This hypothetical mechanism has given rise to many studies on crystal structures and morphology of NR even from the time before the recognition of polymers as high molar mass compounds [4,14–17]. However, the studies using conventional wide-angle X-ray diffraction (WAXD) analysis did not give conclusive mechanisms due to the inability of fast time-resolved measurements during the stretching and the retraction of NR samples [3,18–20]. The observed results have been those inclusive of mechanical stress relaxation during the X-ray measurements [21]. It usually takes a lot of minutes to carry out single WAXD measurement by a conventional technique, while the relaxation is very fast in rubbery materials.

Transmission electron microscopy (TEM) afforded valuable insights on the morphology of NR crystals formed by stretching [22–27]. Again, time-resolved studies by TEM are very difficult, and the mechanism of strain-induced

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crystallization (SIC) of crosslinked NR is to be clarified by some dynamical methods. The advent of powerful X-ray sources at synchrotron facilities has enabled us to carry out the fast time-resolved in situ measurement by WAXD during the tensile measurement of the sample [5–7,9,10,28–31].

In our previous studies, the mechanism of SIC of crosslinked NR has been proposed on the basis of the synchrotron WAXD experiments [9,10,12,31]. The strain-induced crystallites of NR would be formed by homo-epitaxy onto fully extended network chains when the initially coiled chains are stretched and melting temperature of the sample exceeds ambient temperature due to the entropic reason [9,10]. According to this model, the stretched network chains should play a role equivalent to nucleating agents for the formation of oriented crystallites.

Besides SIC, unstretched NR is known to crystallize by standing at low temperature [18,19,32–34], which we mention here as temperature-induced crystallization (TIC). The maximum rate of TIC was observed at ca. −25 °C for uncrosslinked NR [32]. Even at this temperature, TIC starts after several minutes of induction period [35]. The rate of TIC is retarded with the increase in network-chain density [36]. On the other hand, SIC proceeds almost instantaneously even at room temperature when a certain critical strain is applied [9,10,31,37]. In this case (above the critical strain at room temperature), the rate of SIC is faster for the sample with the higher network-chain density [31,38]. It is noted that the relationship between the rate of crystallization and the network-chain density is reversed when the strain is small and the crystallization temperature is lowered [34]. These facts suggest that there is a significant difference between TIC and SIC, and that the latter is more complicated.

It is well known that NR contains non-rubber components such as proteins (1–2% in wt/vol of latex), phospholipids and fatty acids (0.9–1.7%), carbohydrates (1–2%) and inorganic substances (0.4–0.6%) [39,40]. The effects of such non-rubber components on TIC of uncrosslinked rubber have been studied [33,35,41–44]. According to these works, immiscible fatty acids such as stearic acid (SA) act as nucleating agents, while the other non-rubber components do not exhibit the nucleating effect. (In general, a surface of heterogeneity tends to initiate crystallization. Especially, if the surface is a specific crystal plane, epitaxial crystallization can occur.) For example, by the solvent extraction of fatty acids from NR, the rate of TIC was greatly reduced: Addition of SA to the extracted NR sample restored the rate of TIC [35]. On the other hand, the effects of such non-rubber components, especially of SA, on SIC are still not clear, because the vulcanized samples for the study on SIC have always been prepared by mixing SA and ZnO. Because SA has been customarily used for sulfur curing of NR and IR, and NR inherently contains SA, there may be no former report that compared SIC between the crosslinked samples with and without SA.

Our concern in this report is "What is the effect of SA on SIC of crosslinked NR?" Therefore, effect of SA on SIC of crosslinked NR and its synthetic analogue, *cis*-1,4-polyisoprene (IR), was studied by mixing various amounts of SA with them. It is noted that IR does not contain SA otherwise mixing it purposely [39]. That is to say, we compared the behavior of SIC between the samples with and without SA.

2. Experimental section

2.1. Materials

As NR and IR, RSS no. 1 (from Malaysia) and IR 2200 (from JSR Co.) were used, respectively. Formulations of rubber compounds for curing and the curing conditions are listed in Table 1. The amount of SA is indicated in the sample code after the hyphen. The network-chain densities of the crosslinked samples were calculated from their tensile properties as described in our previous papers [9,10], and are also included in Table 1.

2.2. Tensile measurements

In order to evaluate the mechanical properties of rubbery materials, the characteristic of which is a very high elongation, both the onsite tensile measurement at X-ray beamlines and the offline one at the laboratory were carried out. Dumbbell-shaped test specimens were cut from a crosslinked rubber sheet and subjected to the simultaneous tensile (using a small tensile tester, at a strain speed of 10 mm/min) and X-ray measurements at room temperature. Using the same type of sample, usual offline tensile test was carried out with a tensile tester at room temperature. The results of the latter experiment were used for the estimation of the network-chain densities. The specimen was uniaxially stretched to the predetermined strain (well before the failure strain) and then retracted to the original length. The strain ratio, α, was calculated as

Table 1
Formulations of the NR compounds in parts by weight per hundred parts of rubbers

Sample code	Rubber[a]	Stearic acid	Active ZnO	CBS[b]	Sulfur	Total	Curing time[c] (min)	Network-chain density × 10^4 (mol/cm^2)
NR-4SA	100	4.0	1.0	1.5	2.25	108.75	13	1.43
NR-1SA	100	1.0	1.0	1.5	2.25	105.75	13	1.27
NR-0SA	100	0.0	1.0	1.5	2.25	104.75	13	1.34
IR-4SA	100	4.0	1.0	1.5	2.25	108.75	22	1.36
IR-2SA	100	2.0	1.0	1.5	2.25	106.75	21	1.36
IR-0SA	100	0.0	1.0	1.5	2.25	104.75	22	1.35

[a] RSS no.1 and JSR IR 2200 were used for NR and IR series, respectively.
[b] *N*-Cyclohexyl-2-benzothiazole sulfenamide.
[c] Curing temperature was 140 °C.

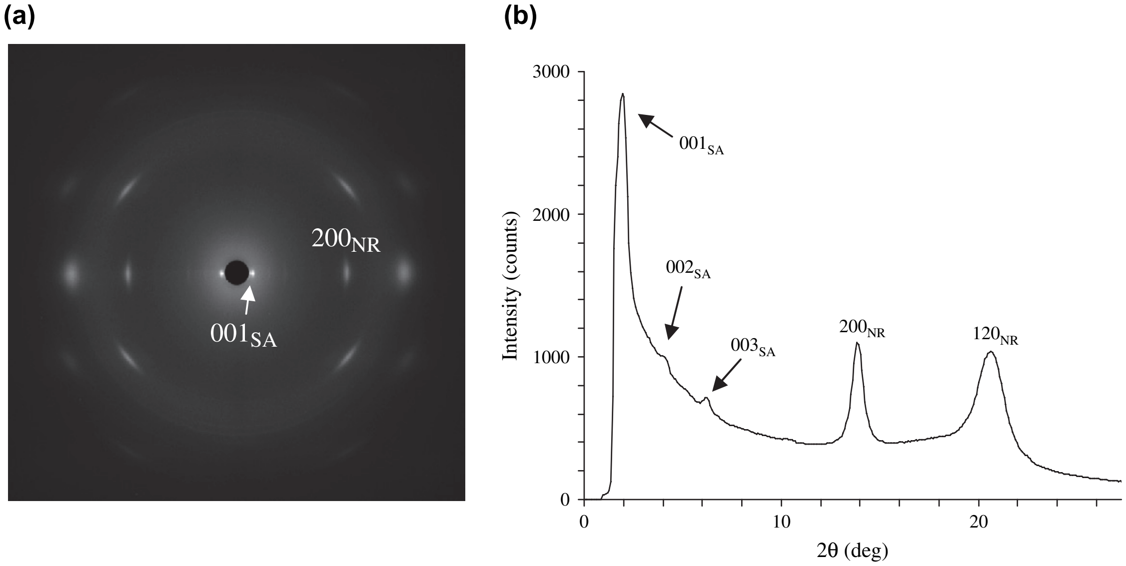

Fig. 1. (a) WAXD pattern of NR-4SA ($\alpha = 8$). Sharp reflections from SA corresponding to ca. 4.2 nm in real space are recognized on both sides of the beamstop. (b) The equatorial intensity profile of part (a). Small peaks are recognized near $2\theta = 4°$ and $2\theta = 6°$.

$\alpha = l/l_0$, where l_0 is the initial length of the sample and l is that of the elongated one.

2.3. Wide-angle X-ray diffraction (WAXD) measurements

WAXD experiments were conducted at X27C and X3A2 beamlines of National Synchrotron Light Source at Brookhaven National Laboratory, Brookhaven, NY, USA. The details of the simultaneous WAXD and tensile measurements are given in Refs. [10,12].

3. Results and discussion

3.1. Stearic acid (SA) in WAXD patterns

It has been reported that SA crystals give small-angle reflections in the X-ray diffraction pattern of stretched NR [45]. Fig. 1a shows the example of the WAXD pattern of NR-4SA. Sharp reflections are clearly observed on both sides of the beamstop. Fig. 1b is the equatorial intensity profile of Fig. 1a, in which the secondary and tertiary peaks are also recognized near $2\theta = 4°$ and $2\theta = 6°$, respectively. The long spacing corresponding to the primary reflection was estimated to be 4.2 nm [10], which is consistent with the spacing of (001) planes of SA crystals [46]. As the SA crystals are flake-shaped [46], they would be oriented as the NR sample is stretched.

Parts a and b of Fig. 2 show the WAXD patterns of NR-0SA just before and after the onset of SIC, respectively. It should be noted that no crystalline sharp rings due to randomly oriented NR crystals are observed in the WAXD pattern (Fig. 2b). Therefore, the initiating species of SIC should certainly be highly oriented entities. Now, we can observe the oriented reflections from the SA also in this figure. Since SA was not mixed to NR-0SA, the reflections in question are due to the inherently contained SA in NR [39,45]. As shown in Fig. 2a, the oriented reflections of SA appeared even before the onset of

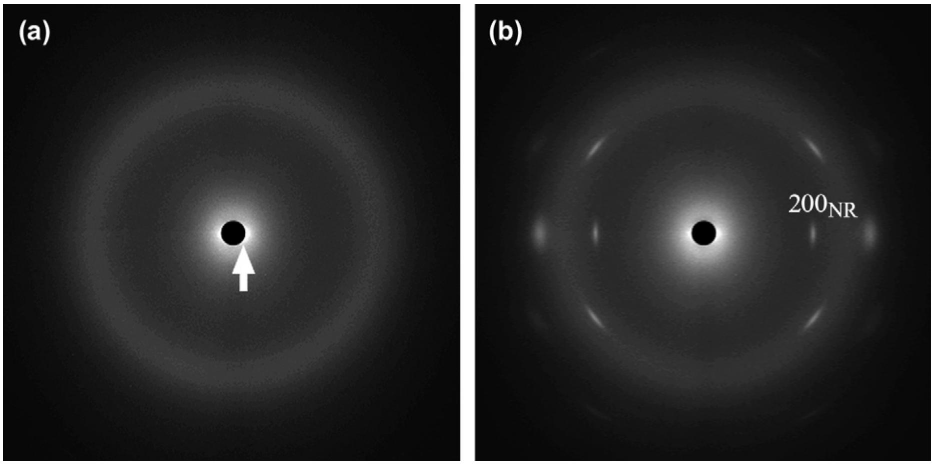

Fig. 2. WAXD patterns of NR-0SA ((a) $\alpha = 3$, (b) $\alpha = 5$). Sharp reflections from SA (indicated by an arrow) corresponding to ca. 4.2 nm in real space are recognized on both sides of the beamstop. The 200 reflection of NR, which is used for the analysis below, is indicated in part b.

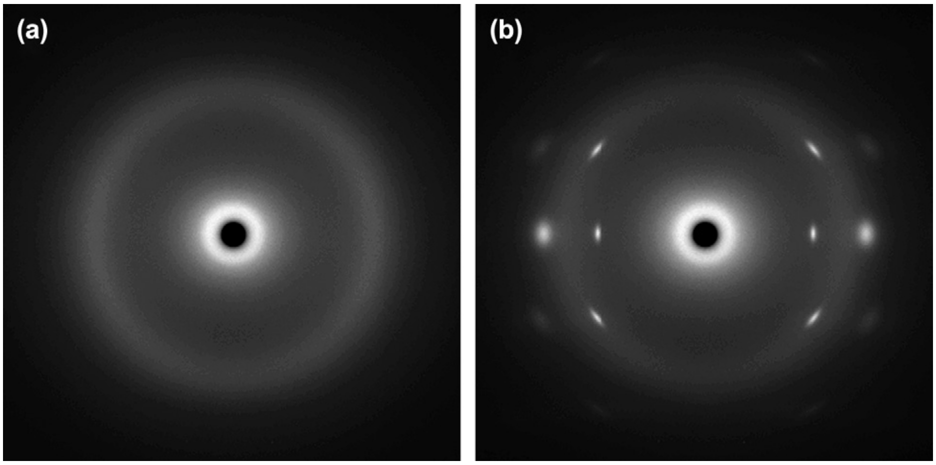

Fig. 3. WAXD patterns of IR-0SA ((a) $\alpha = 3$, (b) $\alpha = 5$). The reflections from SA are absent.

SIC of the NR samples. (One may easily recognize the existence of the reflections from SA by comparing with Fig. 3.) As mentioned in Section 1, the SA has been thought to play the main role in the initiation of TIC of NR in its uncrosslinked state [35,43]. At the same time, if the epitaxial crystallization is the nucleation mechanism, orientation of the SA crystals should satisfy the necessary condition that the initiating species of SIC should be oriented. According to Fig. 2, therefore, SA is tentatively assumed to be a possible candidate as the nucleating reagent also in SIC of crosslinked NR. However, there is another possible candidate. Because the network structure of crosslinked rubber has finite fluctuation, molecular chains along relatively short network trajectories should be extended upon stretching of the sample [47]. The extended chains will also induce the nucleation of SIC homogeneously [9,10,12,31]. The existence of such extended (highly oriented) chains is not doubtful, otherwise the SA crystals would not orient in the rubber matrix.

Even without SA, we could successfully prepare the crosslinked sample of IR. This is noteworthy, considering the fact that SA has been consistently used for the sulfur curing of NR and IR. Fig. 3 shows WAXD patterns of the crosslinked IR without SA (IR-0SA). This sample is solely free from SA in this experiment. Again, highly oriented crystallites were directly formed by stretching (Fig. 3b). Of course, in this case, SA cannot be the nucleating reagent because it is totally absent in this sample. This result evidences that SIC occurs even without SA. In this case, the extended network chains must be the oriented initiation species of SIC. However, this result does not necessarily indicate that SA does not act as the nucleating agent when it is mixed. In the next section, the efficiency of SA in terms of nucleating effect on SIC is compared with that of the extended chains on the basis of crystallization behavior of the rubber samples.

3.2. Initiation and growth of strain-induced crystallization

The crystallization behavior of the rubber samples was assessed by the integrated intensity of the 200 reflection

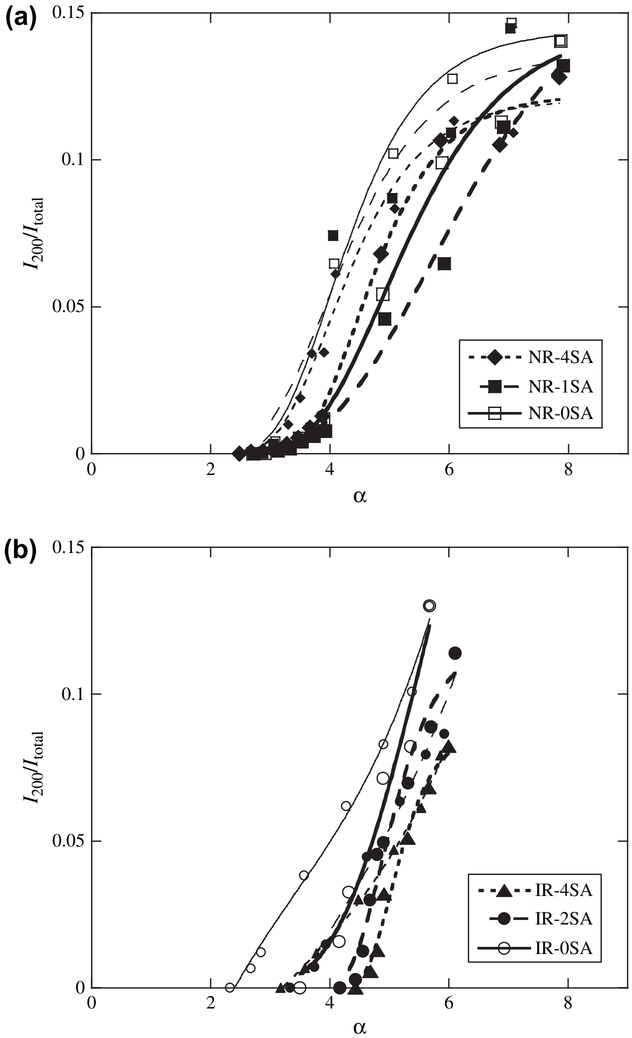

Fig. 4. Variation of I_{200}/I_{total} values with strain for (a) NR and (b) IR samples. Thick lines and larger symbols indicate the stretching process, and thin lines and smaller symbols the retracting process. The strain ratio, α, was calculated as $\alpha = l/l_0$, where l_0 is the initial length of the sample and l is that of the elongated one.

normalized by the integrated intensity of the total diffraction/scattering, namely, $I_{200}/I_{\mathrm{total}}$. Parts a and b of Fig. 4 show the variation of $I_{200}/I_{\mathrm{total}}$ for NR and IR, respectively. Although slight fluctuation was observed, no acceleration or retardation was observed on NR in spite of the increase of SA amount. Especially, when we pay attention to the onset strain of crystallization (α^0), there is no influence by the addition of SA for NR (Fig. 4a). On the other hand, α^0 of IR shifted to the larger side with the amount of SA (Fig. 4b). Among the SA-mixed samples, α^0 of NR is smaller than that of IR in accord with the previous results [9]. Only α^0 of IR-0SA was peculiarly small; it was almost equal to or even smaller than those of NR samples. The results for IR samples suggest that the presence of SA may shift α^0 to the larger strain. This is a totally different situation from TIC reported for uncrosslinked samples, where the existence of SA resulted in significant acceleration of crystallization [19,35,43,44,48–51].

The development of SIC can be discussed on the basis of the slopes of the plots in Fig. 4. Compared with IR-0SA, the slopes of the other IR samples during the stretching process are not so different from each other. That is to say, no remarkable acceleration effect by SA is recognized in Fig. 4. Because α^0 is rather shifted to the larger side by mixing with SA, we can conclude that the initiation and acceleration effect of SA is trivial in the case of SIC. The other initiating species, namely the extended network chain, must be much more effective for the initiation of SIC.

The shift of α^0 with the amount of SA can be explained as follows. From the viewpoint of thermodynamics, melting temperature (T_m) is shifted to higher temperature by stretching a rubber sample [9,10,52,53]. As a result, when T_m exceeds the ambient temperature and sufficient supercooling is attained, SIC would start. Because IR has the poorer regularity in the molecular configuration than NR, T_m of IR in the unstretched state is lower than that of NR [54]. Therefore, IR requires more strain than NR for the onset of SIC [9]. Now, T_m is depressed also by dissolving other compounds to the rubber matrix. Though SA is regarded as immiscible to NR and IR [44], small amount of it can dissolve in the rubber matrix. As a result, T_m of the rubber samples would be decreased by mixing with SA. The dissolved SA may act also as plasticizer in the rubbery matrix to decrease its glass-transition temperature. In the case of TIC, the plasticization effect could facilitate the diffusion of polymer molecules, and at the same time, undissolved SA crystals would act as nucleating agents, accelerating the overall crystallization process. On the other hand, in the case of SIC, the nucleating effect of SA crystals would be trivial, compared to that of the extended chains.

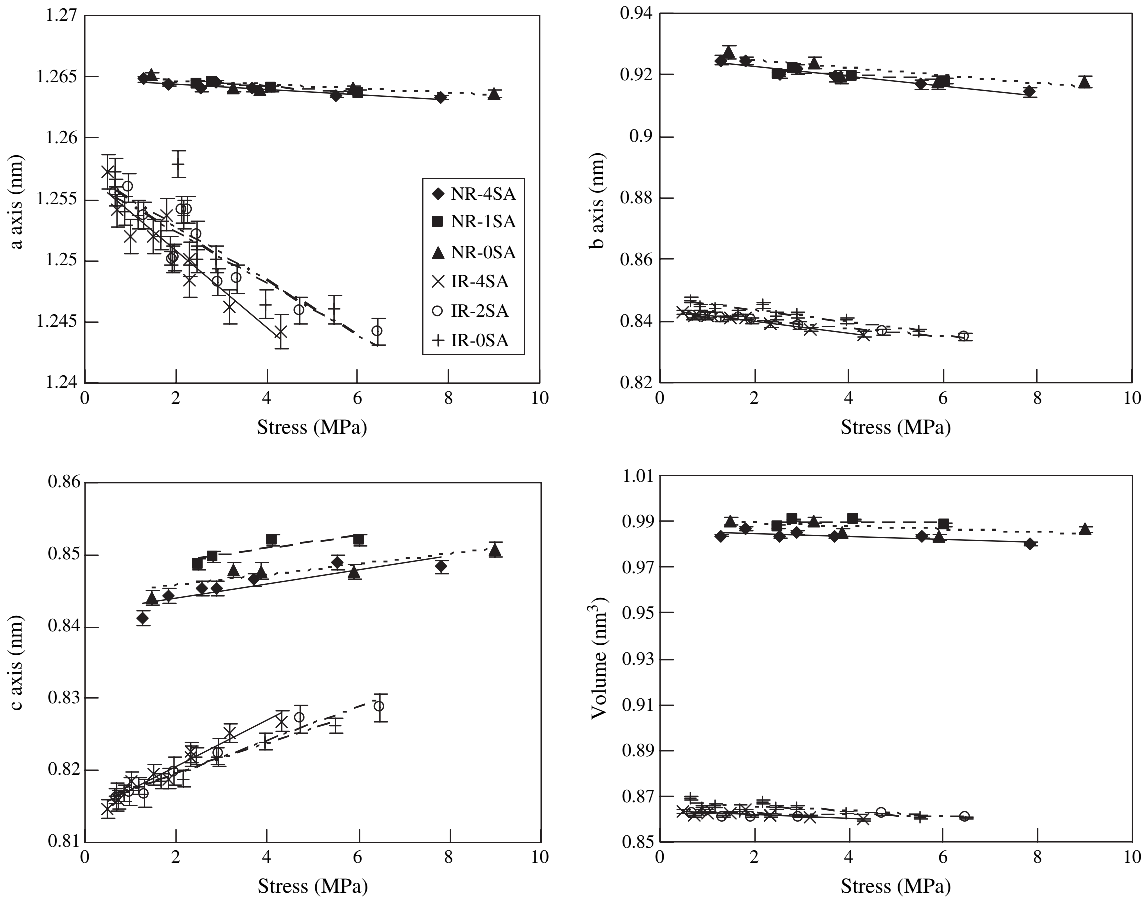

Fig. 5. Lattice constants and volume of the unit cell as a function of nominal stress.

Because some of the other molecular chains are more or less aligned by the tensile strain, the diffusion of molecular chains may also be relatively less important. Thus, by mixing with SA, the depression of T_m would have the major influence on the process of SIC. For IR, the shift of α^0 (Fig. 4b) would reflect the depression of T_m by increasing SA amount. The depression of T_m is also clearly found in Fig. 4b on the retracting process where the reflection intensity disappeared at the higher strain ratio for the samples with the higher SA content. Now, one may wonder why α^0 is almost constant for the NR samples (Fig. 4a) regardless of the SA amount. The amount of SA which is inherently contained in NR exceeds the solubility limit, according to the existence of reflections from the undissolved SA crystals in NR-0SA (Fig. 2). That is to say, SA is saturated in all the NR samples, and the variation of the amount of additional SA would have resulted in the merely negligible effect on α^0. One may also wonder how the slight difference of the slopes for the stretching process (thick lines) in Fig. 4 is explained. The difference would come from the slight difference in network-chain densities among the NR samples. In our former studies using the same experimental method, the slope was steeper for the sample with the higher network-chain density [9,10]. According to Table 1, the order of network-chain density is NR-4SA > NR-0SA > NR-1SA; the slopes in Fig. 4a are consistent with this order.

3.3. Lattice constant and orientational fluctuation of crystallites

In order to examine the other effects of SA on SIC, the WAXD patterns were further analyzed in more detail. Fig. 5 shows the variation of lattice constants as a function of nominal stress, which was estimated as described in our former papers [10,12]. The difference of the absolute values between NR and IR samples came from the difference in experimental settings at the synchrotron beamlines. Here, our discussion is limited only to their relative changes with stress. As already reported on crosslinked NR samples [10,12], the lattice constants changed approximately linearly with the nominal stress. (Even when the network-chain densities are different, the slopes of the lattice constant vs. stress plot are almost constant [10], while compounding with filler particles changes the slopes significantly [12].) In the current study, significant difference of the slope with the amount of SA is not recognized in Fig. 5. The slight difference of the slopes found for *a*- and *c*-axes of IR may be in the range of experimental error, taking the significant change of the slope by mixing with filler particles into account [12]. Accordingly, the fundamental mechanism that transmits the tensile stress to the rubber crystals should not change with the amount of SA.

Fig. 6 shows variations of the half-width of the 200 reflection, β_{az}, in the azimuthal intensity distribution; β_{az} is

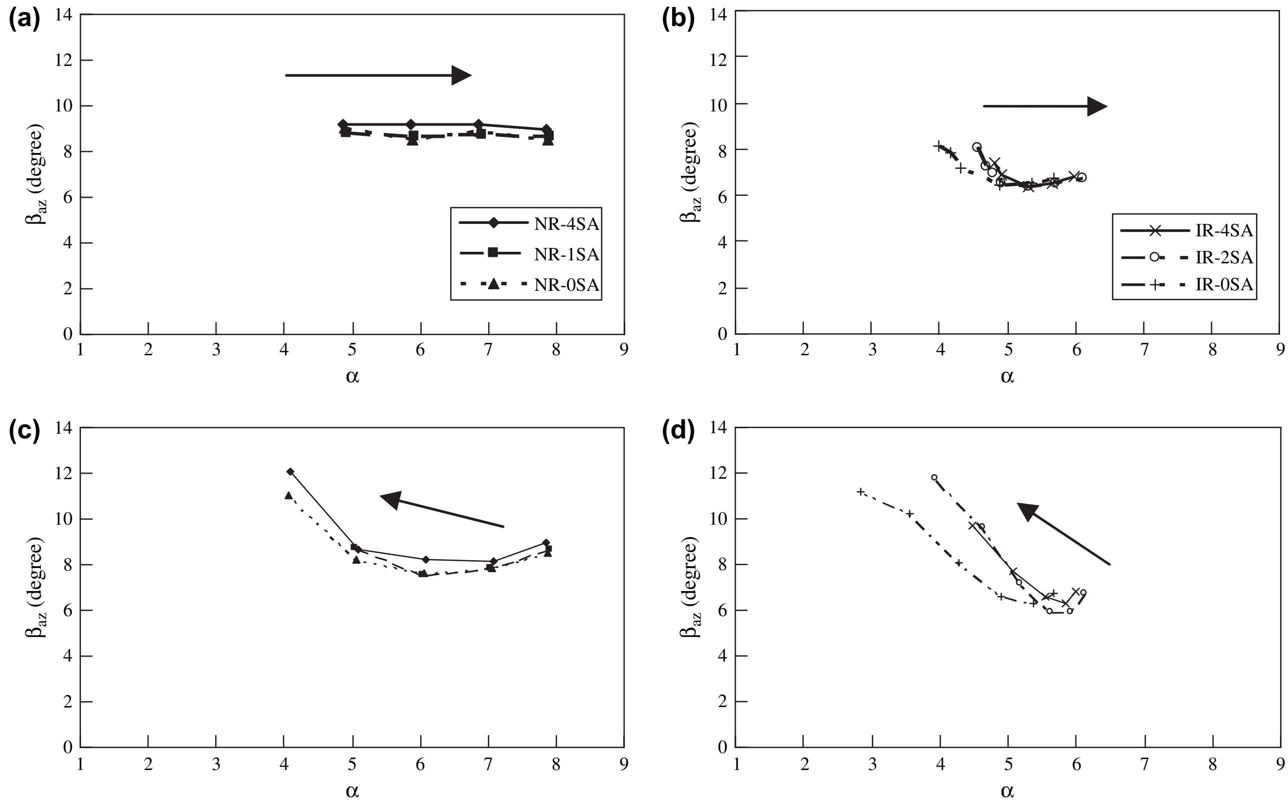

Fig. 6. Variation of azimuthal half-width of 200 reflection, β_{az}, with strain: (a) for NR samples during the stretching process, (b) for IR samples during the stretching process, (c) for NR samples during the retracting process, (d) for IR samples during the retracting process.

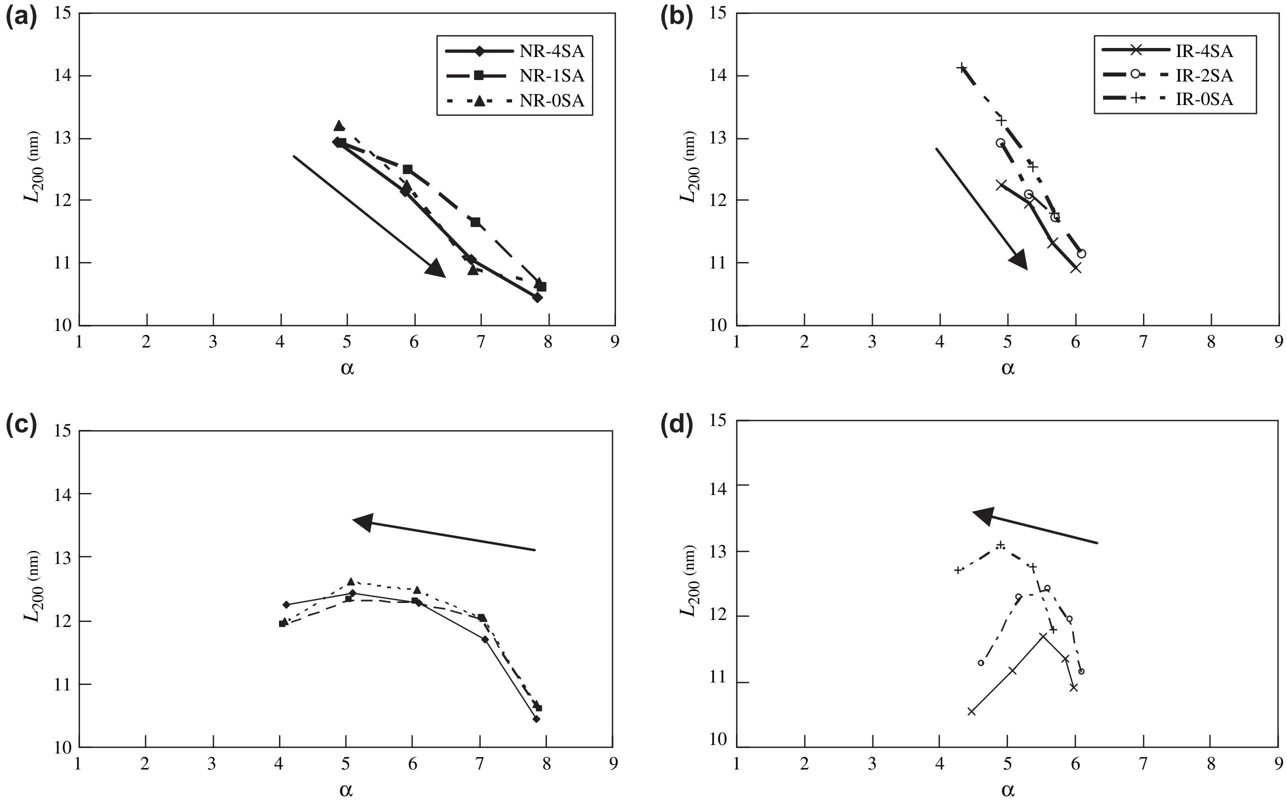

Fig. 7. Variation of lateral crystallite size, L_{200}, with strain: (a) for NR samples during the stretching process, (b) for IR samples during the stretching process, (c) for NR samples during the retracting process, (d) for IR samples during the retracting process.

a measure of the orientational fluctuation of the crystallites, which was also estimated in the same way as in Ref. [10]. That is to say, the 200 reflection was azimuthally scanned to measure the intensity distribution, and the intensity distribution was fitted with the Gaussian function. The β_{az} value was calculated from the fitting parameter. The smaller value of β_{az} indicates the smaller fluctuation in crystalline orientation. There is a slight tendency that β_{az} is smaller for the samples without SA, especially for the retraction process (parts c and d of Fig. 6). This could be due to the plasticization effect of SA dissolved in the amorphous phase of the rubber matrix; IR-0SA without the plasticizer solely showed the somewhat different behavior (Fig. 6d). The orientation of crystallites might be perturbed more in the softer (plasticized) amorphous matrix.

Fig. 7 shows variation of lateral crystallite size, L_{200}, which was estimated from the half-width of the 200 reflection in the equatorial intensity distribution. The detailed procedure of estimation of L_{200} is also described in Ref. [10]. In the case of NR, the differences of L_{200} due to SA were not recognized both for the stretching and retracting processes. Slight fluctuation of the values among the samples may be due to the differences of network-chain density [10]. The changes of L_{200} of IR samples are in conformity with those of NR for the stretching process. On the other hand, for the retracting process of IR, L_{200} apparently decreased with the increase of SA. This could be also due to the plasticized amorphous phase of the rubber matrix; the crystallites might have been broken due to perturbation by the softer matrix during the retracting process. However, further study is necessary to confirm this hypothesis concerning the plasticization effect of SA on β_{az} and L_{200}.

4. Conclusions

SA is thought to be almost inert in the SIC of crosslinked NR and IR. Its role as nucleating agent, which was observed to be the case in TIC, is well overshadowed by the highly active initiating function of extended network chains in the SIC. The mechanism of SIC presented in our former papers [9,10,12] may be valid even when the presence of SA is taken into account. It is important to emphasize that the SIC proceeds with a much different type of nuclei (i.e., the extended network chains) from usual nucleating agents, and that the rate of crystallization [3,10,31] is extremely much faster than that of TIC. Accordingly, we have to definitely distinguish these two phenomena by quite different mechanisms. Even experienced researchers in the field of rubber science have been often unaware of this significant difference. For example, in a review article by Persson et al. [13], they mentioned that SIC *requires certain non-rubber constituents, mainly fatty acids*, referring a result of TIC for uncrosslinked samples. This comment is obviously inconsistent with the experimental evidences for IR-0SA in Figs. 3 and 4b. However, effect of non-rubber constituents has to be investigated and considered further in the SIC, because NR contains many other non-rubber constituents other than SA.

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