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## Transition of rupture mode of strain crystallizing elastomers in tensile edge-crack tests†

Katsuhiko Tsunoda,<sup>a</sup> Yuji Kitamura<sup>b</sup> and Kenji Urayama<sup>b</sup>  <sup>\*c</sup>

We revisit the classical results that the fracture energy density ( $W_b$ ) of strain crystallizing (SC) elastomers exhibits an abrupt change at a characteristic value ( $c_0^*$ ) of initial notch length ( $c_0$ ) in tensile edge-crack tests. We elucidate that the abrupt change of  $W_b$  reflects the transition in rupture mode between the catastrophic crack growth without a significant SIC effect at  $c_0 > c_0^*$  and the crack growth like that under cyclic loading ( $dc/dn$  mode) at  $c_0 < c_0^*$  as a result of a pronounced SIC effect near the crack tip. At  $c_0 < c_0^*$ , the tearing energy ( $G$ ) was considerably enhanced by hardening *via* SIC near the crack tip, preventing and postponing catastrophic crack growth. The fracture dominated by the  $dc/dn$  mode at  $c_0 < c_0^*$  was validated by the  $c_0$ -dependent  $G$  characterized by  $G = (c_0/B)^{1/2}/2$  and the specific striations on the fracture surface. As the theory expects, coefficient  $B$  quantitatively agreed with the result of a separate cyclic loading test using the same specimen. We propose the methodology to quantify the tearing energy enhanced *via* SIC ( $G_{SIC}$ ) and to evaluate the dependence of  $G_{SIC}$  on ambient temperature ( $T$ ) and strain rate ( $\dot{\epsilon}$ ). The disappearance of the transition feature in the  $W_b$ - $c_0$  relationships enables us to estimate definitely the upper limits of the SIC effects for  $T$  ( $T^*$ ) and  $\dot{\epsilon}$  ( $\dot{\epsilon}^*$ ). Comparisons of the  $G_{SIC}$ ,  $T^*$ , and  $\dot{\epsilon}^*$  values between natural rubber (NR) and its synthetic analog reveal the superior reinforcement effect *via* SIC in NR.

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## Introduction

Natural rubber (NR) is one of the most widely used biomaterial polymers. NR has attracted increasing interest in environmental issues and momentum toward realizing a sustainable society.<sup>1–3</sup> A unique feature of NR is strain-induced crystallization (SIC): NR undergoes partial crystallization when subjected to a sufficiently large strain.<sup>4,5</sup> SIC considerably hardens rubber, resulting in a marked stress-upturn in the stress-strain relationship. SIC is a self-reinforcement function that increases the tensile strength and fracture toughness. This beneficial feature distinguishes NR from other non-crystallizing (non-SIC) rubbers.<sup>1–3</sup> Synthetic *cis*-1,4-polyisoprene rubber (IR) is an NR analog. It has long been known that IR is appreciably inferior to NR in several SIC properties, such as the onset strain and the mechanical reinforcement effect.<sup>6–9</sup> The superior SIC abilities

of NR relative to IR are often attributed to the perfect stereoregularity of *cis*-1,4-polyisoprene and a pseudo-network *via* the interaction between the end-functional groups in the rubber chains and non-rubber components such as fatty acids, proteins, and lipids.<sup>10–13</sup> Recently, it has been reported that SIC can occur even in gels with high solvent contents, significantly enhancing the mechanical toughness.<sup>14</sup> SIC has received considerable interest as a key for toughening not only rubbers but also gels.

The SIC near the crack tip subjected to large deformation contributes to enhancing the tear strength or suppressing the catastrophic crack growth.<sup>15–20</sup> The SIC near the crack tip was revealed by investigations using the micro-beam wide-angle X-ray scattering (WAXS) technique.<sup>21,22</sup> However, many aspects of the reinforcement effects *via* SIC remain to be quantified. The reinforcement effect *via* SIC is expected to have an upper limit for each ambient temperature ( $T$ ) and imposed strain rate ( $\dot{\epsilon}$ ) (designated as  $T^*$  and  $\dot{\epsilon}^*$ , respectively), because the crystal has a melting temperature and SIC is a kinetic event. The melting temperatures ( $T_f$ ) of the SIC crystals of NR and IR were investigated using WAXS experiments in the stretched state at various  $T$ .<sup>23–29</sup> The  $T_f$  increased with imposed stretch reflecting an increase in the crystallinity index, which was thermodynamically explained by a reduction in the configurational entropy of network strands.<sup>1–3,30</sup>  $T_f$  is an equilibrium property,

<sup>a</sup> Sustainable and Advanced Materials Division, Bridgestone Corporation, Tokyo 187-8531, Japan. E-mail: katsuhiko.tsunoda@bridgestone.com

<sup>b</sup> Sustainable and Advanced Materials Division, Bridgestone Corporation, Tokyo 187-8531, Japan

<sup>c</sup> Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan. E-mail: urayama.kenji.2s@kyoto-u.ac.jp

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while the SIC kinetics is significantly affected by the ambient temperature ( $T$ ). At  $T^*$  the SIC kinetics becomes so slow that SIC cannot occur at  $\dot{\epsilon}$  of interest.

The effect of  $\dot{\epsilon}$  on SIC was examined by WAXS experiments using custom-made tensile instruments that could achieve high strain rates. The upper limit  $\dot{\epsilon}$  for SIC remains unclear because finite SIC was still observed at high strain rates on the order of  $10^2 \text{ s}^{-1}$ .<sup>31–35</sup> The reinforcement effect *via* SIC is expected to depend on  $T$  and  $\dot{\epsilon}$  and to disappear at sufficiently high  $T$  or  $\dot{\epsilon}$  exceeding  $T^*$  and  $\dot{\epsilon}^*$ . However, in general, the evaluations of  $T^*$  and  $\dot{\epsilon}^*$  in conventional tensile tests using unnotched bulk specimens involve appreciable ambiguity, because the tensile strength (stress at break) data as a function of  $T$  or  $\dot{\epsilon}$  often show scattering owing to the high susceptibility to inherent flaws.<sup>36</sup>

The evaluation of the tearing energy, which is the energy required for crack propagation at given  $T$  and  $\dot{\epsilon}$ , in rubber-like materials has attracted considerable interest since tearing energy is a key property to characterize the fracture behavior.<sup>37–45</sup> A classical tensile fracture test, called the “edge-crack test,” provides an important basis for characterizing the reinforcement effect *via* SIC.<sup>36,46–48</sup> Thomas *et al.*<sup>36,46,47</sup> and Hamed *et al.*<sup>48</sup> investigated the strain energy density at break ( $W_b$ ) for pre-notched NR specimens as a function of the initial notch length ( $c_0$ ) through tensile experiments. They found that  $W_b$  decreased with increasing  $c_0$ , but with an abrupt fall at a characteristic  $c_0$  value ( $c_0^*$ ), whereas this abrupt change was not observed for non-SIC rubber. They regarded this discontinuity as a transition between the tensile fractures with or without a significant SIC effect; at  $c_0 < c_0^*$ , a sufficiently wide region near the crack tip underwent SIC, resulting in an enhancement of  $W_b$ . Hamed *et al.* investigated the influence of cross-links and filler contents on the transition behavior of NR in edge-crack tests<sup>49,50</sup> and discussed the synergetic effects of SIC and filler loading.

In this study, we revisit the discontinuous  $W_b$ - $c_0$  relationships specific to the SIC rubbers and elucidate that the discontinuity results from the transition of rupture mode between the catastrophic crack growth without an appreciable SIC effect at  $c_0 > c_0^*$  and the crack growth like that under cyclic loading ( $dc/dn$  mode) undergoing a significant SIC effect. The occurrence of the cyclic crack growth mode at  $c_0 < c_0^*$  is validated by the characteristic striations on the fracture surface and the result of a separate cyclic loading test using the same specimen. We propose the methodology to quantify the tearing energy enhanced *via* SIC ( $G_{\text{SIC}}$ ) from the  $W_b$ - $c_0$  data and to evaluate  $T^*$  and  $\dot{\epsilon}^*$  from the disappearance of the transition feature. We demonstrate that the comparisons of the  $G_{\text{SIC}}$ ,  $T^*$ , and  $\dot{\epsilon}^*$  values between NR and IR reveal the superior reinforcement effect *via* SIC in NR.

## Theory for the edge-crack test of SIC rubber

Crack growth in rubber has been successfully described using fracture mechanics based on the concept of tearing energy. Tearing energy,  $G$ , which is the required energy to drive a crack

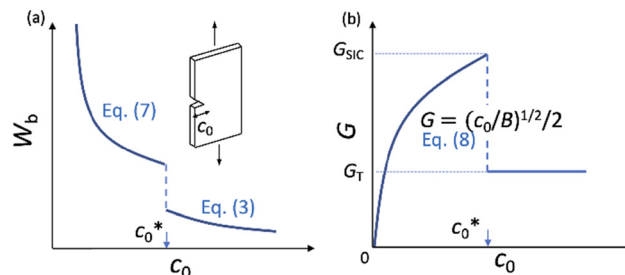


Fig. 1 Schematic illustrations of the theoretical relationships of (a) strain energy density at break ( $W_b$ ) and initial notch length ( $c_0$ ), and (b) tearing energy ( $G$ ) and  $c_0$ . Crack growth of a single-edge crack specimen (inset) undergoes a transition between the catastrophic failure ( $c_0 > c_0^*$ ) and the  $dc/dn$  mode ( $c_0 < c_0^*$ ).

with a unit area in size, is defined as follows:<sup>37,51</sup>

$$G = -\frac{1}{l} \left( \frac{\partial U}{\partial c} \right)_l \quad (1)$$

where  $c$  is the length of a crack in a material with a thickness of  $t$  and  $U$  is the total strain energy. The differential is conducted at a constant specimen length ( $l$ ) or constant strain. For a strip tensile specimen with an edge flaw of length ( $c$ ) (inset of Fig. 1a),  $G$  is given by:<sup>37</sup>

$$G = 2kWc \quad (2)$$

where  $W$  is the strain energy density in the bulk specimen (far from the crack tip) and  $k$  is a slightly varying function of the extension ratio ( $\lambda$ ), given by  $k = \pi/\lambda^{1/2}$ . The tearing energy,  $G$ , reflects the energy required to break the bonds across the fracture plane and the energy dissipated during fracture.

Eqn (2) was experimentally validated using the edge-crack test of non-SIC rubbers by varying the initial notch length ( $c_0$ ):<sup>52</sup> the strain energy density at break ( $W_b$ ) is simply proportional to  $c_0^{-1}$ , reflecting the fact that  $G$  is a material constant for non-SIC rubbers. By contrast, SIC rubbers exhibit a discontinuous transition in the  $W_b$ - $c_0$  relationships:  $W_b$  decreases with increasing  $c_0$ , and notably,  $W_b$  falls abruptly at a characteristic value of  $c_0$  ( $c_0^*$ ),<sup>36,46–48</sup> which is schematically shown in Fig. 1a. Thomas *et al.*<sup>36,46,47</sup> regarded this abrupt change in  $W_b$  at  $c_0^*$  as a transition in the rupture mechanism; at  $c_0 > c_0^*$ , no significant SIC occurs ahead of the advancing crack tip of the specimens, resulting in the catastrophic crack growth process observed in the non-SIC rubbers. At  $c_0 < c_0^*$ , a sufficiently large SIC region emerged near the crack tip, preventing or postponing the catastrophic crack growth process. At  $c_0 > c_0^*$  without a significant SIC effect, when the failure follows the ordinary tearing mode, the  $c_0$  dependence of  $W_b$  can be expressed by eqn (2) as follows:

$$W_b = \frac{G_T}{2kc_0} \quad \text{at } c_0 > c_0^* \quad (3)$$

where  $G_T$  is the critical tearing energy for the onset of catastrophic crack growth. If a specimen undergoes SIC in a sufficiently large area near the crack tip, the crack growth requires a higher  $G$  than the  $G_T$  because the crack propagates through the crystalline region. Thomas *et al.* assumed that the corresponding crack



propagates like crack growth under cyclic loading.<sup>36,46,47</sup> When the notch grows by  $\Delta c$  during the loading,  $G$  is given from eqn (2) as follows:

$$G = 2kW(c_0 + \Delta c) \quad (4)$$

In general, the crack growth rate during a loading cycle ( $dc/dn$ ) is related to  $G$  by a power law according to Paris and Erdogan,<sup>53</sup>  $\Delta c = dc/dn = BG^\alpha$ , where  $B$  is the material constant related to the crack growth, which can be obtained by cyclic crack growth measurement under a large strain. In the case of NR, the power law with  $\alpha = 2$  satisfactorily describes the behavior at moderate and high  $G$  values;<sup>54</sup> the relationship of current interest is written as follows:

$$\Delta c = BG^2 \quad (5)$$

The following relationship is obtained by eliminating  $G$  using eqn (4) and (5) as follows:

$$\Delta c = 4k^2B(c_0 + \Delta c)^2 W^2 \quad (6)$$

Postulating that this quadratic equation for  $\Delta c$  has real solutions provides the condition that the crack grows indefinitely, that is, the rupture occurs.<sup>46</sup> The corresponding postulate gives  $W_b$  in the tensile fracture *via* the cyclic crack growth mode:

$$W_b = \frac{1}{4kc_0^{1/2}B^{1/2}} \quad \text{at } c_0 < c_0^* \quad (7)$$

The transition of the  $W_b$ - $c_0$  relationship between eqn (3) and (7) is schematically illustrated in Fig. 1a. Thomas and co-workers<sup>36,46,47</sup> explained the experimental data for NR at  $c_0 > c_0^*$  and  $c_0 < c_0^*$  using eqn (3) and (7), respectively.

The  $W_b$  values below  $c_0^*$  are significantly larger than those beyond  $c_0^*$ , reflecting the enhancement effect of SIC on the tearing energy. However, the corresponding effect is yet to be quantified from the  $W_b$ - $c_0$  data. Therefore, we extend the analysis to quantify the tearing energy enhanced by the SIC effect ( $G_{\text{SIC}}$ ). Eqn (4) is expressed using eqn (7) by eliminating  $k$  as follows:

$$G = \frac{1}{2} \left( \frac{c_0}{B} \right)^{1/2} \left( 1 + \frac{\Delta c}{c_0} \right) \approx \frac{1}{2} \left( \frac{c_0}{B} \right)^{1/2} \quad \text{at } c_0 < c_0^* \quad (8)$$

The increment  $\Delta c$ , which is characterized by the interval between adjacent striation lines in the fracture surface, is significantly smaller than  $c_0$  (*i.e.*,  $\Delta c/c_0 \ll 1$ ), as will be shown later. Eqn (8) (*i.e.*,  $c_0 \approx 4BG^2$ ) expects that  $G$  increases proportionally to  $c_0^{1/2}$  when  $c_0 < c_0^*$ , reflecting the feature of the  $dc/dn$  mode (eqn (5);  $\Delta c = BG^2$ ). When  $c_0$  exceeds  $c_0^*$ ,  $G$  is expected to drop abruptly to  $G_T$  in eqn (3) because the fracture occurs *via* catastrophic crack growth (ordinary tear manner); there is no significant SIC near the crack tip. Fig. 1b schematically illustrates the  $c_0$  dependence of  $G$  in this scenario. The maximum value of  $G$  at  $c_0^*$  can be regarded as the characteristic tearing energy enhanced by the SIC effect ( $G_{\text{SIC}}$ ). In the case of non-SIC rubber,  $G$  in cyclic crack growth which is a subcritical process is significantly smaller than  $G_T$ . In the edge-crack tensile tests of SIC rubber,  $G$  in cyclic crack growth mode can be larger than  $G_T$ , because the SIC near the crack tip pronouncedly enhances  $G$  at  $c_0 < c_0^*$  whereas it is suppressed at  $c_0 > c_0^*$ .

Investigations of the  $W_b$ - $c_0$  relationships with varying ambient temperatures ( $T$ ) and strain rates ( $\dot{\epsilon}$ ) (Fig. 1a) provide a basis for discussing the effects of  $T$  and  $\dot{\epsilon}$  on  $G_{\text{SIC}}$ . In particular, the corresponding data also enable us to evaluate  $T^*$  and  $\dot{\epsilon}^*$  (the upper limits for the SIC effect on tearing energy) because at  $T > T^*$  and  $\dot{\epsilon} > \dot{\epsilon}^*$ , the transition feature vanishes, and only the ordinary tearing mode ( $G \approx G_T$ ; eqn (3)) appears over the entire  $c_0$  range.

## Experimental section

### Materials

The following compositions were employed for the preparation of the specimens designated as NR-A and IR-A: NR rubber gum (ribbed smoked sheet, RSS#3) or IR gum (IR2200, ENEOS Material Co.), stearic acid (2 phr, *i.e.*, 2 g per 100 g of gum rubber), ZnO (5.0 phr), polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMDQ, 0.3 phr), *N*-1,3-dimethylbutyl-*N'*-phenyl-*p*-phenylenediamine (6PPD, 1 phr), *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS, 1.5 phr), and sulfur (1.5 phr).

First, gum, stearic acid, ZnO, TMQD, and 6PPD were mixed, and the mixture was sheared for 2 min in a chamber at a controlled temperature of 80 °C. Next, CBS and sulfur were added for vulcanization, and the mixtures were subjected to shear for 1.5 min at 80 °C. The mixtures were further sheared using an open-roll mill for 5 min at 60 °C. Finally, specimen sheets were prepared using a hot press method at 160 °C for 8 and 13 min for NR and IR, respectively. We used the NR-A and IR-A specimens for the edge-crack tests in order to investigate the enhancement effects *via* SIC on tearing energy at various  $T$  and  $\dot{\epsilon}$  values.

For comparing the results of the edge-crack and the cyclic loading tests, we employed the NR-B specimen which had almost the same compositions as NR-A but slightly differed in curatives: 1,3-diphenylguanidine (DPG, 0.35 phr), *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS, 1.77 phr) and sulfur (1.4 phr). The processing procedure for the sheet specimens of NR-B was the same as that for NR-A.

NR-A and IR-A exhibited the same magnitudes of equilibrium swelling in toluene within the experimental error, indicating that they have similar cross-link densities. The average molecular weights between neighboring cross-links were estimated to be 7200 g mol<sup>-1</sup> for NR-A and IR-A and 6400 g mol<sup>-1</sup> for NR-B from the equilibrium swelling degrees using the Flory-Rehner equation.<sup>55</sup>

A styrene butadiene rubber (SBR) specimen was prepared as a non-SIC rubber for comparison, using SBR gum (#1500, ENEOS Material Co.). The compositions of stearic acid, ZnO, TMQD, 6PPD and sulfur were identical to those of NR-A. Diphenyl guanidine (1 phr), 2-benzothiazolyl disulfide (0.6 phr), and *N*-oxydiethylene-2-benzothiazole sulfenamide (0.6 phr) were used as cure accelerators. The specimen sheets were made using the same method as for NR-A at 160 °C for 6 min.

### Edge-crack test

A tensile strip specimen (5 mm wide × 50 mm high × 2 mm thick) was used. An initial crack was inserted into the center of



a single side of the tensile strip specimen using a specially designed cutting apparatus. The initial crack length ( $c_0$ ) was varied from 0.25 to 3.5 mm in an approximately 0.25 mm interval. Tensile measurements were performed using a tensile testing machine (Shimadzu AGX-Plus 1 kN and Hydroshot 1 kN) equipped with a controlled temperature chamber. To investigate the effect of  $T$ ,  $T$  was varied from 25 °C to 90 °C, and the measurements were conducted at a fixed strain rate of 0.5 s<sup>-1</sup>. To examine the effect of  $\dot{\epsilon}$ ,  $\dot{\epsilon}$  was varied from 0.005 to 500 s<sup>-1</sup> at 25 °C.

The tensile force at break ( $f_b$ ) of a pre-notched specimen with an initial notch length ( $c_0$ ) was measured under the given conditions of  $T$  and  $\dot{\epsilon}$ . The tearing energy ( $G$ ) was calculated using eqn (2) corresponding to eqn (4) with  $\Delta c/c_0 \ll 1$ . The strain energy density at break ( $W_b$ ) and  $\lambda$  in eqn (2) were obtained with the  $f_b$  value using the  $W$ - $\sigma$  and  $\sigma$ - $\lambda$  relationships for the corresponding unnotched bulk specimen.

### Cyclic loading test

A cyclic loading test was conducted for the pre-notched NR-B specimens (5 mm wide  $\times$  50 mm high  $\times$  2 mm thick) using a tensile tester (Shimadzu AGX-Plus 1kN). The  $c_0$  values were varied from 0.3 to 1.0 mm. The tensile specimen was cyclically loaded and unloaded between the desired extension length and zero position for 5 to 10 cycles at a crosshead speed of 200 mm min<sup>-1</sup> and at 25 °C. The maximum stretch was varied between 3.6 and 7.0 depending on the pre-notch length of each specimen. The maximum force during each cycle was recorded, enabling the evaluation of the elastically stored energy density ( $W_i$ ) and strain function ( $k_i$ ) for the  $i$ -th cycle, using the  $W$ - $\sigma$  and  $\sigma$ - $\lambda$  relationships for the unnotched bulk NR-B specimen. After the cyclic loading test, the initial crack length ( $c_0$ ) and the increment of crack length ( $\Delta c_i$ ) in each cycle were precisely measured utilizing a digital video microscope as described below.

### Observation of the fracture surface

The fracture surface of the specimens was observed using a digital microscope (Hi-rox Co., RH-2000) equipped with a variable lighting adopter. The  $c_0$  values were measured from the fracture surface.

### Wide-angle X-ray scattering measurements

WAXS measurements for the unnotched bulk NR-A and IR-A specimens were performed using synchrotron radiation at beamline BL03XU of SPring-8 (JASRI). The X-ray wavelength was 0.1 nm, and the camera length was 130 mm. A CMOS camera (Hamamatsu Photonics K.K. Orca Flash-4.0) equipped with an image intensifier was used as the detector. Specially designed in-house dumbbell specimens were stretched at a strain rate of 0.1 s<sup>-1</sup>. Sequential WAXS images during the stretching process were recorded every second after the sample extension started. The X-ray scattering intensity at scattering vector  $q$  as a function of stretch ( $\lambda$ ),  $I_x^{\text{OBS}}(q, \lambda)$ , was obtained from the two-dimensional WAXS image by integrating  $\beta = \pm 10^\circ$  ( $\beta$ : azimuth angle) after correcting for the effects of the dark noise of the detector, air scattering, and sample thickness.

Because no reflection from the SIC crystals was observed at  $\lambda < 2$ , the corresponding scattering intensity,  $I_x^{\text{OBS}}(q, \lambda < 2)$ , was regarded as the contribution from the amorphous phase. The scattering intensity from SIC crystals,  $I_x$ , was evaluated as follows:

$$I_x(q, \lambda) = I_x^{\text{OBS}}(q, \lambda) - I_x^{\text{OBS}}(q, \lambda < 2) \quad (9)$$

We employed the peak intensity of the crystal (200) diffraction ( $I_{200}$ ) as a simple measure of the crystallinity index *via* the SIC.

## Results and discussion

### Non-SIC rubber in the edge-crack test

Fig. 2a illustrates  $W_b$  as a function of  $c_0$  for a non-SIC rubber, styrene butadiene rubber (SBR), at 25 °C and a strain rate of 0.60 s<sup>-1</sup> obtained using the edge-crack test.  $W_b$  decreased monotonically with increasing  $c_0$ . The  $G$  values calculated using the  $W_b$  data and eqn (2) are constant in the range of  $c_0 \leq 3.55$  mm examined here (Fig. 2b). It is naturally expected because  $G$  for the non-SIC rubber can be assumed as a  $c_0$ -independent critical tearing energy ( $G_T$ ) for the onset of catastrophic crack growth at given  $T$  and  $\dot{\epsilon}$ . Importantly, the

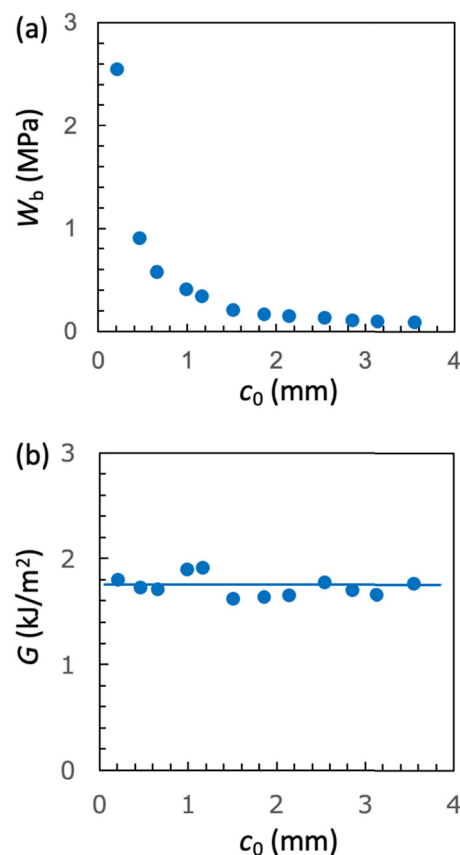


Fig. 2 (a) Strain energy density at break ( $W_b$ ) as a function of the initial notch length ( $c_0$ ) for SBR (non-SIC rubber) at 25 °C and a strain rate of 0.60 s<sup>-1</sup> in the edge-crack test. (b) The  $c_0$  dependence of tearing energy ( $G$ ) calculated using the data in (a) with eqn (2).

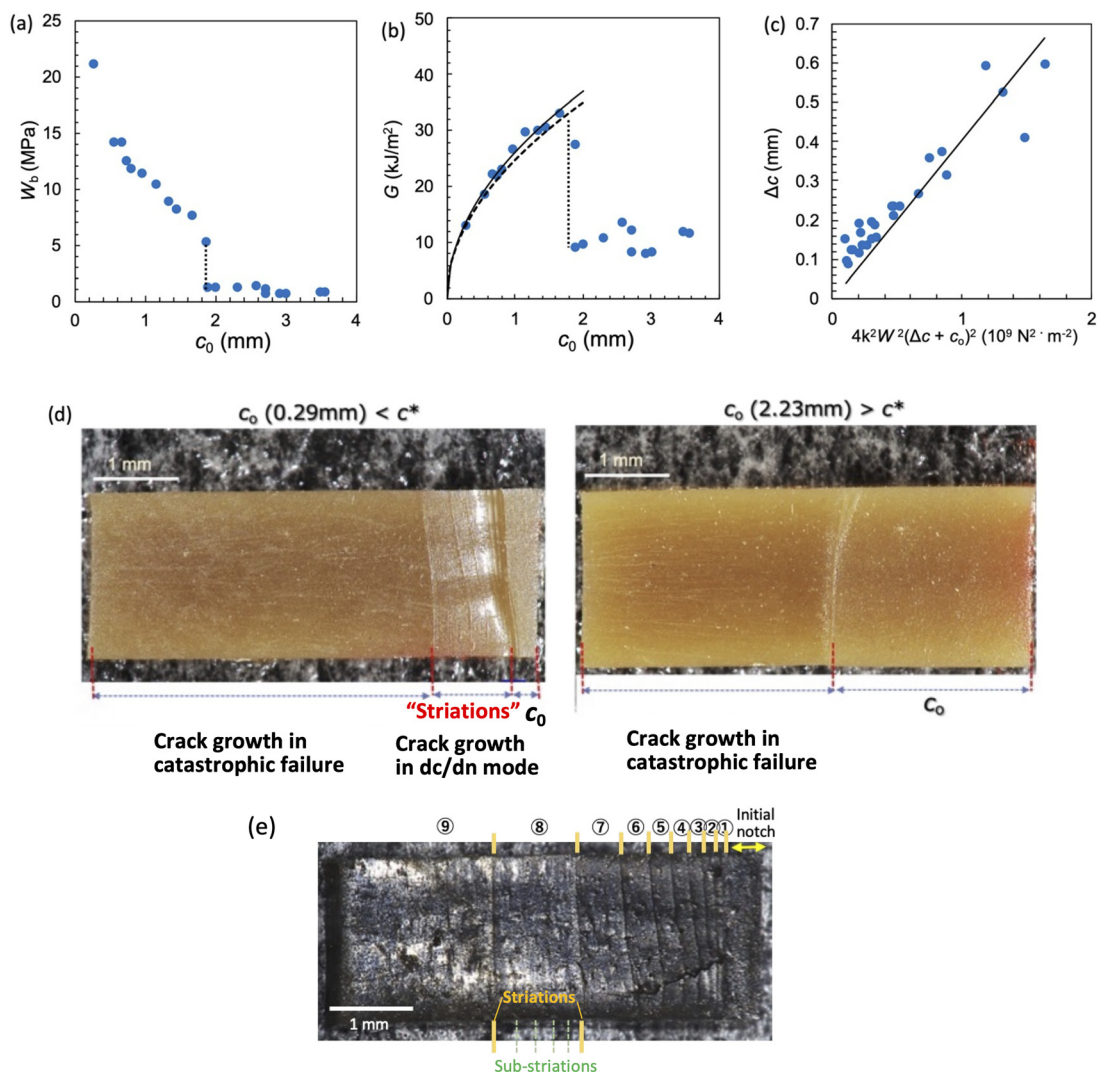


constancy of  $G$  also validates the applicability of eqn (2) in the calculation of  $G$  for the specimens of  $c_0 \leq 3.55$  mm in this experiment.

### SIC rubber in the edge-crack test

Fig. 3a shows the plots of  $W_b$  versus  $c_0$  for a SIC rubber, NR-B, at 25 °C and a strain rate of 0.11 s<sup>-1</sup> in the edge-crack test.  $W_b$  decreased with increasing  $c_0$  but with an abrupt drop at a characteristic  $c_0$  value of  $c_0^* \approx 1.8$  mm, in contrast to the continuous change in a non-SIC rubber (Fig. 2a). The force-displacement data used for the evaluation of  $W_b$  at each  $c_0$  for

NR-B are shown in the ESI.† The  $W_b$ - $c_0$  relationship was qualitatively similar to the observations for NR in earlier studies<sup>36,46-48</sup> and that shown in Fig. 1a. The  $c_0$  dependence of  $G$ , calculated from the  $W_b$  data and eqn (2), shown in Fig. 3b indicates that  $G$  increases with increasing  $c_0$  at  $c_0 < c_0^*$ , whereas  $G$  exhibits a discontinuous change at  $c_0^*$  and tends to become constant at a high  $c_0$ , which agrees qualitatively with Fig. 1b. Importantly, the data at  $c_0 < c_0^*$  obey eqn (8), *i.e.*,  $G = (c_0/B)^{1/2}/2$ , as indicated by the solid line in the figure which is obtained using  $B$  as an adjustable parameter ( $B = 3.65 \times 10^{-13}$  N<sup>-2</sup> m<sup>3</sup>). The dashed solid line depicts the result of eqn (8) using the  $B$  value ( $B = 4.06 \times 10^{-13}$  N<sup>-2</sup> m<sup>3</sup>) which is separately evaluated



**Fig. 3** (a) Strain energy density at break ( $W_b$ ) as a function of the initial notch length ( $c_0$ ) for NR-B at 25 °C and a strain rate of 0.11 s<sup>-1</sup> in the edge-crack test. (b) The  $c_0$  dependence of tearing energy ( $G$ ) calculated using the data in (a) with eqn (2). The dashed line indicates the position of  $c_0^*$  at which an abrupt change occurs. The solid line represents the fitted curve of eqn (8) to the data using  $B = 3.65 \times 10^{-13}$  N<sup>-2</sup> m<sup>3</sup>. The dashed solid line depicts the curve of eqn (8) with the  $B$  value ( $4.06 \times 10^{-13}$  N<sup>-2</sup> m<sup>3</sup>) obtained using the cyclic loading test for the same specimen. (c) Increment of crack length ( $\Delta c$ ) as a function of  $4k^2B(c_0 + \Delta c)^2 W^2$  for NR-B in the cyclic loading test. The line indicates the result of the linear regression. The slope corresponds to the  $B$  value ( $4.06 \times 10^{-13}$  N<sup>-2</sup> m<sup>3</sup>). (d) Fracture surfaces for NR-B of  $c_0 = 0.29$  mm (<  $c_0^*$ ) and  $c_0 = 2.23$  mm (>  $c_0^*$ ). For  $c_0 = 0.29$  mm, the fine striation lines characteristic of the crack growth via the  $dc/dn$  mode are observed. The zone " $c_0$ " indicates the initial notch area. (e) Fracture surfaces including the striations for NR-B in the cyclic loading test.



from the cyclic loading test for the same NR-B specimen at 25 °C: the  $B$  value is obtained using eqn (6) from the slope of the linear regression in the plots of  $\Delta c$  versus  $4k^2(c_0 + \Delta c)^2 W^2$  (Fig. 3c). The  $B$  value obtained by the cyclic loading test satisfactorily agrees with the  $B$  value fitted to the  $G$ - $c_0$  data, indicating without ambiguity that the fracture at  $c_0 < c_0^*$  proceeds similarly to the crack growth under cyclic loading.

The different rupture modes at  $c_0 > c_0^*$  and  $c_0 < c_0^*$  are also appreciable when comparing the fracture surfaces of the corresponding specimens, as shown in Fig. 3d. The fracture surface of the edge-crack specimen with  $c_0 = 0.29$  mm ( $< c_0^*$ ) has characteristic marks (fine striation lines) that show the positions of the crack tip during the incremental growth of a crack. Similar striations are observed in the failure surfaces of NR in the cyclic fatigue tests,<sup>19,20</sup> and Fig. 3e shows the striations accompanied by the sub-striations in the failure surface of NR-B in the cyclic loading tests. As the corresponding features are not observed in the non-SIC rubbers, they are attributed to SIC.<sup>19,20</sup> The fracture surface of the edge-crack specimen of  $c_0 = 2.23$  mm ( $> c_0^*$ ) has no indication of striation (Fig. 3d). The fracture surface including the striations at  $c_0 < c_0^*$  in the edge-crack tests indicates that SIC postpones the catastrophic crack growth.

The successful fit of eqn (8) to the  $G$ - $c_0$  data using the  $B$  value obtained by the cyclic loading test (Fig. 3b) and the striation characteristic of the cyclic crack growth (Fig. 3d) validate the theoretical interpretation of the data described in the previous section. The considerably different  $G$ - $c_0$  relationships beyond and above  $c_0^*$  are attributed to a transition of the rupture mode. The rupture at  $c_0 > c_0^*$  without significant SIC near the crack tip is governed by the ordinary tear mode. At  $c_0 < c_0^*$ , the crack grows through a sufficiently large crystalline region, and the corresponding fracture proceeds similarly to the crack growth under cyclic loading, characterized by eqn (8). The maximum  $G$  value at  $c_0^*$  in Fig. 3b is considered a measure of the tearing energy enhanced by SIC ( $G_{\text{SIC}}$ ). The quasi-plateau  $G$  value at  $c_0 > c_0^*$  is regarded as a critical tearing energy for the onset of catastrophic crack growth without the SIC effect ( $G_{\text{T}}$ ). In Fig. 3b, the  $G_{\text{SIC}}$  is evaluated to be 33 kJ m<sup>-2</sup>, while the  $G_{\text{T}}$  is estimated to be 10 kJ m<sup>-2</sup> from the average of the data at  $c_0 > c_0^*$ .

### Effect of ambient temperature $T$

Fig. 4a and 5a show the  $c_0$  dependence of  $W_b$  at various ambient temperatures ( $T$ ) for NR-A and IR-A, respectively. A discontinuous gap in  $W_b$  at  $c_0^*$  is observed at a sufficiently low  $T$ , and  $c_0^*$  decreases with increasing  $T$  for both NR and IR. Importantly, no discontinuous change in  $W_b$  occurs when  $T$  exceeds a characteristic temperature ( $T^*$ ), and the  $T^*$  values for NR and IR are appreciably different and are estimated to be 80 and 60 °C, the highest temperature at which the abrupt change of  $W_b$  is observed. At  $T > T^*$  the SIC kinetics is so slow that SIC cannot occur sufficiently at  $\dot{\epsilon}$  of interest to enhance the tearing energy.

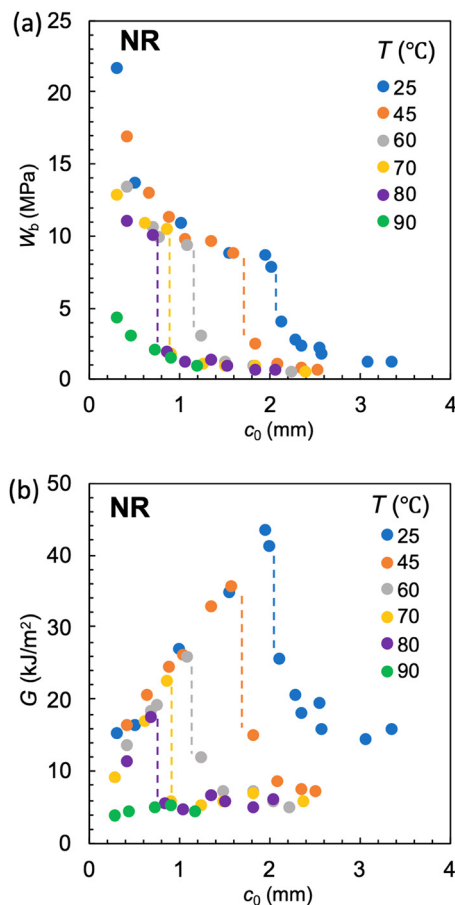


Fig. 4 (a) Strain energy density at break ( $W_b$ ) as a function of the initial notch length ( $c_0$ ) at various ambient temperatures ( $T$ ) for NR-A at a strain rate of 0.5 s<sup>-1</sup>. (b) The  $c_0$  dependence of tearing energy ( $G$ ) calculated using the data in (a) with eqn (2). The dashed lines indicate the position of  $c_0^*$  at which an abrupt change occurs for each  $T$ . No abrupt change is observed at 90 °C.

The  $G$  vs.  $c_0$  plots obtained using eqn (2) and the data in Fig. 4a and 5a are shown in Fig. 4b and 5b, respectively. At  $T < T^*$ , the  $G$  values have the maximum at  $c_0^*$ , allowing the evaluation of the  $G_{\text{SIC}}$  at each  $T$ .  $G_{\text{SIC}}$  tends to decrease with increasing  $T$  in both NR and IR. At  $T > T^*$ , only  $G_{\text{T}}$  is obtained, reflecting the absence of an appreciable SIC effect. In contrast to  $G_{\text{SIC}}$ ,  $G_{\text{T}}$  is almost independent of  $T$  at  $T \geq 45$  °C. Thus, this method reveals the upper limit temperature ( $T^*$ ), beyond which the effect of SIC on tearing energy vanishes, and the  $T$ -dependence of  $G_{\text{SIC}}$ . The  $G$  data in the vicinity of  $c_0^*$  at  $c_0 > c_0^*$  in  $T < T^*$  tend to be larger than the  $G_{\text{T}}$  value obtained at a high  $c_0$ . This tendency implies that a subtle degree of the SIC effect may exist at  $c_0$  slightly beyond  $c_0^*$  although most of the effect vanishes when  $c_0$  exceeds  $c_0^*$ .

Fig. 6 shows the plots of  $G_{\text{SIC}}$  and  $G_{\text{T}}$  obtained in Fig. 4b and 5b against  $T$  for NR-A and IR-A. The  $G_{\text{T}}$  values are nearly insensitive to  $T$ , except for the data at 25 °C, and there is no appreciable difference between these two rubbers. In contrast, for each rubber, the  $G_{\text{SIC}}$  value at a given  $T$  is several times larger than  $G_{\text{T}}$ , whereas  $G_{\text{SIC}}$  decreases with increasing  $T$ . These



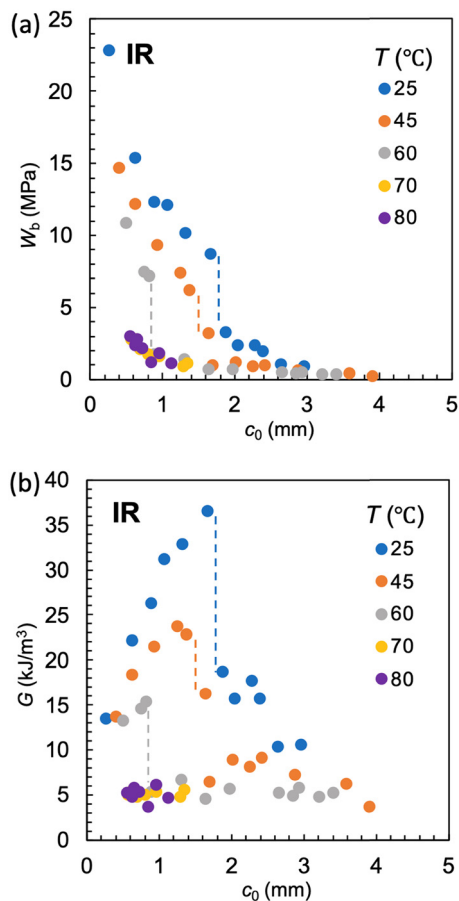


Fig. 5 (a) Strain energy density at break ( $W_b$ ) as a function of the initial notch length ( $c_0$ ) at various ambient temperatures ( $T$ ) for IR-A at a strain rate of  $0.5 \text{ s}^{-1}$ . (b) The  $c_0$  dependence of tearing energy ( $G$ ) calculated using the data in (a) with eqn (2). The dashed lines indicate the position of  $c_0^*$  at which an abrupt change occurs for each  $T$ . No abrupt change is observed at  $T \geq 70 \text{ }^\circ\text{C}$ .

results indicate that  $G$  is significantly enhanced by hardening *via* SIC near the crack tip, whereas this reinforcement effect

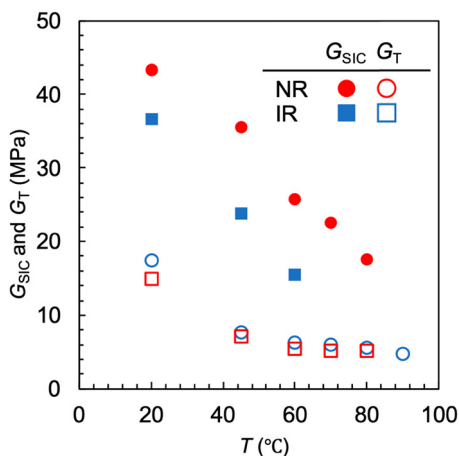


Fig. 6 Temperature dependence of the tearing energy *via* the SIC-reinforcement effect ( $G_{\text{SIC}}$ ) and the tearing energy in catastrophic failure ( $G_{\text{T}}$ ) for NR-A and IR-A. The SIC-reinforcement effect vanishes at  $T > 80 \text{ }^\circ\text{C}$  and  $T > 60 \text{ }^\circ\text{C}$  for NR-A and IR-A, respectively.

decreases with a decreasing crystallinity index. Notably, these two rubbers are considerably different in  $T^*$  and  $G_{\text{SIC}}$ ;  $T^*$  for NR-A ( $80 \text{ }^\circ\text{C}$ ) is approximately  $20 \text{ }^\circ\text{C}$  higher than that for IR-A ( $60 \text{ }^\circ\text{C}$ ), indicating that the reinforcement effect in NR emerges in a broader temperature range. Furthermore, the  $G_{\text{SIC}}$  value for NR at each  $T$  is significantly larger than that for IR.

The effects of  $T$  on SIC are separately investigated using WAXS experiments using unnotched bulk NR-A and IR-A specimens. Fig. 7a and b show the peak area of the crystal (200) diffraction ( $I_{200}$ ) as a function of tensile strain at various  $T$  values. The evolution of  $I_{200}$  beyond the threshold strain reflects a continuous increase in the crystallinity index *via* SIC. The SIC onset strain ( $\varepsilon_{\text{SIC}}$ ) was estimated from the onset of the evolution of  $I_{200}$ . For both rubbers, as  $T$  increases,  $\varepsilon_{\text{SIC}}$  increases, and  $I_{200}$  decreases when compared at a given strain. At a sufficiently high  $T$ ,  $I_{200}$  remains zero over the entire strain range, indicating no occurrence of SIC; SIC can no longer be observed even at a high strain at  $110$  and  $80 \text{ }^\circ\text{C}$  for NR-A and IR-A, respectively, which explains no occurrence of significant SIC at the crack tip in the edge-crack specimens at  $T > T^*$ .

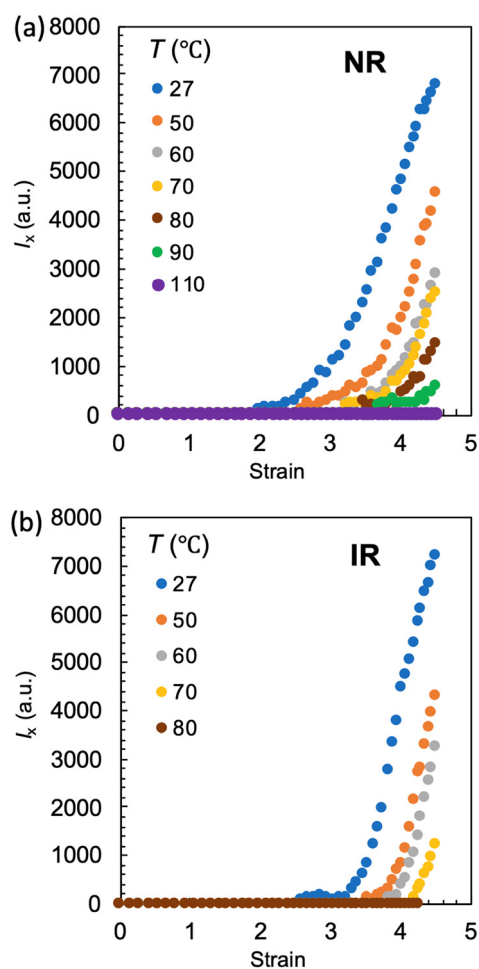


Fig. 7 Scattering intensity of the (200) diffraction of the SIC crystal as a function of the imposed tensile strain for (a) NR-A and (b) IR-A at various ambient temperatures.



The upper-limit temperature for SIC ( $T_{\text{WAXS}}^*$ ), the highest temperature for the finite evolution of  $I_{200}$ , is evaluated to be 90 and 70 °C for NR-A and IR-A, respectively. The  $T_{\text{WAXS}}^*$  for NR-A is approximately 20 °C higher than that for IR-A, which is comparable to the difference in  $T^*$  (Fig. 6). This agreement validates the evaluation of  $T^*$  as the upper-limit ambient temperature in edge-crack tests. For each rubber,  $T^*$  is slightly lower than  $T_{\text{WAXS}}^*$ , probably because of the finite difference in the magnitudes of the effective strain and strain rate in the two measurements; the local strain and strain rate around the crack tip are higher than those in the tensile test of the unnotched bulk specimens. In addition,  $T_{\text{WAXS}}^*$  detects the threshold of SIC at the molecular level, while  $T^*$  reflects the threshold of the SIC effect on macroscopic tearing energy. The emergence of the SIC effect on bulk mechanical properties requires a finite degree of crystallization. This also explains the relationship of  $T_{\text{WAXS}}^* > T^*$  for each rubber.

In each rubber,  $I_{200}$  decreases with increasing  $T$  when compared at the same strain, indicating that the crystallinity index at a given strain decreases as  $T$  increases. This result explains why the  $G_{\text{SIC}}$  decreases with increasing  $T$  for each rubber (Fig. 6).

The effects of  $T$  on the SIC for NR and IR have been studied using in-situ WAXS experiments, mainly in the sustained state with a constant strain beyond  $\epsilon_{\text{SIC}}$  or by analyzing the stress-strain relationships.<sup>23–29</sup> The reported values of the melting temperature of the SIC crystal ( $T_f$ ) of IR range from 60 to more than 100 °C depending on the magnitude of the imposed constant strain. The  $T_{\text{WAXS}}^*$  value (70 °C) for IR-A falls within the range of the reported values.

### Effect of strain rate $\dot{\epsilon}$

Fig. 8a and 9a show the  $c_0$  dependence of  $W_b$  on NR-A and IR-A at various strain rates ( $\dot{\epsilon}$ ). The ambient temperature is 25 °C. The  $G$ - $c_0$  relationships calculated from these data are shown in Fig. 8b and 9b. For NR and IR, the effects of  $\dot{\epsilon}$  on the  $W_b$ - $c_0$  and  $G$ - $c_0$  relationships are similar to those of  $T$  (Fig. 4 and 5). A discontinuous gap in  $W_b$  and  $G$  at  $c_0^*$  is observed at a sufficiently low  $\dot{\epsilon}$ , and the  $c_0^*$  value decreases with increasing  $\dot{\epsilon}$ . The discontinuous feature vanishes when  $\dot{\epsilon}$  exceeds the threshold value  $\dot{\epsilon}^*$ . We regard the maximum  $G$  value at  $c_0^*$  as the  $G_{\text{SIC}}$  at each  $\dot{\epsilon}$ , and the average of the quasi-plateau values at  $c_0 > c_0^*$  as the  $G_T$ .

Fig. 10 shows the plots of  $G_{\text{SIC}}$  and  $G_T$  against  $\dot{\epsilon}$  for NR-A and IR-A. An appreciable reinforcement of SIC on tearing energy ( $G_{\text{SIC}} > G_T$ ) is observed at  $\dot{\epsilon} < \dot{\epsilon}^*$ , while it vanishes at  $\dot{\epsilon} > \dot{\epsilon}^*$ . At  $\dot{\epsilon} > \dot{\epsilon}^*$ , the imposed strain rate is so high that the matrix around the crack tip cannot have enough time to undergo a sufficient degree of SIC, resulting in a catastrophic fracture governed by the  $G_T$ . As this result originates from the competition between the SIC and strain rate,  $\dot{\epsilon}^*$  depends on  $T$  of interest. For convenience, we regard the  $\dot{\epsilon}^*$  from the highest  $\dot{\epsilon}$  value at which finite discontinuity is observed in the  $G$ - $c_0$  relationship because the data as a function of  $\dot{\epsilon}$  are discrete. Notably, the  $\dot{\epsilon}^*$  value for NR-A (50 s<sup>-1</sup>) is considerably higher than that for IR-A (0.5 s<sup>-1</sup>). There exists some uncertainty in the  $\dot{\epsilon}^*$  value for IR-A

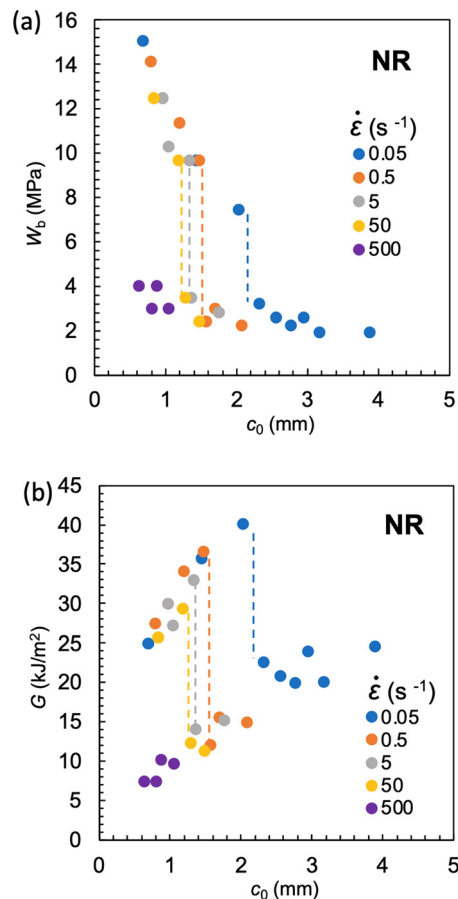


Fig. 8 (a) Strain energy density at break ( $W_b$ ) as a function of the initial notch length ( $c_0$ ) at various strain rates ( $\dot{\epsilon}$ ) for NR-A at 25 °C. (b) The  $c_0$  dependence of tearing energy ( $G$ ) calculated using the data in (a) with eqn (2). The dashed lines indicate the position of  $c_0^*$  at which an abrupt change occurs for each  $\dot{\epsilon}$ . No abrupt change is observed at 500 s<sup>-1</sup>.

because of the ambiguity of the discontinuous feature in the data at 5 s<sup>-1</sup>: Finite discontinuity is appreciable in  $W_b$  (Fig. 9a) but not in  $G$  (Fig. 9b). The  $\dot{\epsilon}^*$  value for IR-A may be slightly higher than 0.5 s<sup>-1</sup>. Nevertheless, we can conclude safely that  $\dot{\epsilon}^*$  for NR-A is at least one order of magnitude higher than that for IR-A because of a definite difference in the discontinuity in the data at 50 s<sup>-1</sup> between them. In addition, the  $G_{\text{SIC}}$  for NR-A is larger than that for IR-A when compared at the same  $\dot{\epsilon}$ . As in the case of the  $T$  effect (Fig. 6), the finite superiority of NR relative to IR in reinforcing ability *via* SIC is appreciable in the effect of  $\dot{\epsilon}$ .

Several researchers have studied the effect of  $\dot{\epsilon}$  on SIC for NR or IR using *in situ* WAXS experiments.<sup>31–35</sup> Recently, Kitamura *et al.*<sup>35</sup> showed that the times required for the occurrence of finite SIC in NR and IR were comparable and less than 0.01 s. Candau *et al.*<sup>34</sup> also reported that the finite superiority of NR relative to IR in SIC ability (observed at slow strain rates) disappeared at high strain rates. According to their results, the occurrence of finite SIC and the disappearance of the difference in the reinforcement effect between NR and IR are expected at high strain rates of more than 100 s<sup>-1</sup>. However, the  $\dot{\epsilon}^*$  values (50 s<sup>-1</sup> for NR-A and 0.5 s<sup>-1</sup> for IR-A) in the edge-crack



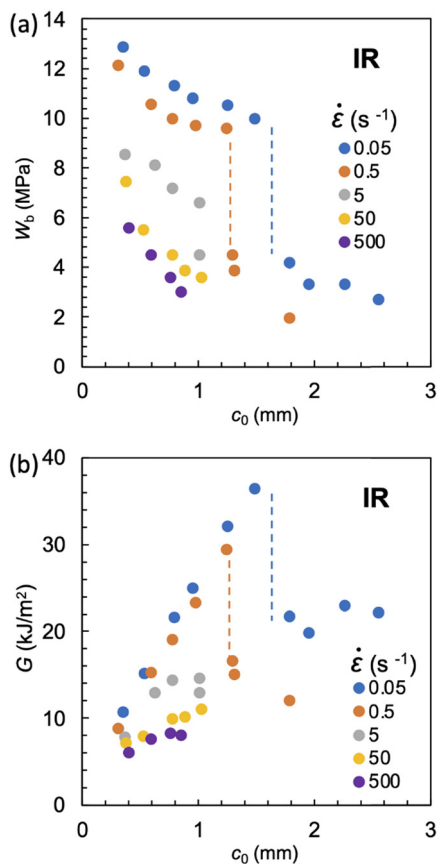


Fig. 9 (a) Strain energy density at break ( $W_b$ ) as a function of the initial notch length ( $c_0$ ) at various strain rates ( $\dot{\epsilon}$ ) for IR-A at 25 °C. (b) The  $c_0$  dependence of tearing energy ( $G$ ) calculated using the data in (a) with eqn (2). The dashed lines indicate the position of  $c_0^*$  at which an abrupt change occurs for each  $\dot{\epsilon}$ . No abrupt change is observed at  $\dot{\epsilon} > 5 \text{ s}^{-1}$ .

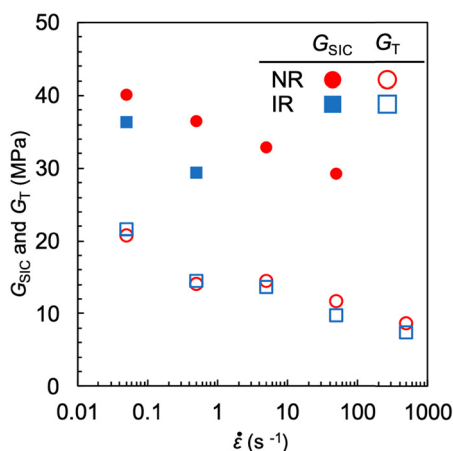


Fig. 10 Strain rate dependence of the tearing energy *via* the SIC-reinforcement effect ( $G_{\text{SIC}}$ ) and the tearing energy in catastrophic failure ( $G_{\text{T}}$ ) for NR-A and IR-A. The SIC-reinforcement effect vanishes at  $\dot{\epsilon} > 50 \text{ s}^{-1}$  and  $\dot{\epsilon} > 0.5 \text{ s}^{-1}$  for NR-A and IR-A, respectively.

tests are appreciably lower than this expectation, and they were considerably different between NR-A and IR-A. These discrepancies

indicate that the threshold for the emergence of the SIC effect on the macroscopic mechanical strength (reflected in the edge crack tests) is different from the onset of SIC at the molecular level (detected by WAXS): the onset of the finite mechanical reinforcement effect requires a significant degree of crystallization. It should also be noted that the magnitudes of local strain and strain-rate near the crack tip are considerably larger than those in the unnotched bulk materials used in the WAXS measurements, when compared at the same degree of imposed macroscopic strain.

## Summary

The present study demonstrates the availability of edge-crack tests to quantify the enhancement effect of SIC on tearing energy and its upper limits of  $T$  and  $\dot{\epsilon}$  for the emergence. In the edge-crack tests using the initial notch length ( $c_0$ ) as a variable, the pre-notched SIC rubber specimens exhibit a discontinuous change in the strain energy density at break ( $W_b$ ) at a characteristic  $c_0$  value ( $c_0^*$ ), as a result of the transition in the rupture mechanism between the ordinary tear mode, simply governed by  $G_{\text{T}}$  at  $c_0 > c_0^*$ , and the cyclic growth mode *via* a significant degree of SIC near the crack tip at  $c_0 < c_0^*$ . We validated the fracture *via* cyclic growth mode at  $c_0 < c_0^*$  by confirming the distinctive relationship  $G = (c_0/B)^{1/2}/2$ , with the  $B$  value separately obtained using the cyclic loading test, and by observing the characteristic striations on the fracture surface.

The maximum  $G$  value at  $c_0^*$ , calculated from the  $W_b$ - $c_0$  data by extending Thomas' theory, is regarded as a measure of the tearing energy enhanced by SIC ( $G_{\text{SIC}}$ ). The magnitude of the  $G_{\text{SIC}}$  is several times larger than that of the  $G_{\text{T}}$ , reflecting that the crack propagates through the matrix hardened by crystallization. The  $G_{\text{SIC}}$  values decrease with increasing  $T$  and  $\dot{\epsilon}$  due to a reduction in the crystallinity index. The upper limits of  $T$  and  $\dot{\epsilon}$  for the finite reinforcement effect *via* SIC ( $T^*$  and  $\dot{\epsilon}^*$ , respectively) are evaluated from the vanishing points of the transition feature.

NR exhibits a higher magnitude of  $G_{\text{SIC}}$  at a given  $T$  or  $\dot{\epsilon}$  than IR, whereas these rubbers show no appreciable difference in  $G_{\text{T}}$ . NR has an approximately 20 °C higher value of  $T^*$  and at least one order of magnitude larger value of  $\dot{\epsilon}^*$  than IR. The WAXS measurements confirm a reduction in the crystallinity index with increasing  $T$  and an approximately 20 °C higher upper-limit temperature for the occurrence of SIC in NR. Comparisons using the  $G_{\text{SIC}}$ ,  $T^*$ , and  $\dot{\epsilon}^*$  values reveal that NR is obviously superior to IR in the mechanical reinforcement effect *via* SIC.

## Conflicts of interest

There are no conflicts to declare.

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