RESEARCH ARTICLE

Effect of Stretching Rate on Tensile Response and Crystallization Behavior of Crosslinked Natural Rubber

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Abstract The performance of natural rubber (NR) relies heavily on the microstructural changes during deformation. This has brought to significant change in the stress response of NR. Besides, the stretching rate may also affect the stress response of NR. In this study, effects of stretching rate on tensile deformation and strain-induced crystallization of crosslinked NR were investigated. Results indicated that increasing the strain rate has increased the stress at given strain where the onset of strain-induced crystallization was shifted to a lower strain. The crystallinity of the crosslinked NR was shown to be higher at a high stretching rate and it corresponded well with the tensile response. The results clearly confirm that chain orientation and crystallization became stronger with increasing deformation rate. The study also suggests that the deformation could improve distribution of crosslinked network structures.

Keywords: Deformation Rate, Tensile Response, Crystallization, Natural Rubber

Introduction

The mechanical performance of rubber materials is normally monitored by various techniques depending on the designed experimental. One of the parameters that frequently set is the strain rate or deformation rate during the testing. This parameter may affect the final result especially in the case of NR. This is because of the different in the ability of rubber to generate crystallization [1-3]. Various techniques have been applied to investigate the effects of strain rate, including dynamic compressive testing [4], tensile impact testing [2], and uniaxial compression testing [5]. The results have usually shown that increasing the stretching rate increases modulus and tensile strength, but maximal elongation decreases.

Uniaxial tensile testing in the vertical direction is the most common and extensively used technique for investigating the mechanical properties of rubbers. This is because the tensile test does not only provide useful information about the ultimate strength and extensibility, but also the modulus across a range of

strains. Moreover, it has been recognized that the results from tensile tests correlate with other physical properties like abrasion resistance, tear resistance, and flex-cracking resistance [6]. Various studies have reported on the influences of strain rate on the mechanical properties and deformation-induced crystallization manner of rubber. Mott et al., [7] measured the mechanical responses of elastomers at different strain rates in horizontal direction. They found that the stress at a given strain and the tensile strength increased with strain rate, but the maximal elongation was independent of rate. Hussein [8] and Cheng and Cheng [9] also reported that stress hardening increases with stretching rate in the blend of Butyl rubber (IIR)/ high molecular weight polyethylene (PE) and ethylene-propylene-diene terpolymer (EPDM), respectively. Miyamoto et al., [10] investigated crystallization and melting of polyisoprene rubber under uniaxial deformation and found that the hardening of rubber progressively decreased with strain rate, and Candau et al., [11] investigated the effects of strain rate and temperature on the onset of strain-induced crystallization in NR. They reported that the onset of crystallization happened earlier as strain rates increased, but how the strain rate affected crystallinity was not clearly discussed.

Although several reports have addressed strain rate effects, no consistent conclusions have been drawn. None of the prior studies have paid attention to the relationship between stress response and structural features impacted by the strain rate. This study was designed to assess key structural features for comparison over a range of deformation rates.

To understand the effects of stretching rate on tensile properties and crystallization behavior with variation of stretching, two stretching rates and two types of vulcanized NR samples were selected. The tensile properties were investigated by using a universal tensile testing machine. The crystallization behavior was studied by means of wide angle X-ray diffraction (WAXD), and the other structural changes were assessed from small angle X-ray scattering (SAXS) measurements.

Materials and methods

Materials

NR of STR5L type was purchased from Chalong Concentrated Natural Rubber Latex Industry Co., Ltd., Songkhla, Thailand. Zinc oxide (ZnO) was manufactured by Imperial Chemical Co. Ltd., Pathumthani, Thailand. Stearic acid was supplied by Global Chemical Co. Ltd., Samut Prakarn, Thailand. N-cyclohexyl-benzothiazyl-sulphenamide (CBS) was purchased from Flexsys America L.P., West Virginia, USA, and sulfur was produced by Siam Chemical Co., Ltd., Samut Prakan, Thailand.

Sample preparation

NR compounds containing stearic acid, ZnO, CBS and sulfur were prepared by using a laboratory-size internal mixer. The list of chemicals and mixing steps as well as mixing times are presented in Table 1. The total mixing time was kept constant at 5 min. The obtained compounds were compression-molded at 160 °C following their respective curing times. To determine the effects of stretching rate on deformation response, tensile properties and micro-structural transformations, two compound formulations with different sulfur and accelerator contents were chosen, and are labelled as S/A 2.5/0.5 and S/A 1.0/2.0.

Table 1. Compound formulations used in this study

Ingredient	Quantity (phr)		Mixing time (min)
	S/A 2.5/0.5	S/A 1.0/2.0	
NR	100	100	2
Stearic acid	1	1	
ZnO	3	3	1
S	2.5	1.0	1
CBS	0.5	2.0	1

Tensile properties

The tensile properties of vulcanized NR were tested by using a universal tensile testing machine (LLOYD Instruments, LR5K Plus, UK). The tensile test was carried out at room temperature with two alternative stretching rates, namely 50 mm/min and 500 mm/min. Five replications were performed and the results reported are averages.

Crystallization behavior and structural changes

Strain-induced crystallization behaviors and microstructural transformations, i.e., crack formation in the vulcanized NR samples under tensile stretching, were investigated by means of wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). Both WAXD and SAXS were performed at the Siam Photon Laboratory, Synchrotron Light Research Institute (SLRI), Nakhon-Ratchasima, Thailand. To correlate the microstructural changes with tensile deformation test, the vulcanized NR specimens were simultaneously tested as they were stretched at a given crosshead speed (50 mm/min or 500 mm/min). The 2D-WAXD and 2D-SAXS data were collected and analyzed by using SAXSIT4.41 software.

The percentage of crystallinity (X_c) corresponding to (200) and (120) planes was calculated as follows [12].

$$X_c (\%) = A_c/(A_c + A_a) \times 100 \tag{1}$$

where, A_c is the area of crystalline peaks assigned to the (200) or (120) planes and A_a is the area of the amorphous halo.

The crystallite size was estimated from the Scherrer equation [12,13].

$$L_{hkl} = K_\lambda/\beta \cos \theta \tag{2}$$

where, L_{hkl} refers to the size of a crystallite in the direction perpendicular to the (hkl) plane, K is equal to 0.89, λ is the wavelength, β is the half-width of a peak at half-height, and θ is the Bragg angle of that peak.

Results and discussion

Tensile properties

Figure 1 shows representative of stress-strain curves of the crosslinked NR samples stretched at 50 mm/min and 500 mm/min respectively. The stress in all cases progressively increased over the deformation. This is a typical shape of the stress response obtained from a rubber vulcanizate sample subjected to a uniaxial tensile test [14]. The ultimate stress and the stress at given strain were found to be higher especially at higher strain rate, i.e., 500 mm/min. The vulcanizate samples appeared to become stronger and stiffer with an increased strain rate. These results disagree with previous reports who found that the hardening progressively decreased over the strain rate [10,11]. However, an increasing trend of stress hardening with stretching rate is corroborated by some prior studies [8,9]. This phenomenon may be explained by the fact that when the deformation rate increased, the molecular chain mobility and reorientation were restricted by kinetic constraints, so the chains responded as apparently stiffer material. On the other hand, these molecular chains have sufficient time to re-orient and relax at a lower deformation rate [5]. It was also observe that the elongation at break decreased slightly at higher strain rate. This finding may be different to the case of butyl rubber and high molecular weight polyethylene elastomer blends reported previously [8], they found out that the strain was found to be higher when higher strain rate was applied due to secondary molecular processes [8,15,16]. Different phenomenon found may be attributed to the completely different choices of tested materials. However, the mentioned study agreed well with the works related to the stress-strain behavior of thermoplastics, especially after yielding point but this phenomenon was unusual for rubber like materials.
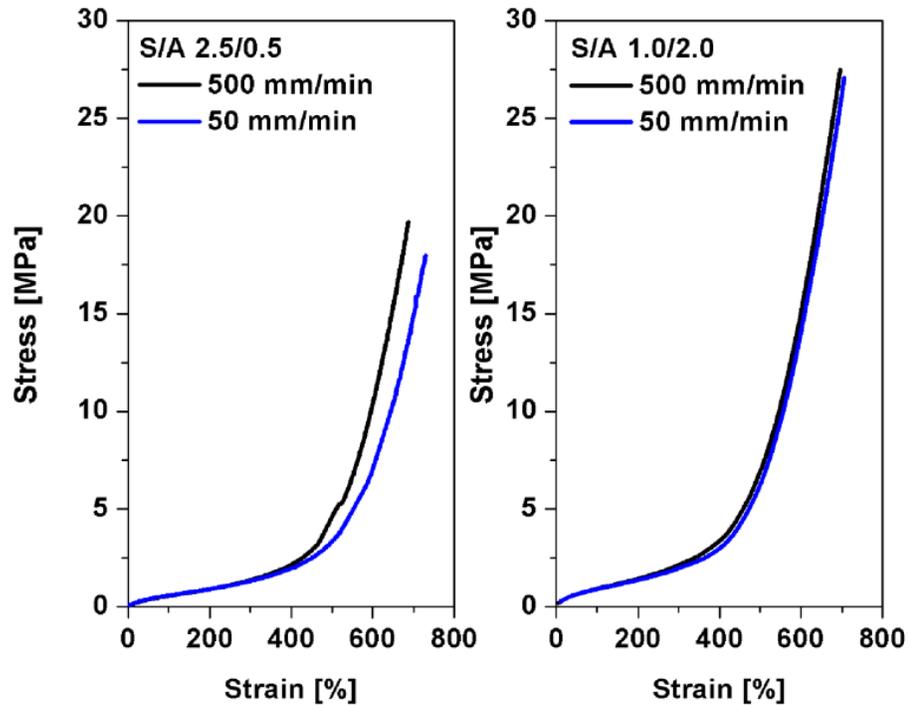
Figure 1. Stress strain curves of two alternative NR samples subjected to different stretching rates.

Crystallization behavior and structural changes

Figure 2 shows typical 2-dimensional (2D) WAXD images of NR samples at various strains and strain rates. In these images, the reflection spots were assigned to various crystallographic planes. Among the most intense reflection spots, the crystallographic planes (200) and (120) are of interest. The WAXD images of all samples with both stretching rates (50 mm/min and 500 mm/min) showed no reflection spots at 0% strain, indicating no initial crystallinity. At over 300% strain, the reflection spots assigned to crystallographic planes (200) and (120) were detected (marked by red circles) confirming strain-induced crystallization. These reflections were more intense at higher strain rate (i.e., 500 mm/min). With further deformation, these reflection spots became clearer as the strain fastened the progress of chain orientation and crystallization [17]. Thus, stronger intensity of the reflections with the higher crystallinity level is expected at larger deformations.

In Figure 3, the patterns showed no crystal peaks at 0% strain unless the amorphous structure. This is simply due to the lack of initial crystallinity. Two diffraction peaks were observed when the deformation over 300% strain. One was located at 2θ of about 14°, corresponding to the (200) plane, while another was at 2θ of about 21° corresponding to the (200) plane [18,19]. These two peaks became more pronounced with further deformation. It is also clearly seen from Figure 3 that the peaks corresponding to (200) and (120) planes were stronger with deformation rate of 500 mm/min than with 50 mm/min. The results clearly confirm that chain orientation and crystallization during stretching increased with deformation rate.
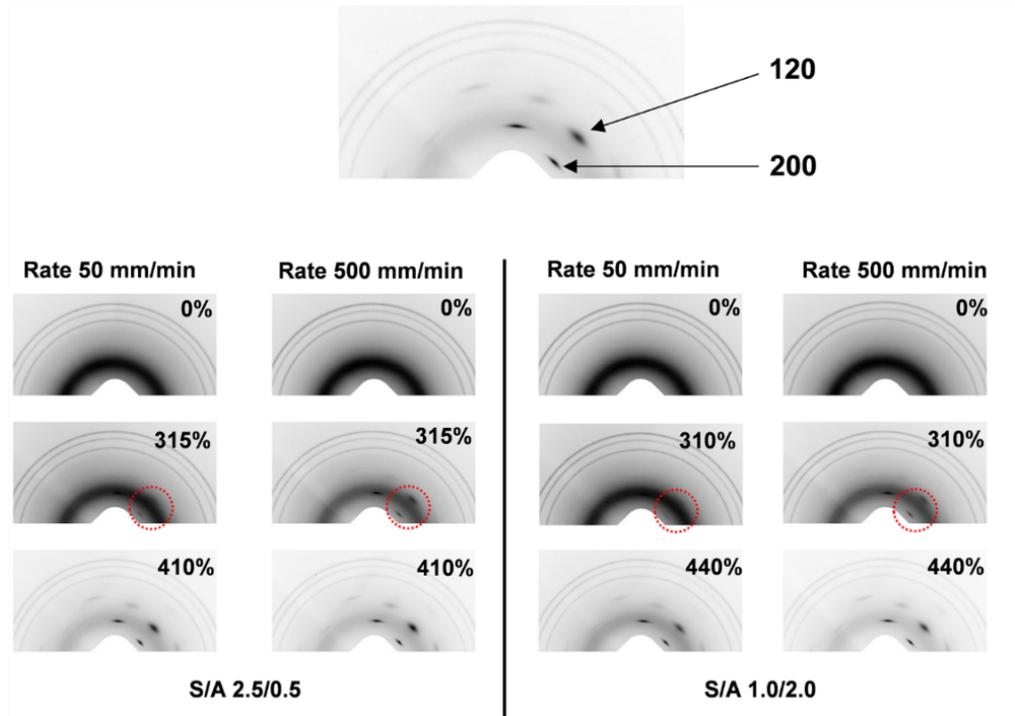
Figure 2. 2D-WAXD images of two alternative NR sample type, stretched at different rates to various strains.
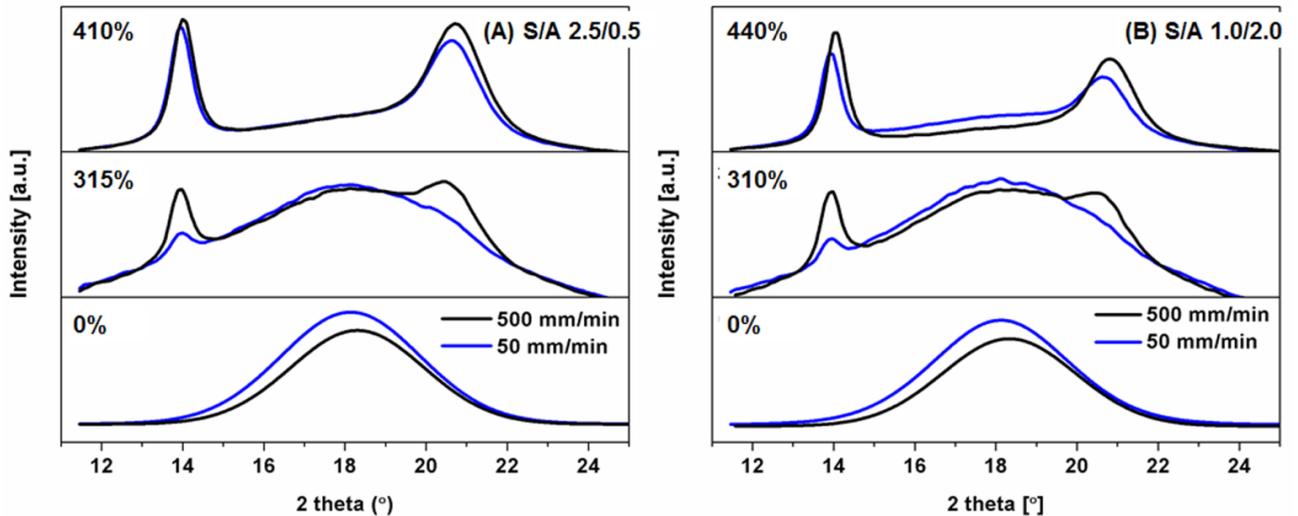

Figure 3. WAXD patterns of two alternative NR samples at different stretching rates, (A) S/A 2.5/0.5 and (B) S/A 1.0/2.0.

Figure 4 shows the degrees of crystallinity corresponding to (200) and (120) planes of two alternative sample types at stretching rates of 50 mm/min and 500 mm/min. For the same type of sample, it is clearly seen that applying the strain rate at 500 mm/min has caused to increase in the degree of crystallinity as compared to that with 50 mm/min, at any given strain (Figures 4 (A) – (D)). Moreover, the strain at which the crystallization appears shifted to a lower strain when the sample was deformed at a higher stretching rate. This implies that strain-induced crystallization became stronger over the strain rate, at least for the two stretching rates tested here. The increase of crystallinity matches well the tensile responses:

increased stress during tensile stretching was (at least partly) due to strain-induced crystallization. Even though the results suggests that orientation of the rubber chains increasing with stretching rate, in some cases strain-induced crystallization can involve unoriented chains from the surrounding amorphous phase [20]. Thus, the details of chain orientation during low and high deformation rates could warrant further investigation, as the mechanisms involved are not simple and straightforward.
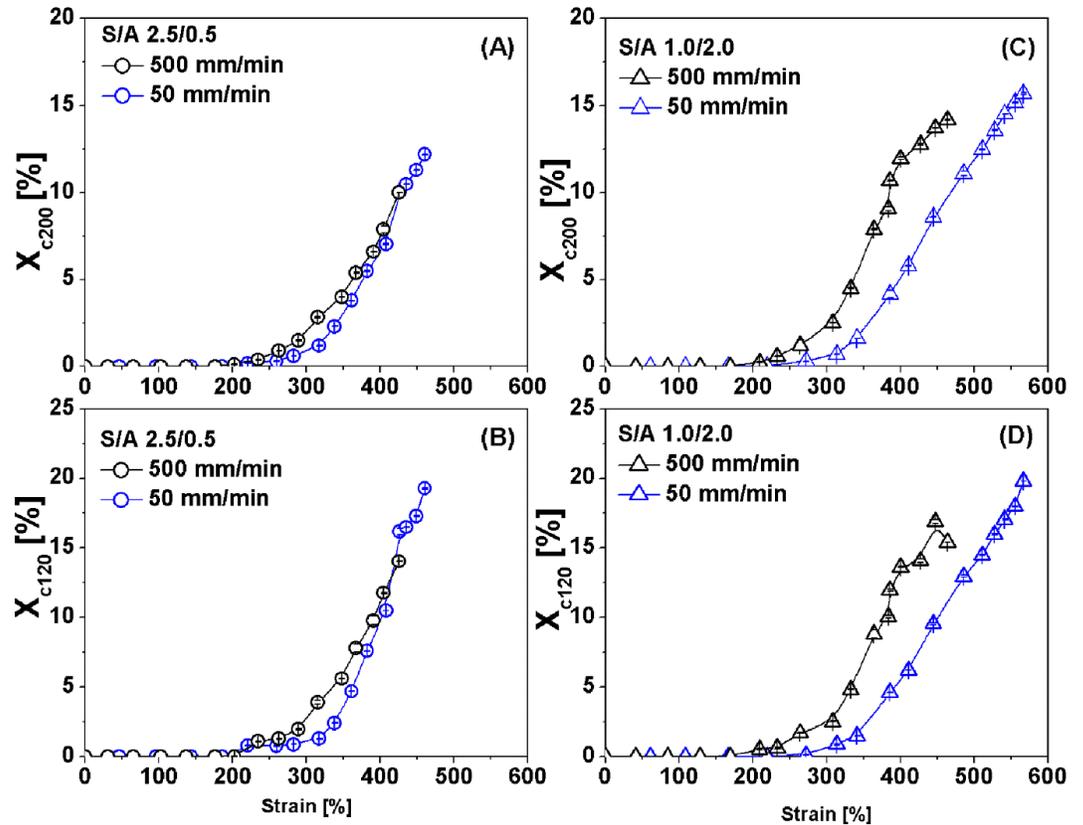

Figure 4. Degrees of crystallinity (Xc) for two alternative sample types at different stretching rates; (A) Xc corresponding to (200) plane of S/A 2.5/0.5, (B) Xc corresponding to (120) plane of S/A 2.5/0.5, (C) Xc corresponding to (200) plane of S/A 1.0/2.0, and (D) Xc corresponding to (120) plane of S/A 1.0/2.0.

Figure 5 shows variations in crystallite size corresponding to (200) and (120) planes of NR samples with strain, assigned to L200 and L120, respectively. The L200 was found to be more sensitive to the deformation than the L120. This is consistent with a previous report [20]. The L200 of both samples tended to decrease slightly with strain at both stretching rates, indicating decreasing mean distance between the stretched chains acting as crystallite precursors [21]. It is also seen that the crystallite size with high deformation rate was slightly smaller than with low stretching rate, for both types of samples. This may have been caused by the higher degree of crystallinity with higher stretching rate, as previously indicated by Figure 4. To further understand the changes of crosslinked network structures, in relation to strain and deformation rate, SAXS was performed.

Figure 6 displays representative plots of intensity I(q) as a function of the scattering vector, q for S/A 2.5/0.5 at the two deformation rates. The q can be defined as $(4\pi/\lambda) \sin \theta$, where λ and 2θ are the wavelength and scattering angle. It should be mentioned that SAXS for S/A 1.0/2.0 had similar trend as for the other sample type, S/A 2.5/0.5. It can be seen from Figure 6 that the intensity gradually decreased with strain at both deformation rates, implying that the changes of network structure during stretching were almost similar. This is because the stretching only reoriented scattering bodies [22], namely

crosslinked network structures. Reduction of SAXS intensity can be also correlated to heterogeneous distribution of the scattering bodies [23]. The network structures in the crosslinked NR was more homogeneously distributed with stretching.
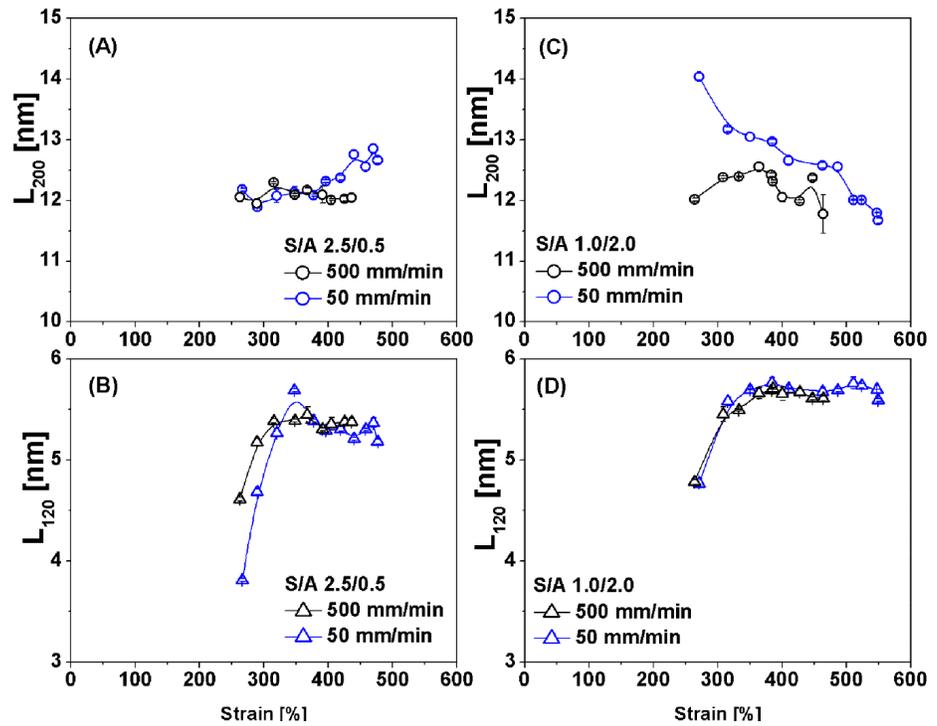

Figure 5. Crystalline sizes of (200) and (120) planes for sample types S/A 2.5/0.5 (A and B), and S/A 1.0/2.0 (C and D) when stretched at 50 and 500 mm/min.
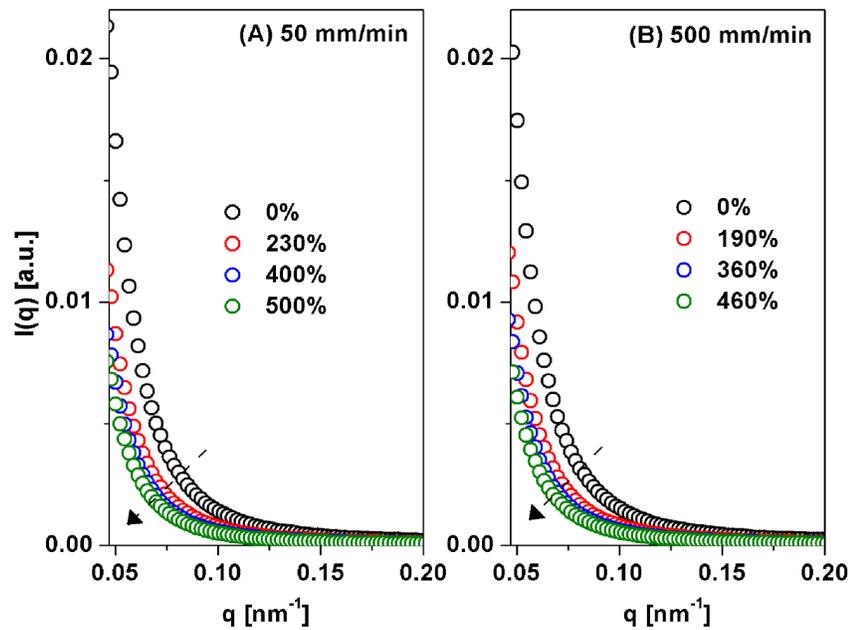

Figure 6. Representative plots of intensity versus strain for S/A 2.5/0.5 sample at the two deformation rates (A) 50 mm/min and (B) 500 mm/min.

Conclusions

Influences of stretching rate, tested at 50 mm/min and 500 mm/min, on tensile response and structural features of crosslinked NR were investigated. Two types of samples were tested to confirm the effects of deformation rate on property changes. The results showed that a high deformation rate increased the stress level at a given strain, gave earlier onset of strain-induced crystallization, and increased chain orientation and crystallinity as compared to a low stretching rate. Stretching facilitated homogeneity of the distribution of crosslinks in networks, and the deformation rate only slightly affected observable changes in microstructure.

Conflicts of interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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