Development of safety tire with enhancement of cut growth and abrasion resistances of natural rubber by controlling strain-induced crystallization

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Summary: Include the outline and conclusions of the research

The influence of strain-induced crystallization (SIC) on the cut growth and abrasion resistances of the carbon black (CB)-filled natural rubber (NR) composites were investigated in this research. Here, the variation of crystallinity degrees in the NR/CB composites were controlled by their cross-linking densities. The relative cut tensile strength, referring to the cut growth resistance of the NR/CB composites tended to increase when the crystallinity degree was higher. The greater NR chain orientation and crystallinity degree of the NR/CB composites probably prevented the simple lateral cut growth across the specimen, but the longitudinal vertical cut growth appeared instead. However, the SIC probably the minor factor controlling the abrasion resistance of the NR/CB composites compared to the moduli and hardness of the composites. The higher moduli of the NR/CB composite gave the better abrasion resistance, where the shorter ridge spacing on the abraded surfaces of the NR/CB composites was observed as pieces of evidence. The finding in this research will be fundamental scientific knowledge for developing the safety tire.

Aim of research

To fabricate the safety and long life expentency tire from natural rubber (NR), an enhancement of the cut growth behavior and abrasion behavior of NR will be controlled by the degree of strain-induced crystallization (SIC). The development of the high-performance NR tire with the long life expentency is expected to increase the safety of driving, reduce air pollution and decrease the number of out of use tires, which helps to resolve the environmental problem from the tire.

Method of research & Progression

The sulfur cross-linked NR for both unfilled and carbon black fillled NRs with the variation in sulfur cross-linking recipes as shown in Table 1 were prepared by conventional two-roll mill mixing. The network-chain density of all the samples were investigated (Table 1). The mechanical properties of all the samples, i.e., tensile strength, edge-cut tensile strength, abrasion resistance were investigated. The SIC behaviour of sulfur cross-linked NR with different network chain densities were investigated using synchrotron Wide-Angle X-ray Diffraction during stretching at Synchrotron Light Research Institute (SLRI), Thailand. The cut growth patterns and abrasion patterns for all the samples were examined by optical microscope and field emission scanning electron microscopy (FE-SEM), respectively.

Table 1. Compound formulations and cross-linking density of unfilled NR and CB-filled NR vulcanizates.

Sample codes	Amount (phr)								Swelling degree	Network-chain density ($\times 10^{-4}$mol/cm^3)
	NR	CB	StH	ZnO	6-PPD	WAX	TBBS	S_8		
NR1.0	100	0	2	4	2	2	0.8	0.70	4.79	0.79
NR1.5	100	0	2	4	2	2	1.2	1.05	3.78	1.23
NR2.0	100	0	2	4	2	2	1.6	1.40	3.27	1.58
NR2.5	100	0	2	4	2	2	2.0	1.75	2.93	1.92
NR3.0	100	0	2	4	2	2	2.4	2.10	2.71	2.21
NC1.0	100	30	2	4	2	2	0.8	0.70	3.14	1.06
NC1.5	100	30	2	4	2	2	1.2	1.05	2.54	1.53
NC2.0	100	30	2	4	2	2	1.6	1.40	2.12	2.11
NC2.5	100	30	2	4	2	2	2.0	1.75	1.90	2.53
NC3.0	100	30	2	4	2	2	2.4	2.10	1.81	2.77

Results and discussion

1. Mechanical properties and, cut growth and abrasion behavior of unfilled NR and CB-filled NR vulcanizates

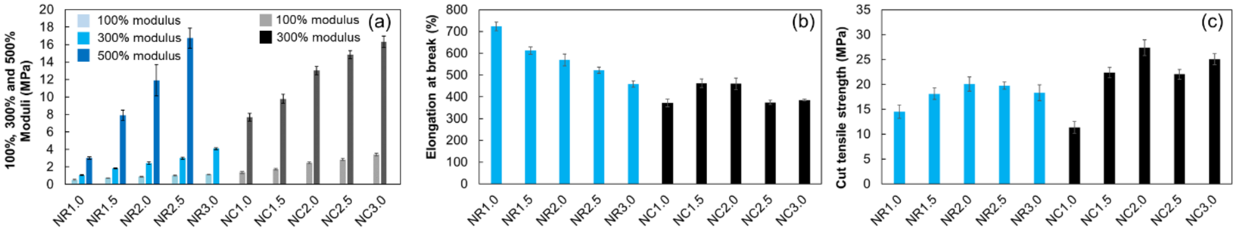


Fig. 1. Tensile properties of the edge-cut tensile specimens of the unfilled NR and CB-filled NR series; (a) 100%, 300%, and 500% moduli, (b) elongation at break, and (c) cut tensile strength. 🟦 and ⬛ represent the unfilled NR series and CB-filled NR series, respectively.

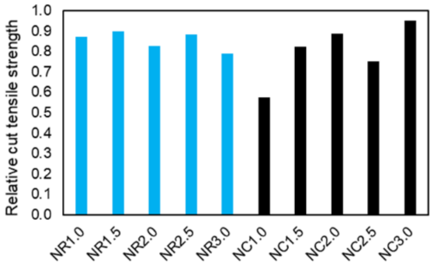
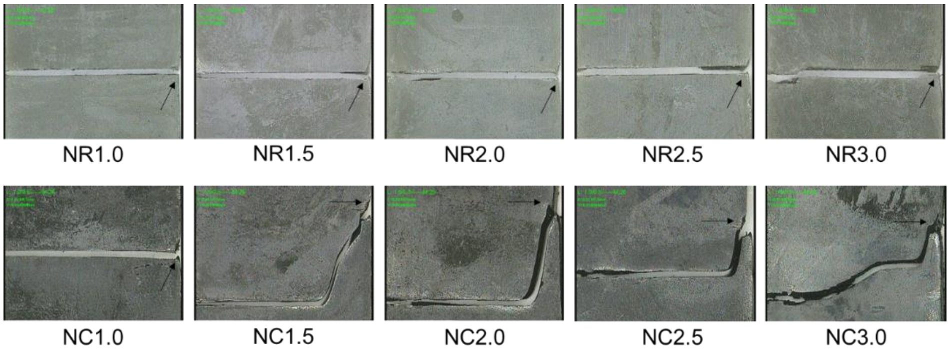


Fig. 2. Relative cut tensile strength of the unfilled NR and CB-filled NR series. 🟦 and ⬛ represent the unfilled NR series and CB-filled NR series, respectively.

Fig. 1 shows the tensile properties, i.e., 100%, 300%, 500% moduli, %elongation at break tensile and cut tensile strength of the unfilled NR and CB-filled NR series. Because of the increasing cross-linking densities, the 100%, 300% and 500% moduli of the unfilled NR and CB-filled NR increased. However, the 500% moduli of the NR3.0 and CB-filled NR series were not observed because those rubber samples became harder and more brittle owing to the higher cross-linking densities. Thus, they were broken before 500% strain. The higher moduli of the unfilled NR led to their shorter elongation at breaks. However, the elongation at break of the CB-filled NR series exhibited the optimum values in the rubber samples containing about 1.5- and 2-times higher amount of curing agents compared to the NR1.0 (Fig. 1(b)). This may be the competitive effects between rubber reinforcement by CB filler and the more brittle rubber with increasing the cross-linking density. As expected, the optimum value of cut tensile strengths for both unfilled NR and CB-filled NR series was observed when their cross-linking densities were varied. The optimum cut tensile strengths of both the unfilled NR and CB-filled NR series were found in NR2.0, i.e., the amount of curing agents are two times higher than those of NR1.0 and NC1.0, respectively. Fig. 2 shows the relative cut tensile strengths of both unfilled NR and CB-filled NR series, where the cut tensile strength of each sample was compared to their normal tensile strengths. This relative cut tensile strength refers to the cut growth resistance of the rubber. The cut growth resistances of the unfilled NR series were not much different when the cross-linking densities increased, while those of CB-filled NR significantly improved when over two times higher amount of curing agents were added, compared to NC1.0. Interestingly, the trend of relative cut tensile strengths of both unfilled NR and CB-filled NR series when the cross-linking densities were varied corresponded to their cut growth patterns after tensile testing as shown in Fig. 3.


NR1.0 NR1.5 NR2.0 NR2.5 NR3.0

NC1.0 NC1.5 NC2.0 NC2.5 NC3.0

Fig. 3. Cut growth patterns of the edge-cut specimens after tensile testing for the unfilled NR (NR series) and CB-filled NR (NC series) at different cross-linking densities. The black arrows indicate the position of an initial cut tip.

The unfilled NR showed only the lateral cut growth pattern (perpendicular to the stretching direction) with increasing the cross-linking densities although a slightly rougher cut growth before rupturing was detected. These results related to the insignificant change of relative cut tensile strength, indicating the comparable cut growth resistances among the unfilled NR samples. Nevertheless, the vertical cut growth near the initial cut tip before rupturing in a simple lateral direction was observed in all the CB-filled NR samples, except the NC1.0. This also agreed well with the much higher relative cut tensile strengths of the NC1.5, NC2.0, NC2.5, and NC3.0 than those of the NC1.0, which exhibited only lateral cut growth patterns. Several researchers have explained that the vertical cut growth is due to the greater orientation of the rubber chains along the stretching direction accelerated by reinforcing CB. This phenomenon prevents the crack from growing simply across the specimen. Additionally, it is well established that the occurrence of longitudinal cracking can reduce the stress concentration at the cut tip with energy dissipation, thus leading to an increase in cut growth resistance. In the case of NR, it is crystallizable during stretching at large deformation, known as the strain-induced crystallization (SIC) phenomenon. The generated crystallites in the NR acting as reinforcing filler are also expected to prevent the lateral cut growth. However, the effect of the orientation of the NR chains or SIC behavior in the unfilled NR and CB-filled NR on the cut growth resistance has been never been examined. Here, the SIC behaviors of both unfilled NR and CB-filled NR investigated using the synchrotron wide-angle X-ray diffraction (WAXD) were considered together with their cut growth properties here for the first time.

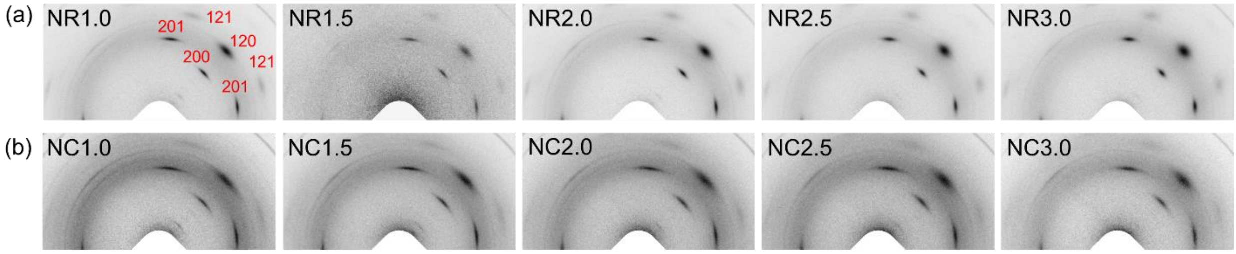


Fig. 4. WAXD images of the unfilled NR series at 700% strain and CB-filled NR series at 400%.

The two-dimensional WAXD patterns of the unfilled NR and CB-filled NR at the 700% and 400% strains were shown in Fig. 4(a) and (b), respectively. Due to the different experimental conditions of WAXD measurement during stretching and tensile testing of the edge-cut tensile specimen, the SIC behaviors and cut growth properties of both unfilled NR and CB-filled NR are comparatively discussed. The WAXD images at the 700% and 400% strains of both unfilled NR and CB-filled NR series clearly showed the spots of the crystalline reflections of NR, i.e., 200, 201, 120, and 121 [(Fig.4(a) and (b)]. These results indicated that the SIC is presented at large deformation for both unfilled NR and CB-filled NR series. Interestingly, the shape of crystalline reflections presented in the CB-filled NR series was longer compared to the unfilled NR series at the same amount of curing agents. This is probably because of the disturbance of the orientation of NR chains by CB filler. However, the change of WAXD images of the both unfilled NR and CB-filled NR series at different cross-linking densities were unclear. Therefore, the quantitative analysis of these WAXD images was conducted and summarized in Fig. 5.

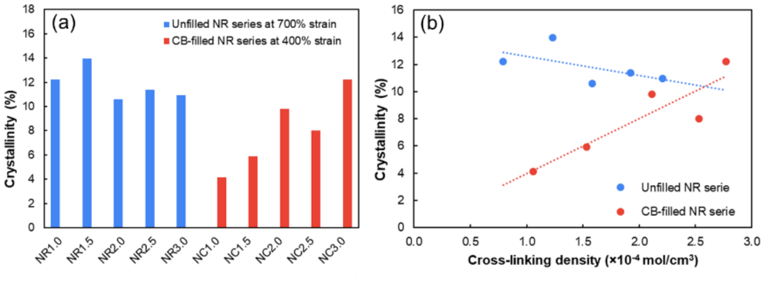


Fig. 5. (a) The crystallinity of the unfilled NR series at 700% strain and CB-filled NR series at 400% strain and (b) the plot of crystallinity of both unfilled NR and CB-filled NR series against their cross-linking densities.

It can be seen that the variation in cross-linking densities provided the different crystallinity degrees in both unfilled NR and CB-filled NR series (Figs. 5(a) and (b)). For unfilled NR samples, the crystallinity tended to decrease with increasing cross-linking densities (Fig. 5(b)). This is because the increased number of cross-linking points restricts the movement of NR rubber chains, resulting in the lower orientation degree of the NR rubber chains and crystallinity, respectively. On the other hand, the crystallinity of the CB-filled NR tended to increase when the cross-linking densities increased. These results suggested that the addition of CB can accelerate the SIC of the NR.

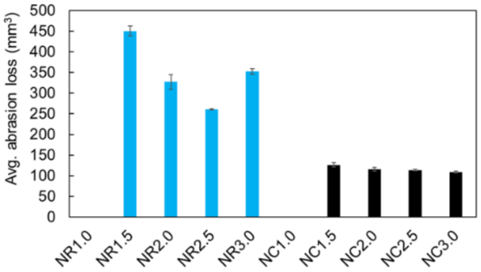


Fig. 6. Average abrasion loss of the unfilled NR and CB-filled NR compounds. 🟦 and ⬛ represent the unfilled NR series and CB-filled NR series, respectively.

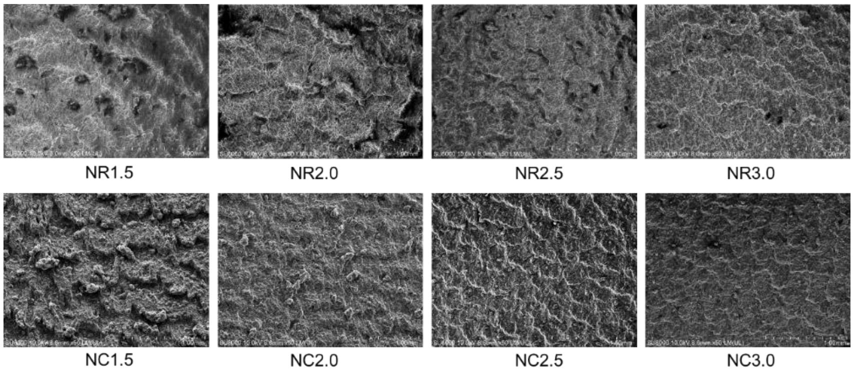


Fig. 7. FE-SEM micrographs of abraded surfaces of the unfilled NR (NR series) and CB-filled NR (NC series) at different cross-linking densities.

Notably, it can be clearly seen that the trend of crystallinity with increasing cross-linking densities as shown in Fig. 5(a) was similar to that of relative cut tensile strength for both unfilled NR and CB-filled NR series in Fig. 2. It can be confirmed that the SIC affects the cut growth resistance of both unfilled NR and CB-filled NR. However, the cut growth resistances of the CB-filled NR tended to be influenced by the SIC more than those of the unfilled NR. The increase of crystallinity in CB-filled NR with increasing cross-linking densities (Fig.5(a)) led to a significant increase in their cut growth resistance (Fig. 2). From those results, it can be said that the greater rubber chain orientation and crystallinity degree in CB-filled NR could prevent the simple cut growth across the specimen, presenting as the longitudinal vertical cut growth before lateral rupturing. Such a vertical cut growth pattern could provide a higher relative cut tensile strength and better cut growth resistance.

Based on the finding in this research, the presence of crystallinity, which can be controlled by cross-linking densities should be greater in order to improve the cut growth resistance of the CB-filled NR for developing the safety tire application. Furthermore, the abrasion behaviors of both unfilled NR and CB-filled NR are investigated. Abrasion resistance of both unfilled NR and CB-filled NR at different cross-linking densities, indicated as abrasion loss is presented in Fig. 6. The rubber sample, exhibiting the lower abrasion loss shows better abrasion resistance. Here, the abrasion testing of the NR1.0 and NC1.0 could not be done because the rubber sample was too soft. The results showed that the abrasion loss of the unfilled NR tended to decrease with increasing cross-linking densities. However, the abrasion loss of the CB-filled NR slightly decreased. Compared to the unfilled NR at the same amount of curing agents, the abrasion loss of CB-filled NR was much lower. This is because the rubber reinforcement by the CB filler, providing the stiffer rubber confirmed by the higher tensile moduli as shown in Fig 1(a). The abrasion loss of each rubber sample also agreed well with its abraded surface. Fig. 7 presents FE-SEM micrographs of abraded surfaces of the unfilled NR and CB-filled NR at different cross-linking densities. A series of ridges were formed on the abraded surfaces for both unfilled NR and CB-filled NR. It has been reported that the formation of ridges on an abraded surface can protect the rubber surface lying behind the ridges from further abrasion by reducing the contact area. Thus, the narrower the ridge spacing, the greater the abrasion resistance. From Fig. 7, the narrower ridge spacing on the abraded surface of the unfilled NR and CB-filled NR were observed when their cross-linking densities were higher. Because the CB-filled NR showed a lower abrasion loss compared to the unfilled NR at the same amount of curing agents, it was proven by the shorter ridge spacing on the abraded surfaces of the former than the latter (Fig. 7(b)). From the macroscopic view, the deformation of the rubber sample is relatively small when it is abraded, but actually, the rubber surfaces are extended microscopically. Thus, the rubber having a greater SIC or greater crystallinity could provide better abrasion resistance. However, the SIC seemed to be a minor factor controlling the abrasion resistance of the rubber, compared to their modulus and hardness.

Future areas to take note of, and going forward: The influence of SIC on the cut growth and abrasion behaviors of the CB-filled NR having a different amount of CB filler should be further investigated. Also, the cut growth and abrasion behaviors of the NR composites prepared using other types of fillers such as silica, carbon nanotube, graphene, etc., or hybrid fillers such as silica/CB, clay/CB, etc. can be concerned.

Means of official announcement of research results: These results will be summarized and published as an article in the academic journal(s) or as a proceeding(s) or presentation in the conference.