

## Pre-strain Induced Anisotropy of Filled Natural Rubber

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(Received September 25, 2000)

### 선 인장에 의하여 유도된 천연고무의 비등방성

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(2000년 9월 25일 접수)

**ABSTRACT:** The objective of this study was to investigate factor that influences the development of anisotropy in carbon black filled natural rubber vulcanizates. Chain orientation affects tensile strength, stiffness. Parallel sample shows low stress at low deformation, but have high stiffness at high deformation compared to isotropic or perpendicular samples. This study shows that natural rubber(NR) exhibits much larger tensile anisotropy at high strains than SBR. It seems that the parallel sample of NR is dominated by orientation effect at high strains. This oriented chain is expected to act as nuclei for following crystallization during second stretching and facilitates the strain-induced crystallization.

**요약:** 이 연구의 목적은 카본블랙이 충전된 천연고무에서 비 등방성 발생에 영향을 주는 인자를 조사하기 위함이다. 고분자 사슬의 방향성은 인장특성에 영향을 준다. Pre-strained 방향의 parallel 시편은 등방성 혹은 perpendicular 시편에 비하여 낮은 인장영역에서 낮은 강도를 보이지만 높은 신장영역에서 높은 강도를 보인다. 고 인장 영역에서 parallel한 천연고무 시편은 비 결정성인 SBR에 비하여 높은 강도를 보여주고 있다. 이것은 parallel 시편의 방향성에 영향을 받는 것으로, 시편의 방향성은 2차 인장시 결정화를 위한 핵으로 작용하여 결정화도를 증가시키는 것으로 보인다.

*Keywords :* filled NR, anisotropy, crystallization.

### I. Introduction

Filled rubbers show anisotropy of strength after an extension is removed, even though original dimensions are nearly regained. When a rubber is subjected to large deformation, there is a decrease in conformational entropy

( $\Delta S$ ). Molecular alignment by stretching induces

crystallization and increases the melting temperature( $T_m$ ) at equilibrium.<sup>1,2</sup>

$$T_m = \Delta H / \Delta S \tag{1}$$

Flory<sup>3</sup> showed that melting temperature( $T_m$ ) depends on the extension ratio,  $\lambda$  as shown by the following equation:

$$1/T_m - 1/T_{m0} = (R/hf) \phi(\lambda) \tag{2}$$

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where  $T_m$  = melting temperature corresponding to  $\lambda$ ,  $T_{mo}$  = extrapolated experimental equilibrium temperature,  $h_f$  = the heat of fusion per segment, and  $\phi(\lambda)$  is a deformation factor describing the changes in the most probable chain's displacement length with elongation. Crystallization takes place only very slowly in NR at ambient temperature, but when a sample is stretched, the rate of crystallization rapidly increases. Shimomura et al.<sup>2</sup> measured strain-induced crystallinity of natural rubber as a function of time at different extension ratios using wide angle X-ray scattering (WAXS) and birefringence-stress data. According to them, the rate of crystallization rapidly increases with increasing extension ratio and crystallization immediately occurs above about 300-400% strain. Strain-induced crystallization (SIC) improves mechanical properties such as modulus and tensile strength. Crystallizing rubber generally shows high tensile strength due to very large mechanical hysteresis induced by crystallization at large deformation.<sup>4,5</sup> Andrews<sup>6,7</sup> investigated the effect of strain on individual lamellae in thin films of synthetic cis-1,4-isoprene vulcanized rubber. They found that strain influences nucleation

rather than crystal growth. NR shows a transition from a spherulitic to fibril morphology in the loading direction on increasing strain.<sup>8,9</sup> This anisotropic structure increases the strength due to orientation of crystals in the loading direction and energy dissipation by crystallization. But, in the transverse direction, the strength is low because of an interlaminar weakness. This study focuses on anisotropy of filled natural rubber (NR) and styrene butadiene rubber (SBR), induced by a single large predeformation. The objective is to understand factors that influence the difference of anisotropy between NR and SBR vulcanized rubbers.

## II. Experimental

The rubber compounding recipes used in this work are given in Table 1. In order to obtain similar tensile strength and elongation at break, N2 contained 2.6 sulfur and 1.4 phr of TBBS. The ratio of sulfur to accelerator for S2 was fixed at 1.7/2.5. A two-step process was employed to prepare compounds that included preparation of a masterbatch in a 250 ml internal mixer, followed by curative addition on a two-roll mill. The fill factor was 0.82-0.86. Final mixing proceeded on a two-roll mill (Farrel, 15cm diameter x 30cm roll length). Stocks were stored at room temperature more than 2 days before vulcanization. The optimum cure time was determined from the Monsanto Rheometer curve, as the time to reach maximum torque ( $t_M$ ). Isotropic sheets of rubber were prepared by compression molding between Mylar films at 160°C for S2 compound, and at 150°C for the NR based compounds. In order to reduce processing-induced anisotropy, flat sheets of about 2.2 mm thickness were prepared by pre-molding at 100°C for 3 minutes. After cooling to room temperature, rubber sheets were kept more than 24 hours, but less than 36 hours. Isotropic sheets of vulcanized rubber were prepared by a Dake press. Test specimens (150mm × 100mm × 2mm) were kept at room temperature

**Table 1. Formulations**

	N1	N2	PN2	S1	S2
SBR 1502	-	-	-	100	100
SMR 5CV	100	100	100	-	-
N330	-	50	50	-	50
ZnO	5.0	5.0	-	5.0	5.0
Stearic acid	1.0	1.0	-	0.5	0.5
Agerite					
Stalite S*	1.0	1.0	1.0	-	-
Sulfur	2.6	2.6	-	1.7	1.7
TBBS**	1.4	1.4	-	2.5	2.5
Di-CUP	-	-	1.4	-	-

\* Agerite Stalite S : mixture of octylated diphenylenes, Vanderbilt Company Inc.

\*\*TBBS : t-butyl benzothiazole sulfenamide, Monsanto.

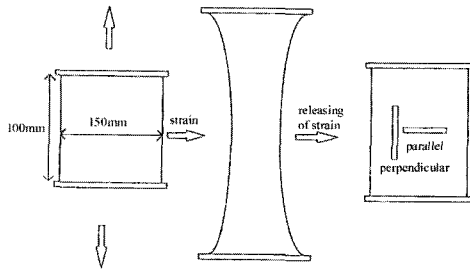
ZnO : C.P.Hall Company

Stearic Acid : from Akrochem Corporation

Carbon black : Cabot Corporation

Di-CUP = Dicumyl peroxide (98.6%)

Fill factor of internal mixer = 0.82-0.88



**Figure 1.** Specimen for inducing anisotropy via uniaxial straining.

at least one week.

**Pre-strained specimens:** A pre-strained specimen was prepared by the steps shown in Figure 1. The physical meaning of each term is followings;

- % of pre-strain( $e_p$ ) :

Sheets were stretched to different levels of pre-strain at room temperature. The prestrained state was maintained for a fixed time and then retracted at the same speed as stretching.

- Hold time at pre-strain( $t_h$ ) :

Testpieces were stretched to a certain pre-strain. The stretched state was maintained for different times, then released. The stress-strain response was measured 45 minutes after load release.

- Time before testing after releasing( $t_r$ ) :

Testpieces were stretched to a certain prestrain. The stretched state was maintained for 3 min. for S2 and 2 hours for N2. The load was then released and the stress-strain response measured as function of time.

The sample gripped with 95 mm initial clamp separation. The sheet was then stretched uni-axially to various pre-strains( $e_p$ ) at a crosshead speed of 50 mm/min. The sample was held at the pre-strain, and then re-tracted at 50 mm/min. After a time  $t_r$ , sheets were cut into dumbbell specimens or simple edge-cut specimens, parallel and perpendicular to the direction of pre-stretching. If we consider the extended sheet, nonuniformity exists near the clamps. Thus this region was avoided when cutting

samples. Samples were cut from a region which underwent uniaxial tension during prestretching.

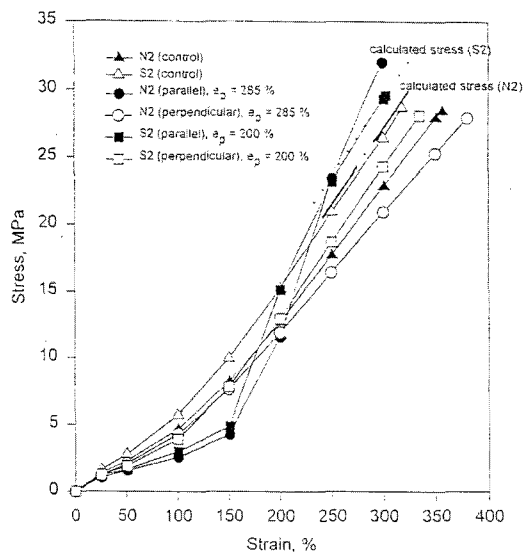
**Tensile testing:** Tensile specimens were cut using an ASTM D-412-89 Type C dumbbell die. Specimens were cut parallel and perpendicular to the direction of prestretching. Bench marks were placed on the middle part of a specimen at 30.0 mm separation. Specimen thickness was measured with a thickness gauge. Three tensile specimens were tested for each case using an Instron model 5567. A video system was used to measure strain during tensile testing. The strain rate was  $0.833 \text{ min}^{-1}$  (cross head speed = 50 mm/min; initial grip separation = 60 mm).

**Differential scanning calorimeter(DSC) measurements:** In order to probe crystallites in natural rubber after releasing a pre-strain, DSC was performed. Sample size was about to 0.25 mg, taken 1 day after releasing of pre-stretching. The sample was scanned from  $10^\circ\text{C}$  to  $100^\circ\text{C}$ ; heating rate was  $10^\circ\text{C}/\text{min}$ .

**Creep test:** Equilibrium stress-strain behavior was determined using creep tests. Benchmarks 40 mm apart were placed on a specimen with a silver pen. The upper part of a specimen was connected to a steel stand, and a weight hung on the lower part. The distance between the two marks was measured using a cathometer after about 20 minutes. The elongation as a function of force was determined and the results analyzed to give Mooney-Rivlin plots.

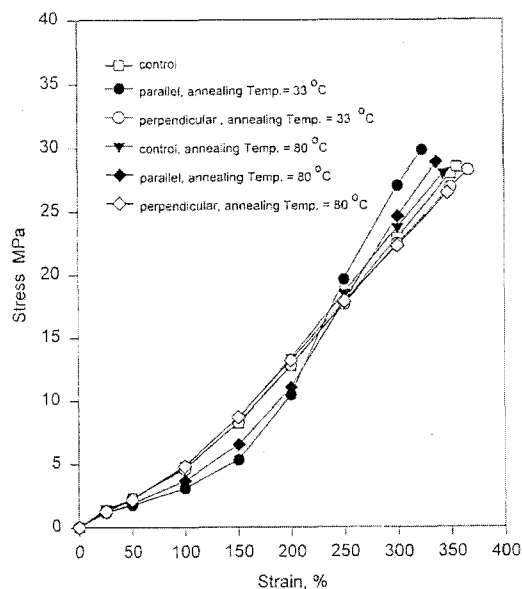
### III. Results and Discussion

As shown in Figure 2, black filled vulcanizates exhibit anisotropy. Although stress-strain response is anisotropic, ultimate strength and extensibility are rather similar in both parallel and perpendicular specimens to the pre-strain direction for composition S2. Because fracture of sample is initiated from flaws present in the bulk or on the surface of specimen, (e.g., from die used to cut a specimen, poor dispersion, or inclusion of foreign material), it is



**Figure 2.** Effect of pre-strain on anisotropy in stress-strain response for composition N2 and S2 ( $t_r=45\text{min}$ ).

very difficult to find a substantial deformation effect on ultimate properties that depend on natural flaw-size. On the other hand, tensile strength of the parallel sample for N2 is decreased with increasing  $t_r$ , but ultimate elongation is increased. At low strains, parallel samples to pre-strain direction exhibit a lower resistance to deformation compared to control or perpendicular samples, but at high strains, parallel samples have high stiffness due to residual network chain orientation. On the other hand, perpendicular specimens have stress-strain curves the same shape as isotropic controls, but slightly lower modulus. As the pre-strain increases, parallel curves of the N2 specimen more substantially change their response than the perpendicular curves. N2 exhibits much larger tensile anisotropy at high strains than S2. The anisotropy of stress-strain response for composition S2 can be explained by the stress softening effect in the parallel direction and the change of the cross section area after pre-strain. Since rubber is nearly incompressible and hence deformed with no change of volume, the change of the cross section area would be expected from the residual extension ratio. When the test strip has



**Figure 3.** Effect of annealing on anisotropy in stress-strain curves for composition N2 ( $\epsilon_p=285\%$ ,  $t_r=45\text{min}$ , annealing time=50hours).

changed by the amount of residual extension,  $(1+\epsilon)$ , after releasing of pre-strain, its cross section area of parallel sample would be expected to decrease  $(1+\epsilon)^{-1/2}$ . The decrease of cross section area of parallel specimen would show a high stress at high strains. At high strain ranges, the stress of parallel sample was quite consistent with the calculated stress from the control sample. However, compared to the calculated stress from the control sample, the parallel sample of N2 has much higher stress than that of S2. Figure 3 shows that as annealed temperature increased, the stress of the perpendicular specimen tends to shift upward compared to the un-annealed perpendicular sample, but the parallel sample has low stress compared to the un-annealed parallel specimen. Figure 4 exhibit normalized anisotropy versus strain for composition N2. By defining a normalized anisotropy and plotting the normalized anisotropy against strain, it is possible to describe the entire behavior of the induced anisotropy. The definition of normalized anisotropy is as follows: <sup>10</sup>

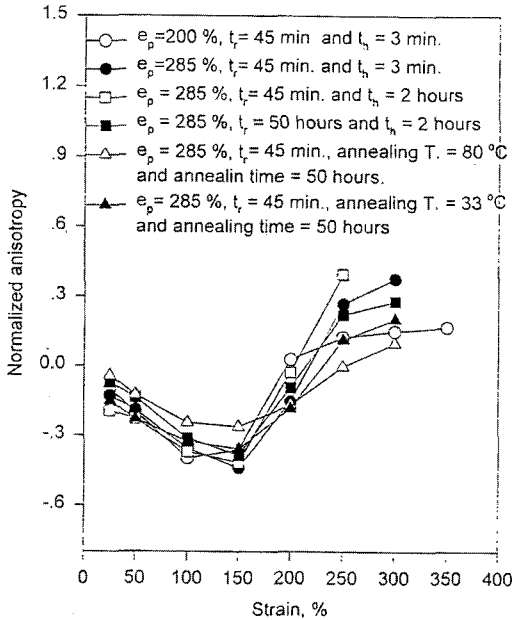


Figure 4. Normalized anisotropy vs. strain for composition N2.

Normalized anisotropy =  $\frac{\{(\text{stress of the parallel curve at a certain strain}) - (\text{stress of the perpendicular curve at the same strain})\}}{(\text{stress of the control curve at the same strain})}$

where the control curve is the stress-strain response for the isotropic specimen. As  $e_p$  or  $t_h$  increases, the normalized anisotropy becomes more negative at low strain, i.e., the parallel curve shows a lower stress than the perpendicular curves. The normalized anisotropy attains more positive values at high strain, i.e., the parallel curve shows a higher stress than the perpendicular curves. At low strain, the softening effect in the parallel specimen is attributed to the breakdown of both structures and agglomerates of carbon black. Other mechanisms are the progressive chain slippage, detachment, or the breaking of network chain attached to filler particles. If a chain breaks at some strain in the first

extension, this broken chain on the first stretch will not able to affect stress on the second stretch. Slipped or detached chains on the surface of carbon black also give stress softening because these chains have longer chain length than that of the initial length. On the other hand, filler assists the development of molecular orientation due to chain slippage at high strains. Stress is more evenly distributed among the molecular chains and the molecular chains are more oriented in the stretching direction. This increase the tendency for strain-induced crystallization of NR at high deformation ranges. In order to determine the causes of this phenomenon, several tests were carried out. The first was an annealing test. Annealing was carried out at 33 °C and 80 °C for 50 hours under vacuum to prevent oxidative chain scission and crosslinking. Hamed<sup>11</sup> proposed that there are two opposing

Table 2. Results of set test of N330 Filled NR compounds

	$L_0$	$L_f$	set(%)
$e_p=285\%$ and $t_r=45$ min.			
Holding Time( $t_h$ )=0.5min.	22.36	26.59	18.92
3.0min.	22.36	26.66	19.23
20min.	22.34	27.02	20.95
120min.	22.19	28.75	29.65
$e_p=285\%$ and $t_r=5$ min.			
Holding Time( $t_h$ )=5min.	27.84	33.25	19.42
20min.	27.93	33.63	20.41
$e_p=200\%$ and $t_r=5$ min.			
Holding Time( $t_h$ )=5min.	28.18	30.44	6.96
20min.	28.38	30.64	7.96
Pre-extension=285%/Annealing**			
Holding Time=3min./remaining time before annealing=56min.			
	$L_b$	$L_a$	$(L_a-L_b)/L_b*100$
Parallel sample (  )	26.414	23.772	-10.0
	26.642	23.663	-10.44
Perpendicular sample (⊥)	26.476	26.579	0.39
	26.468	26.612	0.54
Unextended/annealing**	26.467	26.085	-1.44

\*\*Annealing time is 50 hours at 80 °C under the vacuum condition

\* $L_b$  : distance between marks before annealing

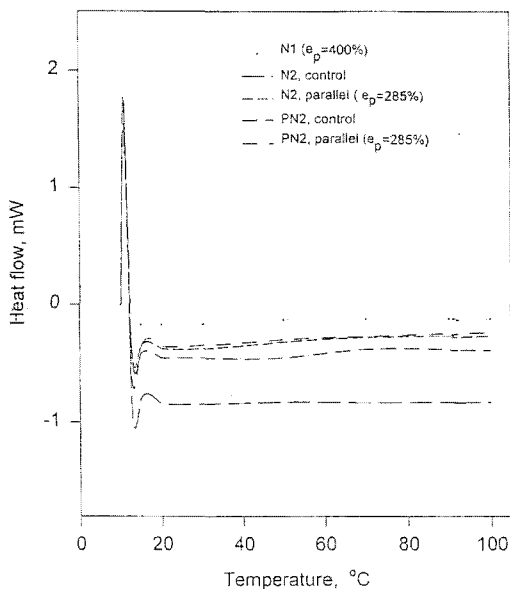
\* $L_a$  : distance between marks after annealing

processes during annealing. While annealing at an elevated temperature, the chain molecular mobility is increased. Simultaneously, heating may induce further attachment between the polymer molecules and carbon black fillers. The former tends to cause material softening, whereas the latter results in stiffening.

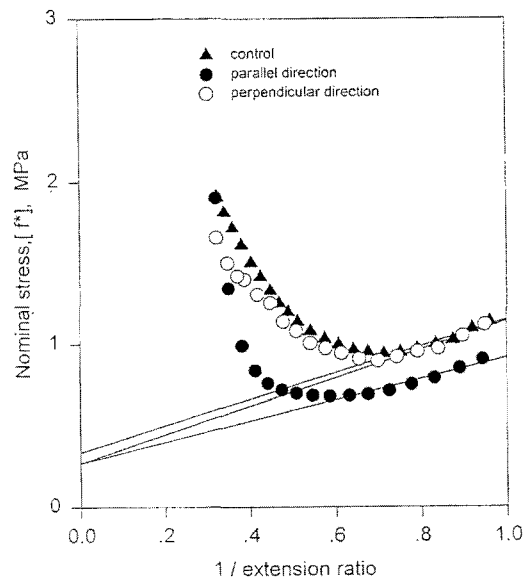
Table 2 provides the results of the annealing test at 80°C for N2. After annealing, considerable shrinkage occurred in the parallel specimens, but there is little change of set in the perpendicular and control samples. The large shrinkage of the parallel specimen seems to be related to the increase of chain mobility. However, compared to the unannealed parallel samples, the annealed parallel samples have remained substantially % set (about 8-9%). It is attributed to the presence of carbon black inhibiting the retraction of chains. This indicates that the anisotropy due to the presence of carbon black is not completely removed by the annealing process. It also implies that the main factor during annealing is the increased attachment between polymer chains and carbon black in perpendicular samples, but the

molecular mobility effect in parallel samples. Another possible cause of the shrinkage in the parallel sample is the melting of remaining crystallites that held NR chains after retracted pre-strain. However, DSC tests did not give any indication of remaining crystallites in the pre-stained specimens as shown in Figure 5. Figure 6 represents Mooney-Rivlin plots of control, parallel and perpendicular specimens for composition N2. Pre-stained specimens exhibit anisotropic equilibrium stress-strain behavior. Compared to control specimen, parallel specimen has low equilibrium modulus and the position of upturn is shifted to a lower strain. In the perpendicular direction, change of equilibrium moduli is insignificant. The upturn of Mooney-Rivlin plots for strain-induced crystallizing rubber is attributed to crystallization.<sup>12</sup> The rapid upturn for the parallel specimen indicates high crystallizability compared to the control and perpendicular specimens.

From stress-strain curves, DSC test, and Mooney-Rivlin plot, the parallel sample of N2 is dominated by orientation effect at high strains. This oriented chain is expected to act as nuclei for following



**Figure 5.** DSC thermogram for parallel samples of pre-stained NR.



**Figure 6.** Nominal stress against elongation for composition N2 ( $e_p=285\%$  and  $t_p=3\text{min}$ ).

crystallization during second stretching and facilitates the strain-induced crystallization effect. Therefore, the parallel sample has the highest stiffness and tensile strength at high strains.

#### IV. Conclusion

Black filled NR exhibit negative anisotropy at lower strains and positive anisotropy at high strains. At high strains, normalized anisotropy increases linearly with increasing residual extension ratio. Perpendicular samples have the same shape of stress-strain curves as isotropic controls, but slightly lower modulus. However, compared to perpendicular samples, parallel samples show low stress at low deformation, but have high stiffness at high deformation. From stress-strain curves, DSC test, and Mooney-Rivlin plot, the parallel sample of N2 is dominated by orientation effect at high strains. This oriented chain is expected to act as nuclei for crystallization during second stretching and facilitates the strain-induced crystallization effect.

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