

## Anisotropy in Gum and Black Filled SBR and NR Vulcanizates Due to Large Deformation

Byung-Ho Park\*

*Kumho Research and Development Center, 555, Sochon-dong, Kwangsan-gu, Kwangju 506-040, Korea*

G.R. Hamed

*Maurice Morton Institute of Polymer Science, College of Polymer Science and Polymer Engineering  
The University of Akron, Akron, OH 44325-3909, USA*

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**Abstract :** After imposing a large pre-strain, anisotropy increases with increasing residual extension ratio. Gums have very low residual extension ratio and exhibit little anisotropy, while black filled SBR and especially sulfur-cured carbon black filled NR have large set and anisotropy. For carbon black filled rubber, samples subjected to tensile loading in perpendicular to the pre-strain direction have the same stress-strain curves shape as the sample without pre-strain (=isotropic samples), but slightly lower modulus. However, compared to isotropic or perpendicular directional samples to pre-strain direction, samples subjected to tensile loading in parallel to the pre-strain direction show low stress at low deformation, but have high stiffness at high deformation. Normalized anisotropy changes with strain. The normalized anisotropy for various deformations is a linear function of residual extension ratio.

### Introduction

A large deformation causes polymer chains to orient in the loading direction.<sup>1-10</sup> If the orientation remains after release of the strain, physical properties are different in parallel and perpendicular direction of to the straining, i.e., the material becomes anisotropic.<sup>1-5</sup> Several factors influence the anisotropy in rubber. The nature of elastomer, the amount and type of filler, cure system and other additives are important factors.<sup>6-9</sup> Processing variables like temperature and the degree of deformation influence anisotropy.<sup>10</sup> During processing, polymer chain is aligned to the direction of flow due to shear stress. If there is not enough time for molecules to be relaxed to a random chain configuration before crosslinking, the resulting vulcanizate becomes anisotropic. However, this kind of flow-induced orientation is small compared to stress-induced backbone and filler alignment.

Some rubbers show anisotropy of strength after an extension is removed even though original dimensions are nearly regained. Generally, anisotropy is enhanced by fillers or strain-induced crystallites. Although many works have been done on the anisotropy of plastics, studies on anisotropy in vulcanized rubber are limited.<sup>1,6</sup> This study focuses on anisotropy of natural rubber (NR) and styrene butadiene rubber (SBR), both filled and unfilled, induced by a single large pre-deformation.

### Experimental

The rubber compounding recipes used in this work are given in Table I. The compounds denoted as "N" and "S" signify NR and SBR formulations, respectively. The numbers, "1" or "2" represent gum or black filled compounds, respectively. PN2 is the peroxide cured black filled NR compound. The curing system for N1 and N2 was a conventional cure system having relatively high sulfur and low accelerator levels. In order to obtain

\*e-mail : bhpark@swan.kumho.co.kr

Table I. 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%).

cf: Fill factor of internal mixer = 0.82-0.86.

similar tensile strength and elongation at break to composition N2, PN2 contained 1.4 phr of peroxide. The ratio of sulfur to accelerator for S1 and S2 was fixed at 1.7/2.5.

**Mixing.** Compounds were prepared by a two-step process 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. The elastomers were added and broken down for 30-45 seconds at 97 rpm. Final mixing proceeded on a two-roll mill (Farrel, 15 cm diameter  $\times$  30 cm roll length). Total milling time was about 6 minutes. Stocks were stored at room temperature more than 2 days before vulcanization.

**Characterization of the Vulcanization Process.** An oscillating disc rheometer (Monsanto Model R-100) was used to determine cure characteristics. The rheometer measured torque versus time for N1 and N2 at 150°C, and S1, S2, and PN2 at 160°C. The optimum cure time was determined from the time to reach maximum torque ( $t_M$ ). Isotropic sheets of rubber were prepared by compression molding between Mylar films at 160°C for S1, S2 and PN2 compounds,

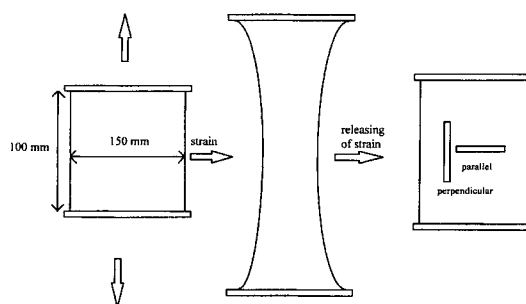


Figure 1. Procedure for inducing anisotropy via uniaxial straining.

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 (150 mm  $\times$  100 mm  $\times$  2 mm) were kept at room temperature for one week.

**Preparation of Pre-stained Specimens.** A pre-stained specimen was prepared by the steps shown in Figure 1. The sample gripped with 95 mm initial clamp separation. The sheet was then stretched uni-axially to various pre-strains ( $e_p$ ) at a cross-head speed of 50 mm/min. The sample was held at the pre-strain, and then retracted at 50 mm/min. Sheets were cut into dumbbell specimens, parallel and perpendicular to the direction of pre-stretching after a time  $t_r$ . If we consider the extended sheet, non-uniformity exists near the clamps. Thus this region was avoided when cutting samples. Samples were cut from a region which underwent uniaxial tension during pre-stretching. Three different types of experiments were carried out to prepare pre-stained specimens.

- Function of pre-strain ( $e_p$ )

Sheets were stretched to different levels of pre-strain at room temperature. The pre-stained state was maintained for a fixed time (3 minutes for N1, N2, S2, and PN2) and then retracted at the same speed as stretching.

- Function of hold time at pre-strain ( $t_h$ )

Test pieces were stretched to a certain pre-strain. The stretched state was maintained for dif-

ferent times, then released. The stress-strain response was measured at 45 minutes after load release.

- Function of time ( $t_r$ ) before testing after releasing

Test pieces were stretched to a certain pre-strain. The stretched state was maintained for 3 minutes for N1, S1, S2, and PN2 and 2 hours for N2. The load was then released and the stress-strain response measured as function of time.

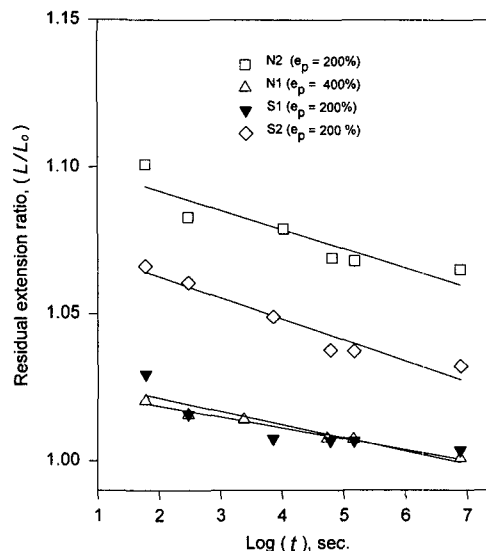
**Tensile Test.** Tensile specimens were cut using an ASTM D-412-89 Type C dumbbell die. Specimens were cut in parallel and perpendicular to the direction of pre-stretching. Benchmarks were placed on the middle part of a specimen at 30.0 mm separation. Specimen thickness was measured with a thickness 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).

**Results and Discussion**

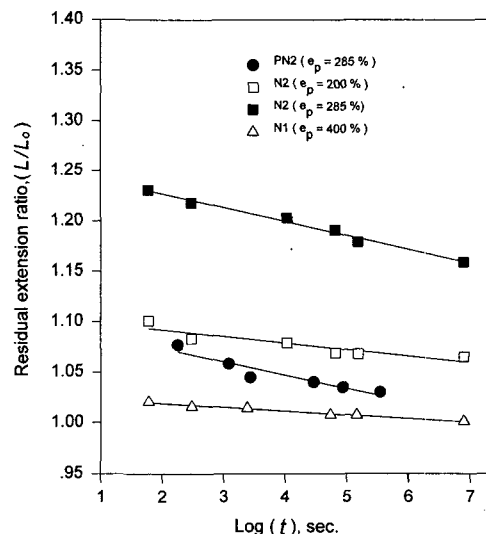
**Residual Extension Ratio.** Figures 2 and 3 show the residual extension ratio versus time after load is released for specimens held in the various stretched states for 3 minutes. Residual extension ratio is defined as follows:

$$\text{Residual extension ratio} = \frac{\left[ \begin{array}{l} \text{The length of a sample at a} \\ \text{certain time after the load release} \end{array} \right]}{\left[ \begin{array}{l} \text{The initial length of the} \\ \text{samples before stretch} \end{array} \right]}$$

Figure 2 shows that gum vulcanizates have very low residual extension ratios. Compared to S1 and N1, S2 and N2 have high value after a long time has passed. It is attributed to carbon black hindering the retraction process of the chain. N2 specimen retained more residual extension ratio than S2 specimen after the extension was removed. One of the resins is the role of remaining crystallites that can restrict the flexibility of the network chains, acting as macroscopic crosslinks after releasing pre-strain. In Figure 3, as the pre-



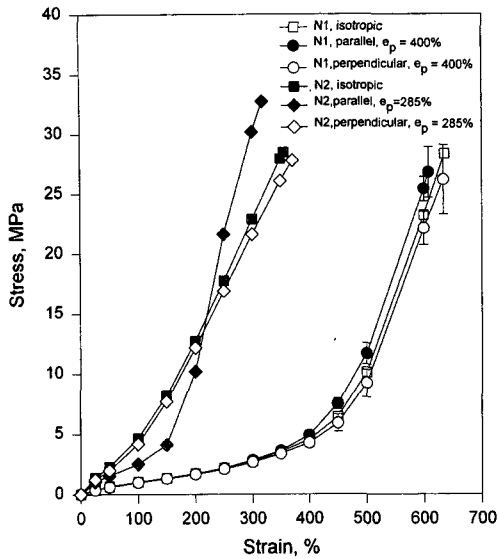
**Figure 2.** Pre-strain effect on residual extension ratio of vulcanized elastomers ( $t_h = 3 \text{ min.}$ ).



**Figure 3.** Pre-strain effect on residual extension ratio of vulcanized elastomers ( $t_h = 3 \text{ min.}$ ).

strain of N2 sample increases, a higher value of residual extension ratio is observed. Another interesting point is that PN2 has a very low set compared to N2. It indicates that the numbers of broken crosslinks in PN2 are very small and their low recombination efficiency gives a very low set. However, compared to N1, the residual extension

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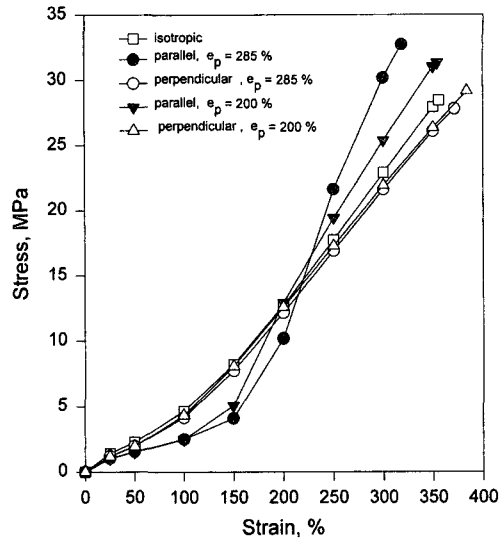


**Figure 4.** Effect of pre-strain on anisotropy in stress-strain response for composition N1 and N2 ( $t_h = 3$  sec. And  $t_r = 45$  min.).

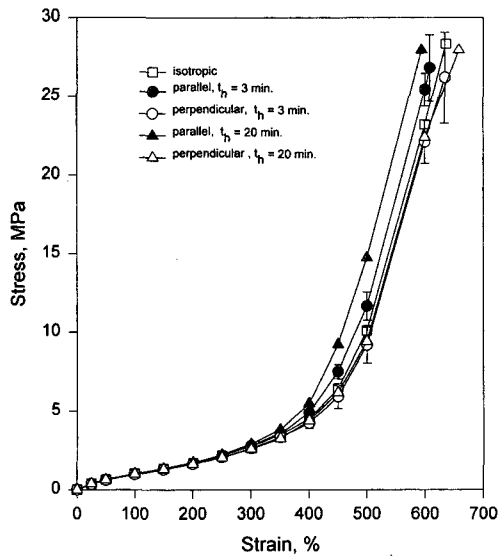
of PN2 is high because of the strain amplification effect of the polymer chain in the presence of carbon black that hinders the retraction process of the polymer chain.

**Pre-strain Effect.** Figure 4 shows the effect of pre-strain on the stress-strain response for parallel and perpendicular samples of N1 and N2 to the pre-extension, which was subsequently relaxed. The specimen was stretched to the pre-strain ( $e_p = 285\%$  for N2 and  $400\%$  for N1), and the stretched state was maintained for 3 minutes. The load was released, and the test specimens were rested for 45 minutes before running tensile tests. Compared to gum NR rubber, black filled NR vulcanizates exhibit anisotropy. 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 the same shape of stress-strain curves as isotropic controls, but with slightly lower modulus.

As the pre-strain increases, parallel curves of the N2 specimen more substantially change their response than the perpendicular curves as shown



**Figure 5.** Effect of pre-strain on anisotropy in stress-strain response for composition N2 ( $t_r = 45$  min. and  $t_h = 3$  min.).

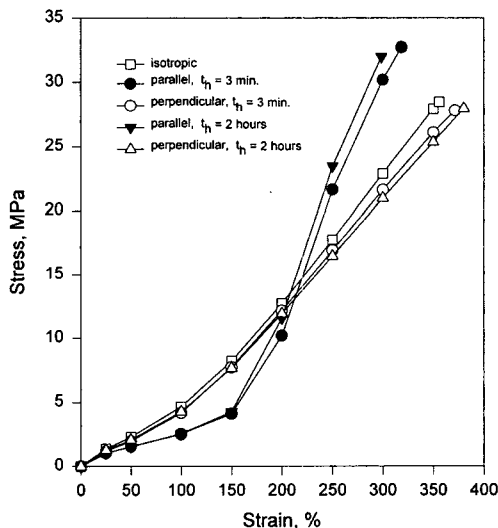


**Figure 6.** Effect of hold time on anisotropy in stress-strain Response for composition N1 ( $e_p = 400\%$  and  $t_r = 3$  hrs).

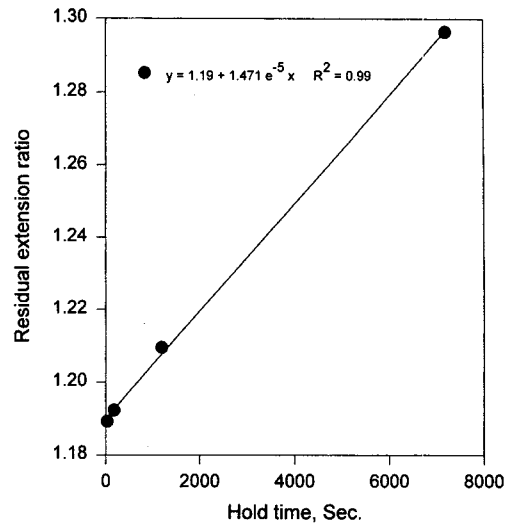
in Figure 5. The anisotropy of stress-strain response can be explained by stress softening in the parallel direction and a change of the cross-sectional area after pre-straining. Since rubber is nearly incompressible and hence deforms with no change of volume, a change of the cross-section

area occurs when there is a residual extension ratio. When a test piece has a residual extension ratio,  $(1+e)$ , after releasing its pre-strain, the cross-sectional area of a parallel samples is expected to decrease by  $(1+e)^{-1}$ . This would give a high stress at high strains.

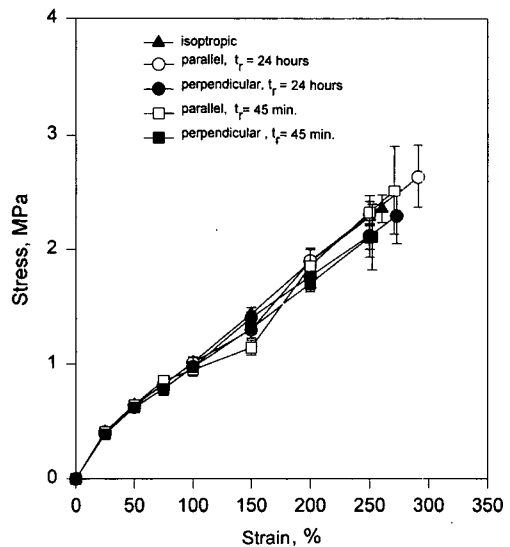
Figure 6 shows the hold time effect at fixed pre-strain for N1. The specimen was stretched to 400% and remained stretched state for a certain time (3 and 20 minutes). Subsequently the load was released. As the hold time increased, the parallel direction curves tended to shift upward, but perpendicular direction curves shifted downward. Figure 7 shows the hold time effect for black filled NR vulcanizate. The parallel sample is displaced well below the curve for the non-stretched counterpart at low strains, but are placed above the curve for the non-stretched sample at high deformation ranges. As the hold time increases, the modulus of the parallel sample decreases at low deformation ranges, but increases at high deformation ranges. In the perpendicular direction, the stress-strain shape is rather similar to that of the isotropic sample, but gives slightly lower modulus. Figure 8 shows the residual extension ratio on the hold time effect for composition N2, which was stretched to 285%. Residual extension ratio was



**Figure 7.** Effect of hold time on anisotropy in stress-strain response for composition N2 ( $e_p = 285\%$  and  $t_r = 45$  min.).



**Figure 8.** Hold time effect on relaxation of N330 filled NR ( $e_p = 285\%$  and  $t_r = 45$  min.).

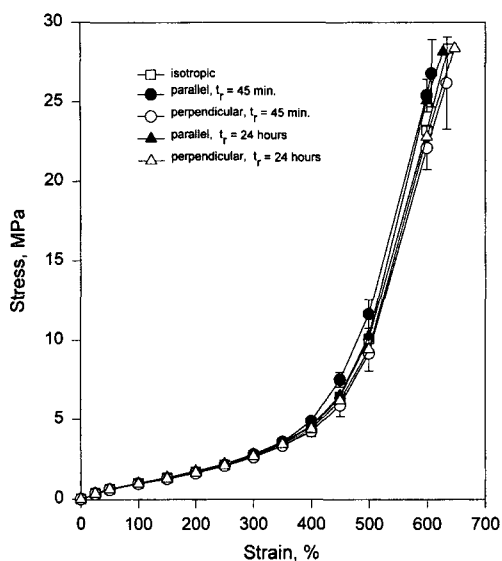


**Figure 9.** The effect of lease time before tensile testing for composition S1 ( $e_p = 200\%$  and  $t_h = 3$  sec.).

checked at 45 minutes after released pre-strain. As the hold time increases, the residual extension ratio continuously increases.

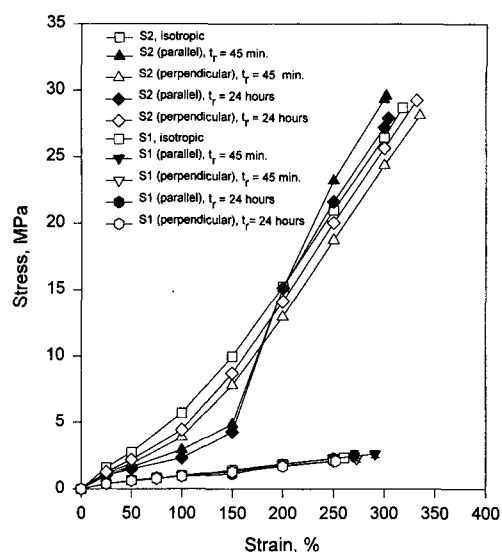
Effect of released time before testing on Figure 9 showed that S1 samples were stretched to 200% pre-strain, and the stretched state was maintained for 3 seconds. Then, the load was released. Stress-strain responses were measured

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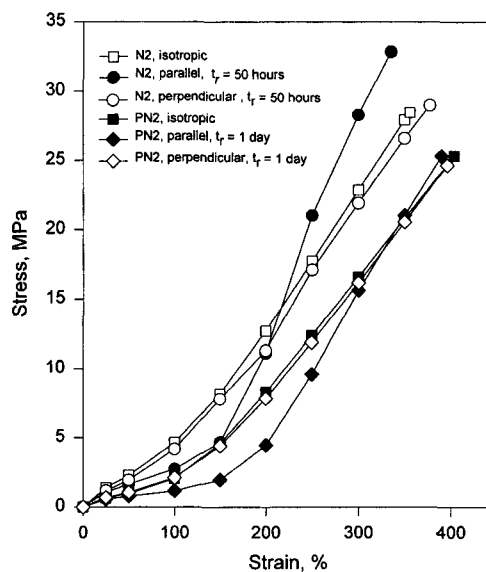


**Figure 10.** Effect of release time on anisotropy in stress-strain response for composition N1 ( $e_p = 400\%$  and  $t_h = 3$  min.).

at different times (45 minutes and 24 hours) after load release. The parallel curve for  $t_r = 45$  minutes exhibited an inflection point from 80% to 200% strain ranges, but the inflection point almost disappeared for  $t_r = 24$  hours. The anisotropy between parallel and perpendicular specimens rapidly decreases with increasing  $t_r$ . It seems that, as the pre-strain increases, some of the crosslinking bonds or main chains may break, and hence affect the stress-strain response on the second stretch. However, the broken chains or broken bonds reheal as the retracted time increases, so that tensile anisotropy rapidly decreases with increasing  $t_r$ . Figure 10 represents released time ( $t_r$ ) effect before testing for composition N1. As the retraction time increases, little tensile anisotropy is exhibited. It indicates that, for gum vulcanizates, the anisotropy induced due to a large deformation can be considered as a temporary anisotropic network. Figure 11 shows the effect of released time before testing gum and black filled SBR on the anisotropy. Black filled vulcanizates have retained a significant anisotropy compared to gum vulcanizates. This is a feature of carbon black filled vulcanizates under deformation due to the strain amplification. Because carbon black particles do not deform under strain, local strain



**Figure 11.** Effect of time after load release on anisotropy in stress-strain response for composition S1 and S2 ( $e_p = 200\%$  and  $t_h = 3$  min.).



**Figure 12.** Effect of release time before tensile testing on anisotropy in stress-strain properties for composition N2 and PN2 ( $e_p = 285\%$ ).

between filler particles is amplified compared to the macroscopic strain. Therefore, the orientation effect of filled rubber is higher than that of unfilled rubber. Another factor is the alignment of carbon black in the direction of pre-stretching. Carbon

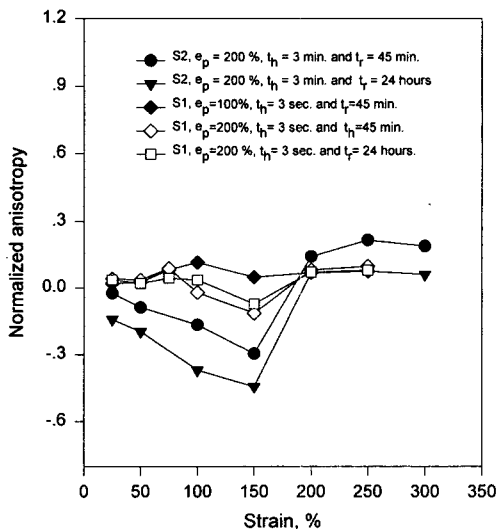
black hinders retraction after releasing strain. Although stress-strain response is anisotropic, ultimate strength and extensibility are rather similar both parallel and perpendicular to the pre-strain-direction for composition S2. For black filled NR vulcanizates, sulfur cured samples have retained considerable anisotropy, but peroxide cured samples showed slight anisotropy at high strains as shown in Figure 12.

**Normalized Anisotropy.** Figures 13 and 14 exhibit normalized anisotropy versus strain for gum and black filled SBR and NR vulcanizates. 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>11</sup>

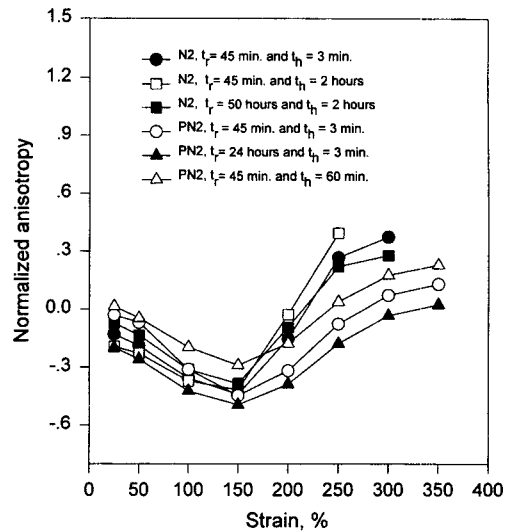
Normalized anisotropy =

$$\frac{\left[ \begin{array}{l} \text{(Stress of the parallel curve at a certain strain)} - \\ \text{(stress of the perpendicular curve at the same strain)} \end{array} \right]}{\left[ \begin{array}{l} \text{Stress of the curve of isotropic sample} \\ \text{at the same strain} \end{array} \right]}$$

where the control curve is the stress-strain response for the isotropic specimen. The anisotropy of unfilled vulcanized rubber is little at low strain ranges, but is substantial at high deforma-



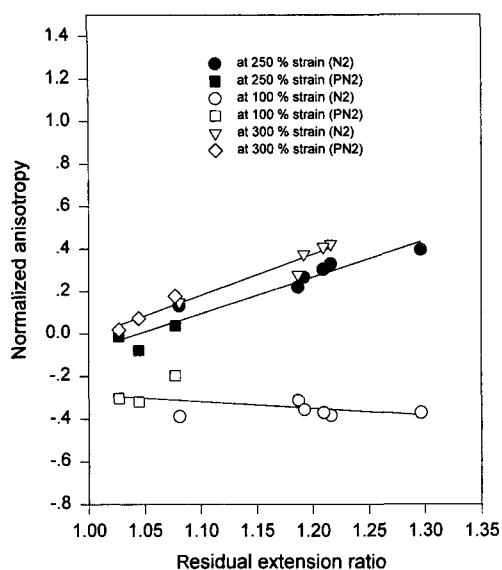
**Figure 13.** The plots of normalized anisotropy vs. strain for composition S1 and S2.



**Figure 14.** The plots of normalized anisotropy vs. strain for composition N2 and PN2.

tion ranges. However, as the released time ( $t_r$ ) before testing increased, unfilled vulcanizates exhibited little anisotropy.

For black filled vulcanized rubber, 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 a strain in the first extension, this broken chain on the first stretch will not be 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 increases the tendency for



**Figure 15.** Normalized anisotropy versus residual strain for composition N2 and PN2.

strain-induced crystallization of NR at high deformation ranges.

Figure 15 displays normalized anisotropy at fixed strain versus residual strain for compositions N2 and PN2 under various pre-conditions. Normalized anisotropy cannot be defined as a single value because it changes with strain. Negative values of normalized anisotropy were observed at 100% strain. However, positive values were observed by selecting high strain at 250% and 300%. The normalized anisotropy for various deformations is a linear function of residual extension ratio. This implies that the extent of set may be primary factor in determining the anisotropic behavior.

## Conclusions

Unfilled rubber vulcanizates have very low residual extension ratios and show little anisotropy, while black-filled SBR and especially NR

have large anisotropy. Black filled NR and SBR, parallel samples exhibit negative anisotropy at lower strains, i.e., the parallel curve shows a lower stress than the perpendicular curves, but has positive anisotropy at high strains, i.e., the parallel curve shows a higher stress than the perpendicular curves. At high strains, normalized anisotropy increases linearly with increasing residual extension ratio. Perpendicular samples have stress-strain curves the same shape 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. Anisotropy increases with increasing residual extension ratio. The normalized anisotropy for various deformations is a linear function of residual extension ratio.

## References

- (1) W. F. Busse, *Ind. Engr. Chem.*, **26**(11), 1194 (1934).
- (2) R. Chasset and P. Thirion, *Rev. Gen. Caoutch.*, **37**, 351 (1960).
- (3) R. Chasset and P. Thirion, *Rev. Gen. Caoutch.*, **35**, 1259 (1943).
- (4) A. G. Thomas, *J. Polym. Sci. Polym. Symp.*, **48**, 145 (1974).
- (5) D. Luch and G. S. Y. Yeh, *J. Macromol. Sci., Phys.*, **B7**(1), 121 (1973).
- (6) A. N. Gent and H. J. Kim, *Rubber Chem. Technol.*, **51**, 35 (1978).
- (7) G. J. Lake, A. Samsuri, S. C. Teo, and J. Vaja, *Polymer*, **32**, 2963 (1991).
- (8) G. R. Hamed, *J. Appl. Polym. Sci.*, **27**, 4081 (1982).
- (9) Y. Udagawa, *Rubber Chem. Technol.*, **61**, 1 (1988).
- (10) Y. Udagawa and M. Ito, *Rubber Chem. Technol.*, **62**, 179 (1989).
- (11) G. R. Hamed and J. H. Song, *Anisotropy Induced in an uncrosslinked Elastomer via Large Strain Deformation*, Presented at a meeting of the Rubber Division, American Chemical Society, Denver, Colorado, October 23-26 (1984).