Elastomer
Vol. 36, No. 4, pp 255~261 (2001)

Temperature Effect on Tensile Strength of Filled Natural Rubber Vulcanizates

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(Received October 4, 2001)

가황 천연고무의 인장강도에 미치는 온도의 영향

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(2001년 10월 4일 접수)

ABSTRACT : This study was related with the effect of elevated temperature on the tensile strength of edge-cut samples. There was a different tensile strength behavior of uncut samples and pre-cut samples under different test temperatures. Tensile strength of uncut sample decreases with increasing test temperature. When pre-cut size(C) is larger than critical cut size(C_{cr}), tensile strength of pre-cut specimen at 80℃ is higher than that of pre-cut specimen at room temperature (RT). Test specimens under 80℃ condition exhibited more secondary cracks at the crack tip region compared to room temperature conditions. However, secondary cracks of pre-cut specimens are not clearly developed at 110℃. Differences in tensile strength induced by different test temperature seem to be responsible for the strain-induced crystallization and micro-cracking patterns.

요 약 : Precut을 가지고 있는 고무 시편에서 서로 다른 온도에서 인장 강도의 영향을 조사하였다. 온도 조건에 따라 precut이 있는 시편과 precut이 없는 시편의 인장 강도는 서로 다른 거동을 보였다. 80℃에서는 임계 Precut 크기보다 더 큰 precut를 가지는 시편은 상온에서 시편보다 높은 인장 강도를 보였다. 상온에서 측정한 시편에 비하여 80℃에서 측정한 시편은 잘 발달된 2차 균열들을 가지고 있는 반면, 110℃에서 측정한 시편의 경우 2차 균열들이 명확하게 발달하지 못하였다. 서로 다른 온도에서 인장강도의 차이는 인장시 발달된 결정화도와 균열 끝 부분에서 형성된 미세 균열 형상과 관계가 있는 것으로 보인다.

Keywords : filled NR, tensile strength, strain-induced crystallization, micro-cracking patterns.

Ⅰ. Introduction

Bueche[1] computed the strength of an elastomer by estimating the number of bonds broken and force needed to rupture them. He proposed that specimen rupture occurred when high local stresses are concentrated on a few chains. When a chain ruptures, it transmits its stress to neighboring chains. The increased loads on the neighboring chains cause additional chain rupture, which finally causes catastrophic failure. In the presence of filler, a broken chain may re-attach to the filler, and thus, more

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chains instead of two neighboring chains will share the load released by the broken chain. The strength (σ_b) of a filled system can be expressed as shown by following equation:

$$\sigma_b = (\nu_e / 3)^{2/3} F_c [1/(1+0.61X) - 1/n] \quad (1)$$
$$X = 2(aF_c/kT\varphi)^{1/3}$$
$$\nu_e = (\rho N/M_c)(1 - 2M_c/M_n)$$

where ν_e is the effective chain density, a is the length of chain between cross-links, F_c is the strength of an individual chain, φ is the number of possible cross-linking sites, ρ is the density of polymer, and n is the number of chain sharing the load.

Equation 1 implies that tensile strength of rubber decreases as the temperature is raised.[1] Amorphous rubber shows a steady fall in tensile strength as temperature or pre-cut size increases, but strain-induced crystallization (SIC) rubber shows a rapid drop at a critical condition.[2,3] Thomas and Whittle[2] observed a rapid drop of tensile strength at critical temperature and a similar sharp drop at critical depth of an edge cut gum NR vulcanizate. He also found that the critical cut size is effectively the natural flaw size at temperature above 80℃. Hamed and Kim[4] investigated cut growth in vulcanizates of NR, BR, and a 50/50 NR/BR blend during single extension. NR and NR/BR specimens showed critical cut sizes and formed secondary cracks that grow a considerable distance parallel to the direction of straining. However, BR samples always grew in a forward direction and secondary cracks did not develop. *Cis*-polybutadiene has insufficient anisotropy of strength at the crack tip to induce secondary cracking because of little strain-induced crystallization. In order to obtain crystallization, it is necessary for molecules or segments of molecules to arrange them in a regular manner on a crystal lattice. This process of rearrangement requires a certain amount of time. NR can be crystallized either by cooling below room temperature or by stretching at room temperature. The effect of temperature on the rate of crystallization can be explained by two factors, nucleation and chain mobility. A reduction of temperature increases the probability of nucleus formation, but at sufficient low temperature reduced chain energy slows their mobility. When a rubber is subjected to large deformation, there is a decrease in conformational entropy (ΔS). Molecular alignment by stretching induces strain crystallization and increases the melting temperature (T_m) at equilibrium.[5,6]

$$T_m = \Delta H / \Delta S \quad (2)$$

Although much work has been done on the influence of elevated temperatures on physical properties of NR, effects of temperature on tensile strength with specimen contained edge-cut is limited. This study focused on the effect of elevated temperature on the crack growth pattern of edge-cut samples.

Ⅱ. Experimental

The compounding recipe used in this work is shown in Table 1. The curing system was a conventional formulation having relatively high sulfur and low accelerator levels. 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

Table 1. Formulations

Recipes	N2
SMR 5CV	100
N330	50
ZnO	5.0
Stearic acid	1.0
Agerite Stalite S*	1.0
Sulfur	2.67
TBBS**	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
N330 : Cabot Corporation
cf : Fill factor of internal mixer = 0.85

mill. The fill factor was 0.85. The elastomers were added and broken down for 30 - 45 seconds at 80 rpm. The mixer was then stopped and one-third of the additives were incorporated into the elastomer and mixed for 1 - 1.5 minutes. The mixer was stopped and the remaining ingredients were added and mixed for 3.5 - 4.5 minutes. The compound was dumped and weighed to check mixing loss. Master-batches were cooled to room temperature for two hours before mixing with curatives. Final mixing proceeded on a two-roll mill (Farrel, 15 cm diameter x 30 cm roll length). Roll speeds were 30 and 35 rpm. Total milling time was about 6 minutes. 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 150℃ 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℃ 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 in a Dake press. Uncut specimens were cut using an ASTM D-412-89 Type C dumbbell die. Pre-cut of varying length of simple strip was introduced perpendicular to the specimen length at the midpoint edge using a razor blade, which had been dipped in a soap solution. Specimen dimensions and shape are shown in Figure 1. Benchmarks were placed on the middle part of a specimen at 60mm separation. Specimen thickness was measured with a thickness gauge. Using an Instron model 5567 carried out tensile test. The strain rate was 0.833 min^{-1} (cross head speed = 50 mm/min; initial grip separation = 60 mm).

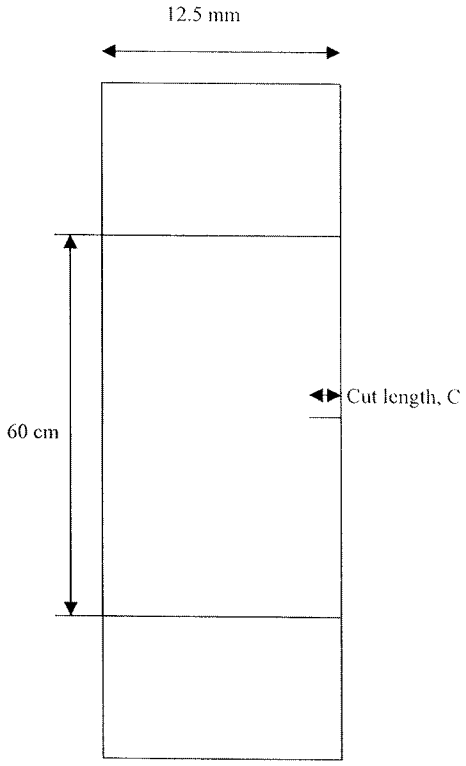

Figure 1. Strip tensile specimen with an edge cut of length, C.

Ⅲ. Results and Discussion

Stress-strain properties of uncut specimens. Figure 2 shows the effect of test temperature on the

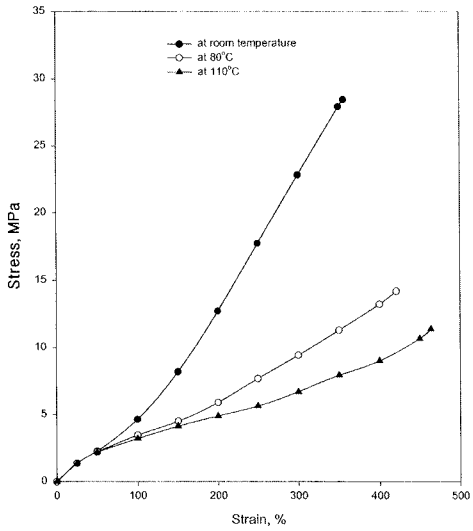

Figure 2. Stress-strain curves under the various test temperature.

stress-strain response for N330 filled-NR samples. Sample exhibits a lower resistance to deformation as the test temperature increases. At low strains, all specimens have stress-strain curves of the same shape, but slightly lower modulus under condition of high temperature. This means that amplitude effect of polymer chain due to carbon black is not completely eliminated at high temperature. In other words, strain amplitude effect is main effect although there is a little softening effect due to the increase of chain mobility. However, at high strain ranges, modulus decreased rapidly with increasing temperature. Specimen at 110℃ exhibited the lowest tensile strength and specimen at room temperature showed the highest tensile strength. At high strain ranges, low modulus is related with increased-chain mobility and suppression of strain-induced crystallization due to the elevated temperature. In order to obtain crystallization, it is necessary for molecules or segments of molecules to arrange them in a regular manner.[5] this process of rearrangement requires a certain period of time. NR can be crystallized either by cooling or by stretching the polymer chain. A reduction of temperature increases the probability of nucleus formation, but at sufficient low temperature, reduced chain energy slows their mobility. According to Flory,[6] the rate of crystallization rapidly increases with increasing extension ratio. SIC improves mechanical properties such as modulus and tensile strength because of large mechanical hysteresis induced by crystallization.[7] As the temperature increases, crystallization takes place only very slowly and gives low strength. Above melting temperature, NR exhibited behavior of amorphous rubber such as crack behavior. This kind of phenomenon will be explained in more detail in the rear parts.

Failure properties of simple edge cut specimen. In order to better understand the role of strain-induced crystallization at the crack tip, simple edge cut test was carried out under the various temperature conditions; room temperature, 80℃ and 110℃ for NR specimens. Figure 3 compare tensile

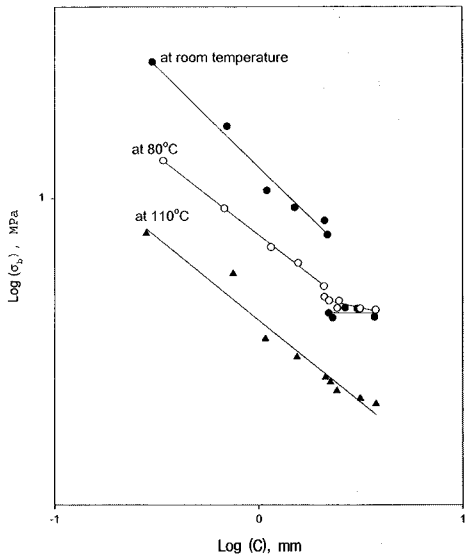

Figure 3. Effect of precut size on the tensile strength under the various test temperature.

strength at RT, 80℃ and 110℃. At room temperature condition, tensile strength of specimen sharply dropped at a critical cut length but a similar sharp drop was not observed in tensile strength at 110℃. The absence of a critical cut length at 110℃ means that crystallization does not occur in the bulk. At 80℃ a similar drop of tensile strength was observed like as room temperature conditions, but the degree of drop is little. The critical cut size (C_{cr} = 1.40 - 1.42 mm) in RT condition is somewhat higher than that of sample (C_{cr} = 1.36 - 1.38 mm) in 80℃. Surprising results is that tensile strength of sample at 80℃ are higher than that of specimen at RT when $C > C_{cr}$. However, tensile strength of specimen at RT is higher than those of samples at 80℃ when $C < C_{cr}$. The question arises why does sample at 80℃ have higher tensile strength than sample at RT if $C > C_{cr}$. As Thomas[2] pointed out, the bulk remains amorphous state above 80℃, the highly-strained polymer continuously proceed crystallization at the crack tip region, although the bulk remains amorphous state above 80℃. It seems that specimen continues to crystallize, although there is suppression of crystallization at 80℃

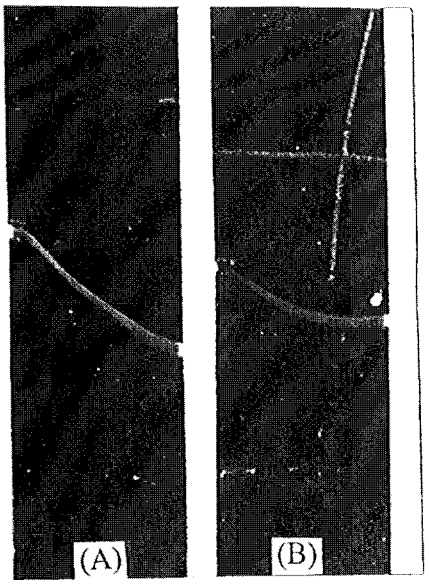

Figure 4. Crack growth surface morphology for filled NR specimens at room temperature.
(A) C_o=2.17mm, σ_b = 8.04 Mpa.
(B) C_o=2.20mm, σ_b = 5.03 Mpa.

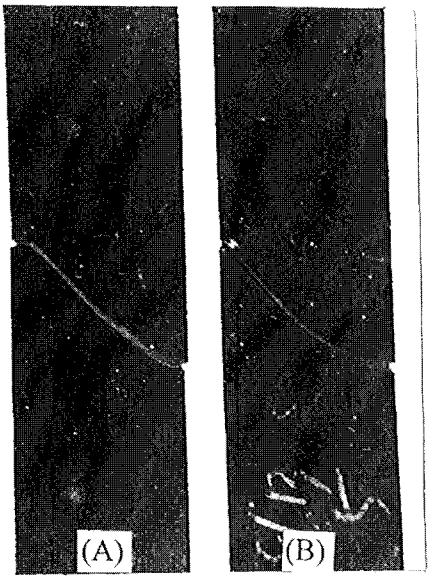

Figure 5. Crack growth surface morphology for filled NR specimens at 80℃.
(A) C_o=2.21mm, σ_b = 5.17 Mpa.
(B) C_o=1.15mm, σ_b = 7.46 Mpa.

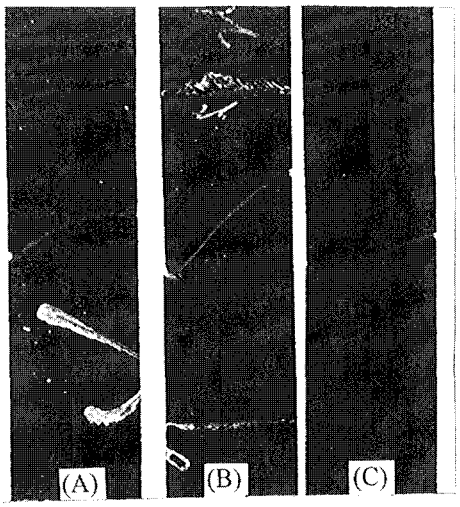

Figure 6. Crack growth surface morphology for filled NR specimens at 110℃.
(A) C_o=2.12mm, σ_b = 3.42 Mpa.
(B) C_o=2.24mm, σ_b = 3.32 Mpa
(C) C_o=1.54mm, σ_b = 3.86 Mpa

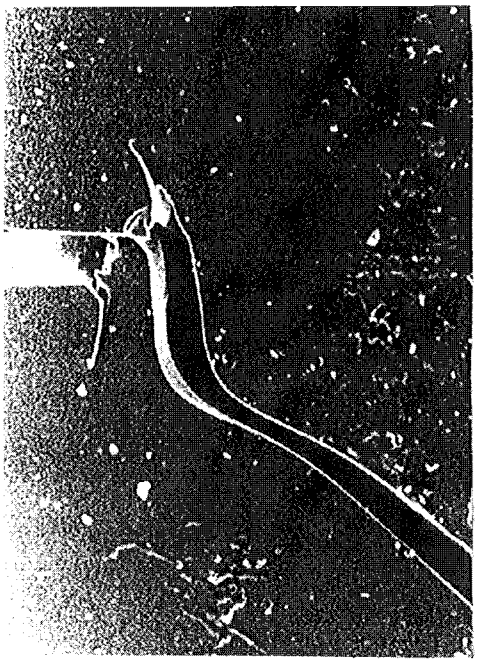

Figure 7. Micrograph of the region near the crack tip of sample at room temperature.
(C_o=2.30mm, σ_b = 4.89 Mpa.)

Figure 8. Micrograph of the region near the crack tip of sample at 80℃.
(C_o=2.47mm, σ_b = 5.41 Mpa.)

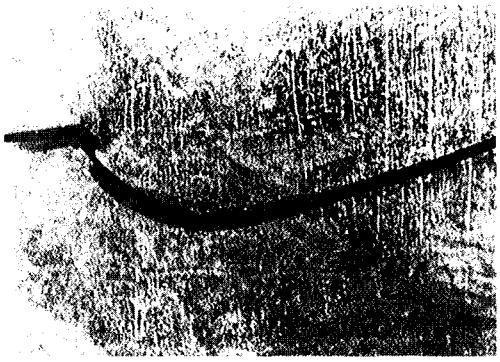

Figure 9. Micrograph of the region near the crack tip of sample at 110℃.
(C_o=2.41mm, σ_b = 3.15 Mpa.)

compared to RT. However, at above melting point 110℃, strain-induced crystallization can not occur in bulk and tip regions and it lead to low tensile strength and modulus. Figures 4-6 show that the angles of crack deviation of specimens at 110℃ are small, compare to those of RT and 80℃ condition. Figures 7-9 exhibit microcracking patterns near the crack tip regions; at room temperature, 80℃, and 110℃. Specimen at RT has well-developed longitudinal cracks before catastrophic tearing, but this kind of crack is not clearly developed at 110℃. Compared to room temperature test results, 80℃ test specimens exhibit multiple microcracking at the crack tip region and tensile strength remained high. The increased microcracking at 80℃ seems to be related high tensile strength. This suggests that the increase of chain mobility favor chain orientation and crystallization at the tip region. However, heating above the melting temperature precludes crystallization in the tip region. Thus, at 110℃ microcracking is not seen as shown figure 9.

The results of this study indicate that the tensile strength of specimen with an edge cut is caused by the orientation of NR chains, which is amplified by SIC. Differences in tensile strength induced by different test temperature are responsible for the critical cut size and microcracking patterns in specimens.

Ⅳ. Conclusion

Uncut sample exhibits a lower resistance to deformation as test temperature increases. Compare to uncut samples, there is a different behavior in pre-cut samples. At room temperature condition, tensile strength of specimen sharply dropped at a critical cut length but a similar sharp drop was not observed in tensile strength at 110℃. At 80℃ a similar drop of tensile strength was observed like as room temperature conditions, but the degree of drop is very little. The critical cut size (C_{cr} = 1.40 - 1.42 mm) in RT condition is somewhat higher than that of sample (C_{cr} = 1.36 - 1.38 mm) in 80℃. Tensile strength specimen at RT is higher than sample 80℃ if $C < C_{cr}$. However, tensile strengths of sample at 80℃ are higher than those of specimen at RT if $C > C_{cr}$. Compared to room temperature test results, 80℃ test specimens exhibit complex micro-cracking patterns at the crack tip region.

Differences in tensile strength induced by different test temperature are responsible for the micro-cracking patterns.

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