

The Tensile Properties of Strain-Crystallising Vulcanisates. I. A New Theory to Explain Strengthening

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ABSTRACT: The tensile properties of conventional and peroxide vulcanisates were studied over a range of crosslink densities at room temperature and at 90°C. At 90°C the tensile strength and elongation at break of vulcanisates of lower crosslink density are superior to those at room temperature, while for vulcanisates of higher crosslink density the reverse applies. When strain-induced crystallites form, they act as crosslinks shortening chains within the network. Shortened chains have lower entropies and a larger force is required for their continued extension, i.e., for a further reduction in their entropy. It is proposed that because these stiffer chains resist deformation, other less stiff chains are preferentially extended. This alters the network deformation pattern, forcing more chains to become load bearing and delaying the development of taut chains or chain sequences. Thus the formation of strain-induced crystals leads to the

slope of the stress–strain curve rising rapidly. At elevated temperatures the rate of nucleation of strain-induced crystallites is slower but data on stress–strain curves obtained with different temperature programs show that, while strain-induced crystallization is essential for the development of high tensile strength, delaying their formation to higher elongations is advantageous for high tensile properties. In vulcanisates of higher crosslink density the rate of crystallization at high temperatures becomes too slow. Rupture occurs before strain-induced crystallites can form and protect the network by altering the network deformation pattern. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1562–1569, 2006

Key words: strain-induced crystallization; tensile strength; temperature effects; strengthening mechanism

INTRODUCTION

Vulcanisates of stereoregular polymers have an increased tendency to crystallize upon being strained, and such rubbers typically have larger ultimate tensile strengths than rubbers that do not undergo strain-crystallization. Rubber vulcanisates that undergo strain-induced crystallization usually display a sharp upturn in the stress–strain curve.

The stress required to extend an affine network increases with extension according to eq. (1)¹

$$\text{stress} = c_p k T \left(\lambda - \frac{1}{\lambda^2} \right) \quad (1)$$

where c_p is the number density of chains; λ , the extension ratio; k , the Boltzmann constant; and T , the absolute temperature. For a Gaussian distribution of chain ends, the rate of increase in the slope of the stress–strain curves, in terms of eq. (1), levels out to an

essentially linear relationship at higher extensions. For a real, non-Gaussian distribution, in which the chain end distribution is finite and consequently the extension of chains is limited to the distance between crosslinks, an upturn in the stress–strain curve can be predicted.² Extensions at which non-Gaussian behavior predicts an upturn in the stress–strain curves coincide roughly with the onset of strain-induced crystallization. Flory³ attributed the upturn in the stress–strain curve to strain-induced crystallization, though subsequently Wang and Guth⁴ showed that the shape of the stress–strain curve of natural rubber (NR) changes only to a small degree when the extension is conducted at 100°C, even though crystallization would have been greatly reduced. It was suggested by Smith et al.⁵ that crystallization does have an effect on the stress–strain curve, but only at higher extensions and that non-Gaussian behavior is responsible for the initial upturn in the stress–strain curve.

At room temperature (RT) crystallization can be detected in vulcanisates of stereo-regular elastomers, such as NR, when subjected to strains of 200–250% or more,^{6–9} though Toki et al.¹⁰ have pointed out that, in most studies, there is a time lapse between extension and the measurement of crystallization. They found that strain-induced crystallites formed only after 400% elongation at an extension rate of 50 mm min⁻¹.¹⁰

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The marked upturn in the stress-strain curve can be attributed to the interplay of four factors: (1) non-Gaussian behavior, (2) strain-induced crystallites, which act as additional crosslink points, (3) the volume fraction of extendable material, which decreases as crystallization occurs, and (4) the stress relaxation that is caused by crystallization. The first three factors will increase the slope of the stress-strain curve while the fourth factor will moderate this increase in slope.

The number of strain-induced crystalline crosslinks increase with strain, increasing the number of chains, c_p , in eq. (1). This raises the stress required to extend the sample to a given strain. The superior tensile properties of stereo-regular gum vulcanisates is generally associated with the development of strain-induced crystals but it is contended that, to develop high tensile strength, strain crystallization must occur sufficiently fast to prevent crack propagation, i.e., high tensile strengths are attributed to strain-induced crystallites blocking crack propagation.¹¹⁻¹⁵ A higher stress would be required for the advancement of the crack deflected at right angles to the applied stress. The increased number of effective crosslinks with strain-induced crystallite formation is not referred to in this type of strengthening mechanism. Mention has also been made in the literature to crystallization at the crack tip causing stress relaxation,¹⁶ thereby increasing the apparent stress required for failure. It is not clear how crack deflection can lead to an increase in tensile strength without, during the strengthening process, generating a network that is riddled with micro-cracks. The mechanism suggested¹⁶ specifically relies on the deflected micro-crack requiring a higher stress for it to advance further. This, it is argued, is why the stress increases. Such micro-cracks, however, should persist when the strain, and consequently the "crack blocking/deflecting" crystallites, are removed, and the network should be subject to ready failure on reloading. The already present micro-cracks would act as preformed stress raisers and could propagate before crystallization can occur. As is well known, and was specifically pointed out by Erman and Mark,² stress-strain isotherms are generally reversible up to the rupture points, indicating that failures in the network, that subsequently lead to catastrophic failure, occur only near the sample rupture point.

The tensile strengths of vulcanisates are reported to decrease with an increase in temperature.^{11,14,15,17} This has often been ascribed to a decrease in the amount of strain-induced crystallization. Strain-induced crystallites not only increase the number of crosslinks in the network [c_p in eq. (1)], but chain shortening affects the entropy of chains and the force required for their continued extension. This paper examines the effect of temperature on the tensile behavior of vulcanisates over a range of crosslink densities, and interprets the effect of strain-induced crystalline crosslinks in raising

tensile strength in terms of entropy changes, resulting from the shortening of subchains between crosslinks, rather than in terms of the deflection of micro-cracks that develop prior to rupture.

EXPERIMENTAL

Vulcanisates

Peroxide vulcanisates of synthetic *cis*-1,4-polysioiprene (IR) (Nipol IR 2200, Dunlop, Durban, South Africa) were obtained by curing with dicumyl peroxide (DCP) (Fluka, Steinheim, Germany). Conventional vulcanisates were cured with 2-bisbenzothiazole-2,2'-disulfide (MBTS) (Orchem, Sasolburg, South Africa) and sulfur (S_8) (AECI, Modderfontein, South Africa). The MBTS/ S_8 mass ratio was 1 : 2. Compounding was done in a Brabender internal mixer fitted with an 80 mL N50 elastomeric mixing head using a fill factor of 0.95. The rubber was added to the mixer with the rotors spinning at 45 rpm and a water cooled unit held the mixing head temperature below 90°C. First, $\frac{3}{4}$ of the rubber was added and left to masticate for 1 min before the curatives were added over a period of 2 min, after which the remainder of the rubber was added. The mixing speed was then increased to 60 rpm and mixing continued for 3 min. The compound was removed and milled on a two-roll mill four times before it was reintroduced to the mixing head, spinning at 60 rpm, and mixed for another 3 min. The compound was then removed and passed through the mill another four times. The finished compound was left for 24 h before being vulcanized. All vulcanized rubber samples were compression molded at 150°C as flat sheets. The cure time was determined as the time needed to obtain 95% of maximum torque from rheometer cure curves. The crosslink density of samples was determined by swelling in toluene in the dark (SMM Instruments, Vorna Valley, South Africa) for 72 h. Solvent was exchanged for fresh every 24 h. Crosslink density was calculated using the modified Flory-Rehner equation¹⁸ from the masses of the swollen and dried vulcanisates. The compounds used for the bulk of the investigations and referred to as IR/DCP(i) and IR/MBTS/ S_8 (i) were cured using 1 phr DCP (crosslink density of 4.66×10^{-5} mol mL⁻¹) and 3 phr MBTS, and 6 phr S_8 (crosslink density of 4.54×10^{-5} mol mL⁻¹) respectively. Other compounds contained different DCP or MBTS/ S_8 (ratio 1 : 2) loadings and these are indicated in the text in parentheses as phr. All peroxide vulcanisates contained 0.5 phr of the antioxidant *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) (Bayer, Leverkusen, Germany) and MBTS vulcanisates 1 phr IPPD.

Tensile tests

Tensile test were conducted using an Instron 4411 Tensiometer fitted with a 1 kN load cell and an Instron

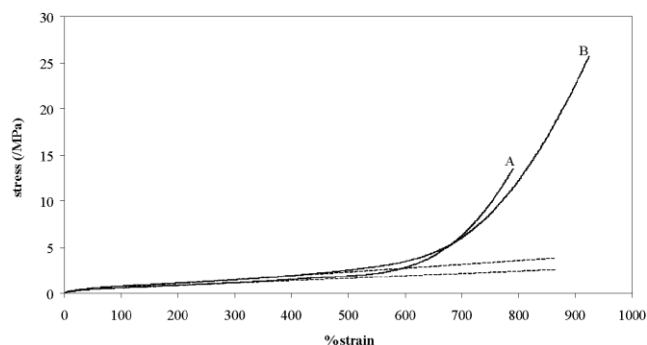


Figure 1 The RT stress–strain curves of (A) IR/DCP(i) and (B) IR/MBTS/S₈(i).

long travel elastomeric extensometer. A crosshead extension speed of 500 mm min⁻¹ was used. Some tensile tests were conducted with a D size ASTM D412 dumbbell sample. For work above room temperature, samples were extended in a water tank fed from a thermostatted water reservoir. This necessitated the use of a customized dumbbell sample with a gauge length of 8 mm and neck width of 2 mm. The sample was clamped in a self adjusting elastomer grip fixed at the bottom of the tank and the self adjusting elastomer grip was attached via an extender arm. Countercurrent air cooling was supplied to the load cell. Failure to protect the load cell from the heat in the bath led to a drift in the stress recorded at constant strain. Unfortunately the extensometer could not be operated in the tank, and the length of the test piece had to be reduced drastically to ensure that it did not extend above the water level in the tank.

X-ray diffraction

X-ray diffraction patterns were obtained of “D” size dumbbells stretched to 700% strain (measured by extensometer) and held at that strain by an aluminum clamp. The strained sample was removed from the tensile tester and placed in the X-ray diffractometer (Phillips PW 840, using Cu K α (1.541 Å) radiation, set at 40 kV and 35 mA). Spectra were scanned at 2 θ from 15° to 27° at 0.02°/s with a slit width of 0.3 mm.

RESULTS

Strain-induced crystallization and the upturn in the stress–strain curve

The stress–strain curves for IR/DCP(i) and IR/MBTS/S₈(i) vulcanisates at room temperature (RT) (± 23 °C) are shown in Figure 1. These curves were obtained using “D” size dumbbell samples and an extensometer to record the strain. They are the average of five replicate tests.

From Figure 1 it is clear that the IR/MBTS/S₈(i) vulcanisate has a higher ultimate tensile strength (UTS) and can extend further before breaking than the IR/DCP(i) vulcanisate, even though they have the similar crosslink densities. In Figure 1 and in other stress–strain curves depicted, the initial, near-linear portion of the curve is extended as a broken line to emphasize the strain at which the upturn initiates. The stress–strain curves for both vulcanisates show an upturn at elongations between 400 and 500%, the change in slope being more pronounced in the case of IR/DCP(i).

X-ray diffraction patterns of both IR/DCP(i) and IR/MBTS/S₈(i) vulcanisates at 700% strain (after the stress upturn) showed a diffraction peak with a maximum at 2 θ of 21°. This is indicative of the development of a strain-induced crystallization.⁷ Unstrained samples did not have this diffraction peak.

Effect of temperature on the shape of the stress–strain curve

The effect of temperature on the stress–strain curve was studied in the IR/DCP system over a range of crosslink densities ($1/2M_c = 2.49 \times 10^{-5}$ to 8.02×10^{-5} mol mL⁻¹). Stress–strain curves were obtained at RT and 90 °C for the custom size dumbbell using the water tank apparatus. Because the extensometer could not be used, extension is expressed as the distance moved by the upper grip in mm.

Figure 2 illustrates the effect of increased temperature on the stress–strain curves of two of the peroxide cured IR formulations studied. At high temperature the moderately crosslinked (IR/DCP (0.8)) samples extend further and break at a higher UTS than the RT samples, while the higher crosslinked samples break at a much reduced extension and UTS than the RT samples. The high temperature stress–strain curve of

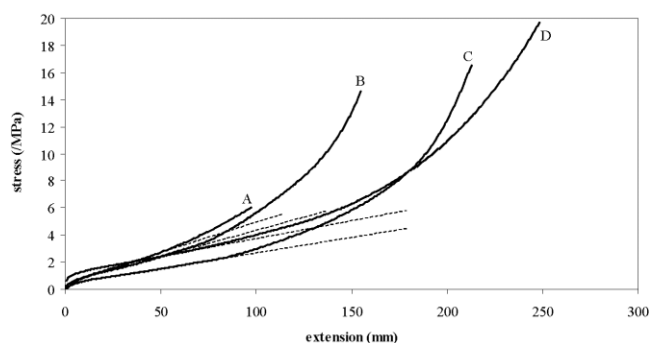


Figure 2 The effect of increased temperature (RT vs. 90°C) on the stress–strain curves for IR/DCP vulcanisates at two different crosslink densities (IR/DCP (0.8) 4.12×10^{-5} mol mL⁻¹ and IR/DCP (1.6) 6.45×10^{-5} mol mL⁻¹). (A) IR/DCP (1.6) 90°C, (B) IR/DCP (1.6) RT, (C) IR/DCP (0.8) RT, (D) IR/DCP (0.8) 90°C.

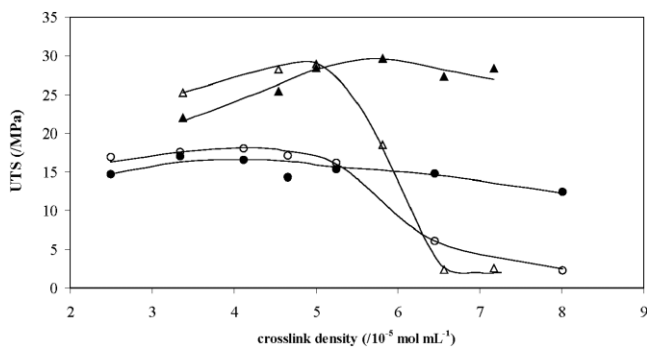


Figure 3 The UTS of IR/DCP and IR/MBTS/S₈ vulcanisates at RT and 90°C, over a range of crosslink densities ($1/2M_c$). (○) IR/DCP 90°C, (●) IR/DCP RT, (▲) IR/MBTS/S₈ RT, (△) IR/MBTS/S₈ 90°C.

IR/DCP (0.8) shows a very extensive upturn in stress prior to break; this upturn occurs at a longer extension than in the RT extension and this is attributed to delayed crystallization, a larger entropy decrease (elongation) being required before strain-induced crystallization occurs at higher temperatures. The rate of the upturn in stress is also smaller than in the RT sample. The RT stress-strain curve of IR/DCP (1.6) shows a strong upturn in stress, while at high temperature the upturn in stress is severely limited.

The upturn in stress in Figure 2 is less pronounced than the upturn seen in Figure 1 because in Figure 2 curves were obtained without the aid of an extensometer, and extension of the wide part of the dumbbell is included in the strain.

Effect of temperature on ultimate properties

The effect of increased temperature on the ultimate properties (UTS and ultimate elongation) of IR/DCP and IR/MBTS/S₈ vulcanisates over a range of crosslink densities was investigated. The effect on tensile properties and elongation at break are summarized in Figures 3 and 4 respectively.

In agreement with literature data,^{19–21} the room temperature UTS versus crosslink density curve for IR/MBTS/S₈ lies above that of IR/DCP (Fig. 3). Both curves have a maximum, that of IR/DCP occurring at a lower crosslink density than IR/MBTS/S₈. The curves do not cross in this range of crosslink densities.

At low to moderate crosslink densities the 90°C UTS versus crosslink density curves of both IR/DCP and IR/MBTS/S₈ lie above their RT counter parts. This is in sharp contrast to what is expected from the literature.^{11,17,22} It should, however, be noted that the systems studied had higher crosslink densities than the bottom end of the range measured here. The crosslink densities studied by Gent et al.¹⁷ were in excess of $5.6 \times 10^{-5} \text{ mol g}^{-1}$ while Nomara et al.²² studied even more highly crosslinked samples (in excess of 1.5

$\times 10^{-4} \text{ mol g}^{-1}$). With an increase in crosslink density, there is a sudden and dramatic decrease in the UTS of both IR/DCP and IR/MBTS/S₈ at 90°C. A similar sharp decrease is not seen in the RT curves. In the IR/MBTS/S₈ system the UTS drops from 28.9 to 2.3 MPa over the crosslink density range of 4.9×10^{-5} to $6.6 \times 10^{-5} \text{ mol mL}^{-1}$. The UTS for the IR/DCP system decreases from 16.2 to 6.0 MPa over the crosslink density range of 5.3×10^{-5} to $6.5 \times 10^{-5} \text{ mol mL}^{-1}$ and the decrease at 90°C is larger for IR/MBTS/S₈ than for IR/DCP, the UTS values for IR/MBTS/S₈ at 90°C fall to below those of IR/DCP at high crosslink densities ($> 6.5 \times 10^{-5} \text{ mol mL}^{-1}$).

At RT both IR/DCP and IR/MBTS/S₈ vulcanisates undergo a steady decrease in ultimate elongation with an increase in crosslink density (Fig. 4) and at all crosslink densities IR/MBTS/S₈ samples have a larger ultimate elongation than IR/DCP at RT. At low to moderate crosslink densities both IR/MBTS/S₈ and IR/DCP extend further at high temperature than at RT. As the crosslink density increases the high temperature extension curves cross the RT curves. There is a particularly sharp decrease in ultimate elongation at 90°C with an increase in crosslink density for IR/MBTS/S₈. This sharp decrease takes place over the same crosslink density range as the drop in UTS at 90°C (Fig. 3). At 90°C IR/MBTS/S₈ vulcanisates of high crosslink density fail at lower extensions than IR/DCP vulcanisates.

Delayed crystallization

As seen in Figure 2, the upturn in the stress-strain curve at elevated temperatures is delayed to higher elongations. This is to be expected because an increase in temperature will necessitate a larger decrease in entropy, resulting from chain alignment, before conditions become favorable for strain-induced crystallization. This is because the melting point of these crystals is the heat of fusion divided by the entropy of

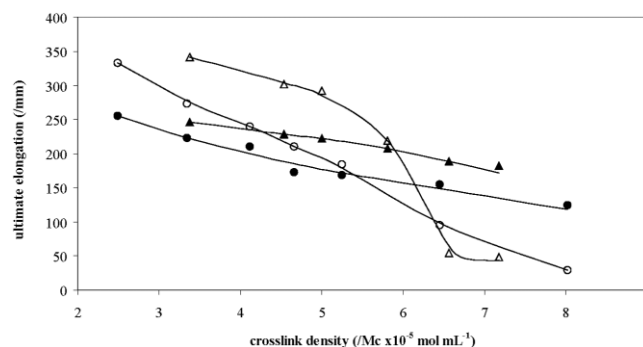


Figure 4 The ultimate elongation of IR/DCP and IR/MBTS/S₈ vulcanisates at RT and 90°C, over a range of crosslink densities ($1/2M_c$). (○) IR/DCP 90°C, (●) IR/DCP RT, (▲) IR/MBTS/S₈ RT, (△) IR/MBTS/S₈ 90°C.

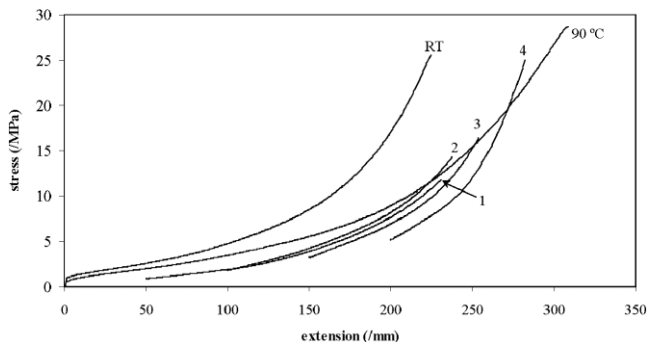


Figure 5 The effect of delaying crystallization on stress-strain curves of IR/MBTS/S₈(I). Curves 1–4 are the further extensions, the normal RT, and 90°C curves are shown for reference.

fusion ($T = \Delta H/\Delta S$). At higher temperatures, the entropy change that thus occurs upon crystallization must be smaller. This necessitates the melt, just prior to crystallization, to be more ordered at higher temperatures than at lower temperatures. Consequently a much greater degree of elongation is required before crystallization at higher temperatures.

This will be referred to as delayed crystallization. At low to moderate crosslink densities, delayed crystallization clearly improves ultimate tensile strength (Figs. 3 and 4).

It is important to understand the effect of delayed crystallization on the stress-strain curve. To investigate this phenomenon further, the following series of experiments were conducted. Samples of IR/DCP(i) and IR/MBTS/S₈(i) were extended at 90°C to various extensions (50, 100, 150, and 200 mm), and held at these extensions for 30 min, during which time stress relaxation occurred. The samples were then cooled to room temperature by the addition of cold water to the water tank and, after allowing 5 min equilibration at this temperature, were extended to break.

Figure 5 shows the stress-strain curves on further extension of IR/MBTS/S₈(i) as well as reference stress-strain curves at RT and 90°C. Similar curves were found for IR/DCP(i). The stress at which the extension starts after samples were held at a given extension and then cooled down, is lower than that of the RT reference curve at the corresponding extension (Fig. 5). This is due, in part, to stress relaxation (crystallization), which occurred when the samples were held at a given strain at 90°C and in part to crystallization and relaxation that resulted on cooling. On further extension the stress-strain curves lie well below that of the RT reference. The initial slopes on further extension are less than slopes of the RT curve at the same extensions, and these differences become more marked as the initial extension before cooling is increased. Note that the 90°C curve has a delayed and less steep upturn in stress than the RT curve (similar to the peroxide vulcanisates in Fig. 2).

The ultimate extensions at break and UTS resulting from the experiments for IR/DCP(i) and IR/MBTS/S₈(i) are compared in Table I. The values are presented as a percentage of the RT maximum values. Delaying crystallization allows the samples to extend further before breaking than a normal RT sample would. Increasing the initial extension results in increased ultimate elongation of the samples. This increase is more dramatic for IR/MBTS/S₈(i) than for IR/DCP(i).

Although delaying crystallization allows all samples to extend further than normal before breaking, IR/MBTS/S₈(i) has a lower UTS than the room temperature extension. The lower the initial extension before cooling, the smaller the UTS value, and only at the highest initial extension (200 mm) measured is a UTS value comparable to the normal (engineering) UTS value. It is not possible to calculate true tensile strength values at break since an extensometer could not be employed, but it is evident from Figure 5 that, in the case when the sample was extended to 200 mm before cooling, the true tensile strength was considerably higher than obtained in a normal RT extension. In the IR/DCP(i) system the UTS values show considerable scatter (Table I), but are generally larger than the (engineering) UTS value of the RT reference. For all vulcanisates the increase in ultimate elongation values follows the same trend as the UTS values.

Thus delaying crystallization allows the samples to extend further before breaking and could increase UTS, depending on the system and the delay.

DISCUSSION

This study confirms that high temperatures delay the development of strain-induced crystalline crosslinks, as indicated by the delayed upturn of the stress-strain curve (Fig. 2). High temperatures will decrease the extent of crystallization that develops. Yet, at lower crosslink densities, both peroxide and MBTS/sulfur vulcanisates have superior tensile strength and ultimate elongation at elevated temperatures (Figs. 3 and 4). At higher crosslink densities the reverse applies.

Stress is dependent on crosslink density [c_p in eq. (1)], and the steep rise in the slope of the stress-strain

TABLE I
The Effect of Delaying Crystallisation on the Tensile Properties of Peroxide and MBTS/S₈ Cured IR

Initial extension at 90°C (mm)	% of RT UTS		% of maximum RT extension	
	IR/DCP	IR/MBTS/S ₈	IR/DCP	IR/MBTS/S ₈
50	126.2	46.1	109.0	102.5
100	90.6	56.0	103.6	105.6
150	131.9	64.3	112.9	112.7
200	112.9	97.8	113.4	125.6

curve at high elongations (Fig. 1) suggests the development of a very large number of strain-induced crosslinks, a much higher number than that are present as chemical crosslinks in the most highly crosslink sample prepared for this study. According to data in Figures 3 and 4, a network containing such a large number of chemical crosslinks should fail at a low strain, and if extended at elevated temperature, at a very low stress. Why then does the increased number of effective crosslinks not simply lead to a brittle network?

It is concluded that it is not simply the number of strain-induced crystalline crosslinks that are important in determining tensile properties, but their distribution within the network. As noted in the Introduction, the crack deflection mechanism would suggest a weakening of a re-extended network, which in turn is not supported experimentally.

Proposed strengthening mechanism

The force (f) required to overcome the decrease in entropy on extension of a chain is given by eq. (2)¹

$$f = \frac{3kT}{R_0^2} \Delta L = b\Delta L \quad (2)$$

where k is the Boltzmann constant; T , the absolute temperature; R_0 , the end-to-end distance in the undeformed chain; ΔL , extension; and b , a stiffness factor.

The force to reach a given extension is greater for a shorter chain, since R_0 is proportional to chain length. Thus shorter chains are effectively "stiffer" than longer chains. In a vulcanisate network, crosslinks represent chain ends, i.e., points of reference that move apart under stress. Equation 2 cannot, however, be applied to vulcanisates, for equivalently spaced crosslink points can be joined by chains of different length. It does still remain true that the shorter a chain, the larger the force required for its extension, i.e., the distance crosslink points are moved apart.

The formation of strain-induced crystals subdivides network chains. On average a chain which undergoes crystallization will be halved in length, creating two stiffer chains, and a larger force will be required to extend these new shorter subchains than for a similar extension of the original longer chain; thereby changing the deformation pattern within the network and forcing other regions of the network to make a larger contribution to load bearing. This decreases the rate of extension of shortened chains and delays their being drawn taut to the point of failure. Thus the site of potential failure (chains or short chain sequences that could become taut to the point of failure) is eliminated by their inclusion in strain-induced crystalline crosslinks and by the redistribution of the deformation

to longer less stiff chains. Only at much larger extensions is a situation reached where chain failure becomes inevitable and a flaw is initiated that propagates and causes catastrophic failure. Strain-induced crystallization not only restricts the extension of certain chains, but by doing so disturbs the chain displacement/extension pattern and delays the development of taut chains that would otherwise lead to early failure. The proposed mechanism increases network strength by delaying failure to a larger extension, and consequently a larger stress. It does not rely on microcracks to form first before the strengthening mechanism comes into play. Note that this mechanism relies only on the formation of a stable crystal nucleus, not the growth thereof.

The addition of more crosslinks on strain-induced crystallization increases the number of chains that have to be extended by the applied force, but this, it is proposed, is not in itself the most important factor in raising the stress because after all too highly crosslinked networks become brittle). Rather, it is the chain shortening, and thereby stiffening of such chains as a consequence of the introduction of strain-induced crystallites as crosslinks, that is important for the strengthening of the network.

Effect of crosslink density

Figure 3 shows that, under the test conditions, strain-induced crystallization occurs sufficiently fast at RT for high tensile values to be achieved over a range of crosslink densities in both peroxide and MBTS/sulfur vulcanisates.

Though shorter chains have lower entropies, they will not necessarily be the first to become part of strain-induced crystalline crosslinks since such shorter, stiffer chains will be more resistant to deformation, i.e., they will resist a further decrease in their entropy. Furthermore, on extension, chains in a solid will not expand uniformly, as would an isolated chain. Instead chain movement will be sporadic and localized, the extension of a sequence of chain segments being determined by transient entanglements and the cooperative movement of segments on neighboring chains. Thus, on extension, the entropy of a portion of the network, comprising segments of adjacent chains in a given region, may momentarily be decreased sufficiently for nucleus formation to occur. As noted earlier, these strain-induced crystalline crosslinks shorten and stiffen chains emanating from the crystallites, forcing further extension to result from the deformation of other, less stiff chains in the network, i.e., the network deformation pattern is altered vis-a-vis deformation in the absence of the introduced crosslinks. The greater degree of alignment of chains at high extensions will further promote strain-induced crystallization, as evidenced by the accelerated in-

crease in slope of stress–strain curves, but at low extensions, strain-induced crystallization will be a more random process, nucleation, in part, being promoted by entanglements of longer chains. This is in accord with literature results, which suggest that the elongation at which crystallization is initiated is almost independent of crosslink density.²³

In vulcanisates of progressively higher crosslink density the chain stiffening is associated with shorter chains, and the increased number of chains opposing deformation will lead to a gradual increase in tensile strength but, at some point, the reduced number of strain-induced crosslinks generated in the stiffer, less entangled network will decrease the contribution such crosslinks make to the network deformation pattern and to load redistribution, and the UTS will decline, as evidenced by the maximum in Figure 3. Increased crosslink densities decrease the average length of chains in the network and this, coupled with reduced load redistribution, will lead to chains being drawn taut to the point of fracture at progressively lower extensions (Fig. 4).

At higher crosslink densities the greater number of subchains and the lower entropy of short chains, which require higher forces for their extension, combine to ensure that the stress–strain curve rises more steeply than for vulcanisates of lower crosslink density (Fig. 2). Furthermore, the lower average entropy of shorter chains will allow an increased number of strain-induced crystallites to form at lower strains and, in terms of the proposed strengthening mechanism, ensure the earlier upturn of the stress–strain curve, as seen in Figure 2.

The more rapid upturn in the stress–strain curve of IR/DCP(i) than that of IR/MBTS/sulfur(i) (Fig. 1) suggests that strain-induced crystallization occurs more rapidly in the peroxide vulcanisate, particularly at high extensions. This is in accord with low temperature crystallization studies of unstrained vulcanisates.^{24–26} The difference in behavior of the vulcanisates will be discussed more fully in a later paper in the series.

Effect of temperature

Literature suggests that increasing the temperature leads to a decrease in physical properties of rubbers that undergo strain-induced crystallization^{11,17,22} (normally ultimate elongations are not reported, only UTS), and that tensile properties relate to the amount of crystallization that occurs on extension.¹⁴ The data in Figure 3 conflict with this.

At elevated temperatures the entropy of chains is raised and a greater decrease of extension is required before nucleation becomes possible because at these temperatures the decrease in entropy on crystallization is smaller. Hence the onset of the upturn in the

stress–strain curve is delayed and slower nucleation ensures that the curve rises less steeply (Fig. 2). The superior tensile properties at elevated temperatures shown by networks of lower crosslink density suggest that, the greater the degree of alignment of chains before they become incorporated into strain-induced crosslinks, the larger the overall extension of the network, and the higher is its load bearing ability. At low crosslink densities delayed crystallization is clearly advantageous.

At high temperatures the upturn in stress is delayed and becomes very small in highly crosslinked samples (Fig. 2). The slower nucleation rate and higher elongation required for nucleation, coupled with reduced entanglements and the reduced crystallizability of highly crosslinked networks,^{14,25,27} prevent sufficient strain-induced crystallization from occurring rapidly enough to ensure chain shortening and a redistribution of the load before rupture. Consequently there is a rapid drop off in UTS and elongation at break at high crosslink densities (Figs. 3 and 4).

The improved physical properties of less crosslinked vulcanisates at elevated temperatures (Figs. 3 and 4) clearly show that the amount of crystallization that forms is irrelevant in determining physical properties, while the very poor physical properties of highly crosslinked samples, that do not undergo strain-induced crystallization before rupture at elevated temperatures, emphasizes the importance of strain-induced crystallization in redistributing the extension pattern of chains.

The deflection of micro-cracks by strain-induced crystallites is not denied, but such deflection is seen as the “last line of defense” before rupture. Such deflection will only occur immediately prior to rupture and will raise the tensile strength marginally; the steady rise in the stress–strain curve observed over an extended range of strain values prior to fracture cannot be supported by the experimental data.

Delayed crystallization

On further extension at RT the initial slope of the stress–strain curve is higher than that of the sample extended at 90°C to the same elongation (Fig. 5), indicating an increase in the number of strain-induced crosslinks or load bearing chains, but lower than that of a sample extended to this strain at RT, indicating a smaller number of crosslinks when compared with that in a RT extended sample.

It was suggested that strain-induced crystal nuclei will form at random in the network, the nonuniform extension of chains due to their transient impediment by entanglements and the degree and extent of cooperative movement of segments on adjacent chains, giving rise to regions in which the entropy is sufficiently low for nucleation. On re-extension after cool-

ing, both DCP and MBTS/S₈ vulcanisates exhibit higher elongations than are achieved on simple extension at RT (Table I). This is attributed to the delay in sporadic nucleation during the high temperature extension. The delay permits a greater degree of extension of chains before their incorporation into randomly generated strain-induced crosslinks and, while the redistribution of the network deformation pattern is essential to prevent chains prematurely being drawn taut to the point of fracture, the early incorporation of chains into crystallites lowers the average chain length in the network and ultimately limits its overall extendability. Ideally, strain-induced crosslinks should form only when and where required to protect vulnerable chains, and not randomly.

In DCP vulcanisates higher UTS values are also achieved than on extension at RT (Table I) and this supports the contention that strain-induced crosslinks should only form as required to prevent premature fracture. With MBTS/S₈ vulcanisates, high UTS values are obtained only when the initial high temperature extension exceeds 200 mm (Table I). When strain-induced crystallization is markedly delayed, both vulcanisates show improved UTS.

The above improvements resulting from delayed crystallization are consistent with the higher UTS and elongation shown by DCP and MBTS/S₈ vulcanisates of lower crosslink density at elevated temperatures. It is not the percentage crystallinity but the distribution of crystalline crosslinks and their effect on the network deformation pattern that determines UTS. Furthermore, early, rapid crystallization may introduce network defects, such as loops, which will at no stage be able to contribute to load bearing.

CONCLUSIONS

In vulcanisates of low crosslink densities an increase in temperature leads to an improvement in tensile properties, but in vulcanisates of higher crosslink density poorer properties result at higher temperatures. Existing theories of strengthening could account for the decrease, at high temperature, in tensile strength of more highly crosslinked vulcanisates in terms of a decrease in the number of strain-induced crystallites available to deflect or impede the propagation of flaws within the network, but it is difficult to adapt the theory to explain the improvement in tensile properties at high temperatures for vulcanisates of lower crosslink density. Instead a new theory to explain the effect of temperature on tensile properties is proposed. Because of the reduction in the entropy of chains as a result of their being shortened by strain-induced crystallization, higher stresses are required for their further extension. The stiffening of these chains results in the preferential extension of other, less stiff chains, and the network deformation pattern is altered.

Strain-induced crystallites form at potentially vulnerable sites in the network, pre-empting rupture, and the slope of the stress–strain curve increases steeply as further strain-induced crystallization increases the force required for continued extension. If strain-induced crystallization is delayed, forcing chains into making a larger contribution to load carrying before chain stiffening transfers further deformation to other chains, higher tensile strengths and elongations at break are possible. At increased temperatures the rate of crystallization is reduced, delaying crystallization and resulting in superior tensile properties. However, where the rate of crystallization is greatly reduced, as in more highly crosslinked networks, rupture may occur before crystalline crosslinks, necessary to alter the deformation pattern, can develop.

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