

Tear Strength of Pre-stressed NR Black-filled Vulcanisates

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Parallel-sided test-pieces prepared from conventional natural rubber (NR) sulfur vulcanisates filled with 50 p.p.h.r. HAF black were pre-stressed to a pre-determined stress level for one minute, after which the loading stress was removed. They were swollen in toluene for 72 hours after which time they were deswollen to remove residual strain, and to allow for rapid elastic recovery. The test-pieces were dried down to a constant weight before carrying out the tear test. Tear deviations from the intended tear path took place if the stress level during pre-stressing was lower than 18 - 20 MPa (ca. 350% strain). Above 20 MPa stress level, the tear did not deviate but propagated along the intended tear path. However, if the samples were cycled a few times even below 18 MPa, no tear deviations from the intended path were observed. Tear measurements on all samples pre-stressed to 23 MPa were conducted at four different temperatures and at various different test speeds. Within the range of test speeds and test temperatures covered in this investigation, tearing energy increased with increasing test speeds. The tearing energy data were amenable to WLF transformations indicating that the tearing process was predominantly associated with viscous processes. Tearing energy of the pre-stressed samples was closely associated with the amount of permanent set produced during pre-stressing (single loading or cyclic loading). The higher the amount of set, the lower the tearing energy.

Keywords: Pre-stressing; cyclic pre-stressing; set; tearing energy; tear rate; mastercurve

It is generally known that vulcanised natural rubber (NR) has excellent tear resistance attributed to its ability to crystallise when highly strained. The tear resistance is further enhanced with the addition of a reinforcing filler. The mechanism for enhancement of tear resistance of the filled NR vulcanisate is due to the phenomenon of knotty tear where the crack splits and deviates sideways, almost perpendicular from the intended tear path. The phenomenon of knotty tear in black-filled vulcanisates is not new. It was

noted by Busse¹ in 1934. However, knotty tear is a complex phenomenon and has attracted wide research work in this area²⁻⁷. Knotty tear not only occurs in vulcanisates containing reinforcing fillers, but also in NR latex films containing no filler⁷. An excellent lecture on “Some Outstanding Problems in the Mechanics of Rubbery Solids” was given by Gent⁸ who delivered his Keynote Lecture at the IRC’08. According to Gent⁸, knotty tear is one of the strengthening features in particle-filled compounds; although the conditions

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under which crack splitting occurs are well known, the cause is still obscure.

However, if the reinforced black-filled NR rubber is pre-stressed to a large strain for a short time scale, after which the stress is removed completely, the tearing energy to propagate tear in the direction of the previously applied pre-stressing is very low⁴. The tearing energy correlates strongly with the amount of set, where tearing energy decreases progressively with increasing amount of set⁴. The set is believed to occur during pre-stressing due to the ability of the broken crosslinks to recombine and form new network consistent with the two-network theory of Green and Tobolsky⁹. The application of such a theory gives a quantitative measure of the proportion of crosslinks which break and recombine under the influence of an applied stress^{10,12}. *Figure 1* below shows the relationship between permanent set and the recombination efficiency n_2/n_1 ¹⁰.

The amount of set produced is very dependent on types and nature of the crosslink network. The type of crosslinks produced is dependent upon the type of vulcanisation system employed in the rubber mix formulation. There are two main sulfur vulcanisation systems, namely the conventional vulcanisation (CV) and the efficient vulcanisation (EV) respectively. The former employs higher sulfur to accelerator ratio than the latter. The CV system produces predominantly polysulphidic type of crosslinks where adjacent rubber chains are bridged by 3 to 6 sulfur atoms. In contrast, the EV system produces predominantly monosulphidic type of crosslinks where the adjacent rubber chains are bridged by one sulfur atom. It is well established that polysulphidic type crosslinks are weak and labile¹¹. Weak crosslinks such as the polysulphidic type usually give higher tensile strength than do stable crosslinks such as the monosulphidic type, because of their ability to relieve local stress through

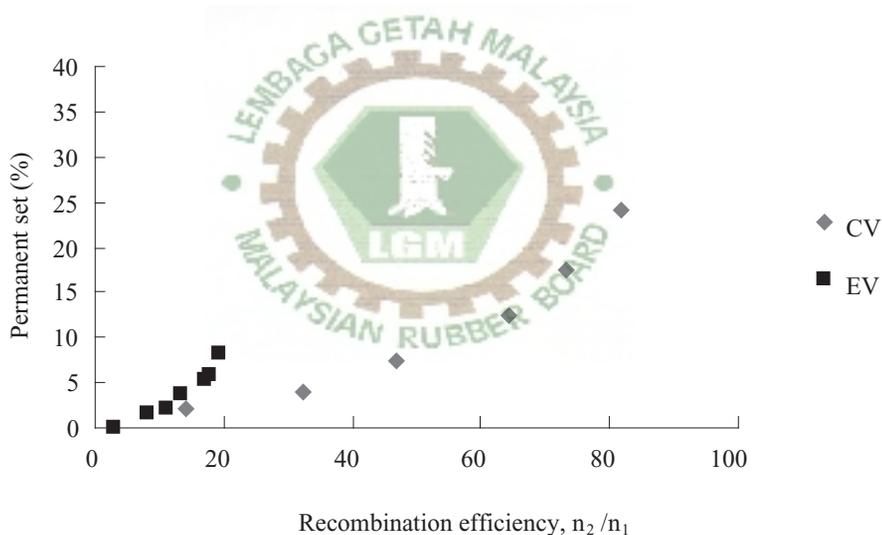


Figure 1. Plot of permanent set against recombination efficiency n_2/n_1 of conventional vulcanisation system (CV) and efficient vulcanisation system (EV) black-filled (50 p.p.h.r. HAF) NR vulcanisates (reproduced from ref. 10).

“yielding”, thereby permitting a more uniform distribution of stress¹¹. This hypothesis has been supported by an independent investigation into the breaking and reforming of crosslinks during stressing¹². Here, the permanent set provides an indication of the number of bonds which have recombined whilst in the deformed state, and the changes in equilibrium volume swelling indicate the fraction of crosslinks which break¹². The earlier findings by the present author *et al.*^{4,10} is very significant in this context because it implies that: in vulcanisates produced by the conventional sulfur system, once the set has occurred during pre-stressing, it is no longer necessary to maintain the stress giving the molecular orientation since the anisotropy associated with the set is adequate to cause crack propagation in the direction of molecular orientation^{6,13,14}. This is clearly an undesirable feature because it can lead to premature failure of the product.

This paper reports and discusses further work on investigating the effect of pre-stressing on the tear behaviour of black-filled NR vulcanisates. Previous work by this author employed single stressing for deformation. In this subsequent work, the effect of repeated stressing was investigated since in practice, rubber products such as tyres, conveyor and V-belts, and rubber mounts are subjected to repeated stresses (dynamic deformations). Thus, this approach is more relevant to practical situations than merely applying a stress in a single cycle.

As a useful adjunct, the method of introducing set at low stress through a two-stage vulcanisation technique is also described; the first stage involves curing the rubber to 95% of its maximum state of cure. The second stage involves curing the rubber (held in a strained state) fully to its maximum state of cure. Thus, the second network is formed in a strained state. This study also has some practical applications, for example in continuous

vulcanisation and in injection moulding. In these cases, vulcanisation is carried out at a high temperature, of 190°C and above, using very fast accelerator systems; because of the very short vulcanisation time (less than a minute), vulcanisation may take place before the rubber completely fills the mould. The effect is analogous to the formation of two networks in the vulcanisates investigated. It is not surprising that the strength properties, such as tensile and tear strengths of injection-moulded test-pieces show a strong dependence on the direction of orientation¹⁵.

Finally, this paper also discusses work to investigate the dependence of tearing energy of pre-stressed black-filled NR on tear rates and temperatures. It is of interest to see whether the tear behaviour of pre-stressed black-filled NR show a similar behaviour to that of unfilled SBR vulcanisates at different test temperatures and tear rates.

EXPERIMENTAL

Materials and Formulations

Tables 1 and *2* show the formulations for natural rubber black-filled compound and unfilled (gum) styrene butadiene rubber compound respectively. All the compounding ingredients are expressed in parts per hundred of rubber (p.p.h.r.).

Mixing and Moulding

All rubber compounds were prepared by mixing the rubber with the compounding ingredients in a laboratory internal mixer in accordance with the formulations shown in *Tables 1* and *2* respectively. The starting mixing temperature was 50°C and the rotor speed was 80 r.p.m. The mixing time was four min. At the end of the four min the mix was discharged

TABLE 1. NATURAL RUBBER CARBON BLACK-FILLED FORMULATIONS

	CV	EV
Natural Rubber (SMR L)	100	100
Zinc oxide	5	5
Stearic acid	2	2
Carbon black (HAF N330)	50	50
*Antioxidant	2	2
Sulfur	2.5	0.6
** MBS	0.5	4.8
# TMTD	-	3.0
Cure time at 150°C (min)	27	50

CV – conventional cure system

EV – efficient vulcanisation system

* Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline

** Morpholinylbenzothiazole-2-sulphenamide

Tetramethylthiuram disulphide

TABLE 2. STYRENE BUTADIENE RUBBER GUM MIX FORMULATIONS

Mix No.	1	2	3	4	5	6
SBR (Intol 1500)	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
*Antioxidant	2	2	2	2	2	2
Sulfur	1.5	1.8	2.0	2.5	3.5	4.0
**MBS	0.3	0.38	0.4	0.5	0.7	0.8
Cure time at 150°C (min)	120	90	80	80	60	60

* Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline

** Morpholinylbenzothiazole-2-sulphenamide

onto a two-roll mill, curatives were added into the mix on the two-roll mill and further mixing took place to disperse and homogenise the mix. The finalised rubber mix was sheeted out to about 4 mm thick sheets. Samples were taken from each rubber mix to determine the cure characteristics using an oscillating disc rheometer at 150°C.

Vulcanised rubber sheets of uniform thickness measuring 150 mm × 130 mm × 0.5 mm were prepared by moulding the rubber

compound in a compression mould heated in an electrical press at 150°C vulcanised to the optimum state of cure. For the case of unfilled SBR, 150 mm × 130 mm × 2.0 mm vulcanised sheets were prepared.

Introduction of Set at Low Stresses by a Two-stage Vulcanisation Process

The rubber mix was initially vulcanised to 80% – 95% state of cure in a compression

mould heated in an electrical press. The reason for choosing these states of cure was to avoid prolonged vulcanisation in the autoclave that might cause degradation. Furthermore, polysulphidic crosslinks are thermally unstable, and prolonged vulcanisation might cause chemical changes within the first network introduced during the first-stage vulcanisation. The second-stage vulcanisation was carried out in an autoclave to the point of maximum state of cure 24 hours later. However, the samples were slightly strained by means of a suitable jig so that the crosslinks introduced during the second stage vulcanisation formed a second network whilst in the strained state, thus simulating the recombination process believed to occur in a polysulphidic network necessary to give the set. Since the rubber was not fully vulcanised, the stress required to extend to 100% extension was low, being less than 2.5 MPa. It is unlikely that such low stresses would rupture the crosslinks.

Pre-stressing of NR Black-filled Vulcanisate

A parallel sided test-piece, measuring 75 mm × 10 mm × 0.5 mm was prepared by using a die on a flat 150 mm × 130 mm × 0.5 mm vulcanised black-filled NR sheet. Two gauge marks of distance l_o , (drawn at the central region of the test-piece) referred to the unstrained state was measured accurately by means of a vernier scale. The test-piece was pulled at a rate of 100 mm per min to a pre-determined stress level. The corresponding extension ratio was noted. The test-piece was held in the extended state for one minute, before unloading the stress. The two ends of the test-piece were cut and discarded since they were compressed by the grips. The uniformly pre-stressed portion of the test-piece was weighed and then swollen in toluene for 72 hours to eliminate both short and long term viscoelastic effects.

The test-piece was then deswollen and dried by evaporation under a strong current of air in a fume chamber. The weight was regularly monitored until it was constant. The permanent set was calculated using *Equation 1* below^{4,10}.

$$\text{Permanent set} = (l_d/l_o) - l \quad \dots 1$$

where l_d is the deswollen dried down length (distance between the two gauge marks), and l_o is the initial distance of the gauge marks on the test-piece before prestressing.

Finally, a cut of about 40 mm was introduced parallel to the direction of the extension previously applied. Unstressed samples were also taken from the same vulcanised sheet as controls. They were swollen under the same conditions as those used for the prestressed samples to avoid complications arising from effects which the solvent might have had upon the samples.

Repeated Pre-stressing

The parallel sided test-piece described above was pulled to a stress level of 12.4 MPa, and then relaxed to zero stress before pulling it again to the same stress level for the desired number of cycles required. The apparent set was measured one minute after the completion of all the cycles. The apparent tension set was calculated using *Equation 2* below.

$$\text{Apparent tension set} = (l_e - l_o)/l_o \quad \dots 2$$

where l_e is the length of the gauge mark in the central region of the test-piece measured one minute after the completion of the cycle, and l_o is the original gauge mark before pre-stressing.

A cut was introduced parallel to the direction of cyclic pre-stressing.

Tear Measurement

Tearing was carried out by separating the legs of the trouser test-piece using an Instron tensile machine at test speeds ranging from 5 mm per minute to 1000 mm per minute. A temperature cabinet was used for measurements at temperatures above 24°C. Outside the range of test speeds covered by the machine, tearing was done by using the constant load method. In the case of constant rate separation method, the tear rate was half the crosshead speed (extension rate)¹⁶. In the case of constant load method, the tear rate was obtained from the slope of the straight line of the crack length versus time plot. The tearing energy, T , for the trouser test-piece was determined using Equation 3 given below^{4,16}.

$$T = F(\lambda + 1) / h \quad \dots 3$$

where F is the force to propagate tearing, λ is the extension ratio in the legs of the test-piece and h is the average nominal thickness of the test-piece.

Measurement of Relative Crosslink Concentration

The crosslink concentration measurement was done by means of an equilibrium swelling technique as suggested by Porter¹⁷. Samples were weighed accurately using an electronic analytical balance. They were then swollen in n-decane at 25°C until equilibrium swelling was attained (*i.e.* when the swollen weight became constant). The equilibrium swollen weight was determined first before drying the samples in a vacuum oven at 50°C until the weight was constant. The final weight of the dried samples was noted. The crosslink concentration of the vulcanisate was calculated using the familiar Flory-Rehner¹⁸ equilibrium swelling Equation 4 given below.

$$-\ln(1 - v_r) - v_r - \psi v_r^2 = 2 \rho V_o [X]_{phy} v_r^{1/3} \quad \dots 4$$

where v_r is the volume fraction of rubber in the swollen sample, ψ is the rubber-solvent interaction parameter, ρ is the density of rubber hydrocarbon, V_o is the molar volume of solvent and $[X]_{phy}$ is the physically manifested crosslink concentration. Correction for the filler occupied in the vulcanisate was made using Equation 5 below¹⁷.

$$[X]_{act} = [X]_{phy} / (1 + kc) \quad \dots 5$$

where $[X]_{act}$ is the actual crosslink concentration, k is a constant characteristic of the filler and has a value of 2.6 for HAF black, and c is the volume fraction of carbon black in the vulcanisate.

RESULTS AND DISCUSSIONS

Effect of Repeated Stressing on Tension Set

Figure 2 shows the variations of permanent set as a function of the applied stress. The permanent set increased as the magnitude of applied stress during pre-stressing was increased. This was attributed to the fact that the recombination efficiency of the broken crosslinks increased since the probability of the broken links to recombine was high as fractions of crosslinks broken increased with increasing stress level¹⁰. Results in Figure 2 show that if the applied stress during pre-stressing was below 15 MPa, the permanent set was lower than 10%. Previous work^{4,10} indicated that knotty tearing still took place if the permanent set was lower than 10%. However, this paper discusses the effect of repeated pre-stressing at low stress on the set and tearing energy of conventional cure black-filled NR vulcanisates. The result of this investigation is as shown in Figure 3 where the “apparent set” is plotted against the

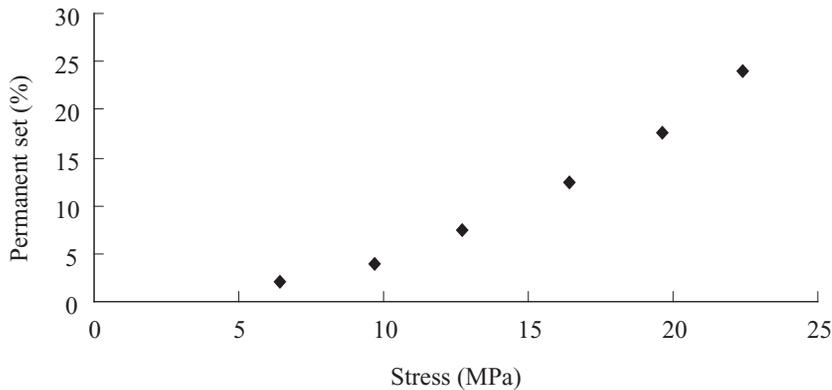


Figure 2. Permanent set vs. stress of conventional cure black-filled NR vulcanisate.

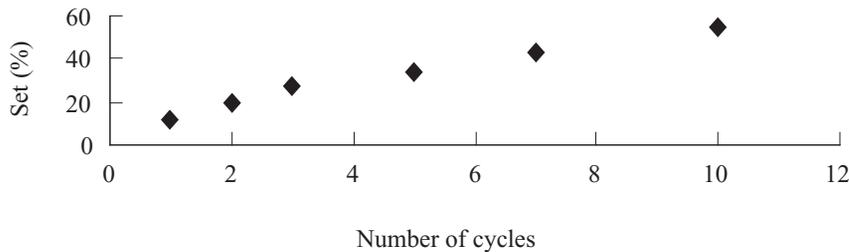


Figure 3. Effect of repeated stressing on set (measured 1 minute after the completion of the cycles) of NR black-filled vulcanisate. The stress at each cycle was maintained at 12.4 MPa.

number of cycles. The apparent set increased with the number of pre-stressing cycles. The apparent set was more than 30% after five cycles. The apparent set is different from the permanent set since the former includes contribution from viscoelastic effects as well as that of recombination of broken crosslinks. In the case of the permanent set, the amount of set excludes that of viscoelastic effects. For this reason the apparent set is higher than the permanent set.

Effect of Set on Tearing Energy

The effect of set on tearing energy of black-filled NR in the direction of pre-stressing is

shown in Figure 4. The tearing energy decreased progressively as the amount of set was increased. The decrease in the tearing energy is associated with the set which introduces anisotropy as a consequence of the formation of a second network during pre-stressing¹²⁻¹⁴. According to Rivlin and Thomas^{13,14}, if the number of links per chain segment in the second network is much less than that in the first network, the tearing energy is much less for tearing parallel to the direction of pre-stressing than for tearing perpendicular to it. Indeed, Gent *et al.* developed model cracks and used FEA to calculate the tearing energy both in the forward and sideways directions. They found that a crack will turn or split sideways if the strength in that direction

was about 40% less than that of the forward direction⁶. It was observed that below 10% set, knotty tearing still took place. However, when the set was more than 15%, steady or smooth tearing took place. Thus, it appears that 15% set is adequate to provide the 40% less energy for the tear to split and propagate in the direction parallel to pre-stressing imposed to meet the anisotropic requirements as proposed by Gent *et al.*⁶. The results obtained here are consistent with the work reported earlier⁴.

Set Introduced During Second Stage Vulcanisation

Set was measured 7 days after the completion of the second stage vulcanisation after allowing the samples to relax at 24°C, to eliminate any viscoelastic effects. When swelling and deswelling were carried out after the 7-day period, the set value was still the same confirming that the set measured after 7 days was associated solely with the second network introduced by the crosslinking which occurred during the second stage

vulcanisation. *Table 3* shows some important data from this study.

Very high set can be obtained from second stage vulcanisation depending on the magnitude of strain imposed during vulcanisation, although the percentage of cross-link introduced during the second stage vulcanisation, q_2 was relatively low. During tear measurements it was found that the tearing energy to propagate tear in the direction parallel to the applied stress decreased substantially with increasing set. The magnitude of the tearing energy was about one tenth of the control sample (fully cured during 1st stage vulcanisation) which produced knotty tear with high tearing energy. Tear measurements across the orientation (perpendicular to the direction of imposed strain during 2nd stage vulcanisation) was about a factor of 9 or 10 higher than tearing energy parallel to orientation. This clearly indicates that a two-network vulcanisate indeed produced anisotropy of strength as reflected by the difference in the tearing energies for crack propagation in the direction parallel and

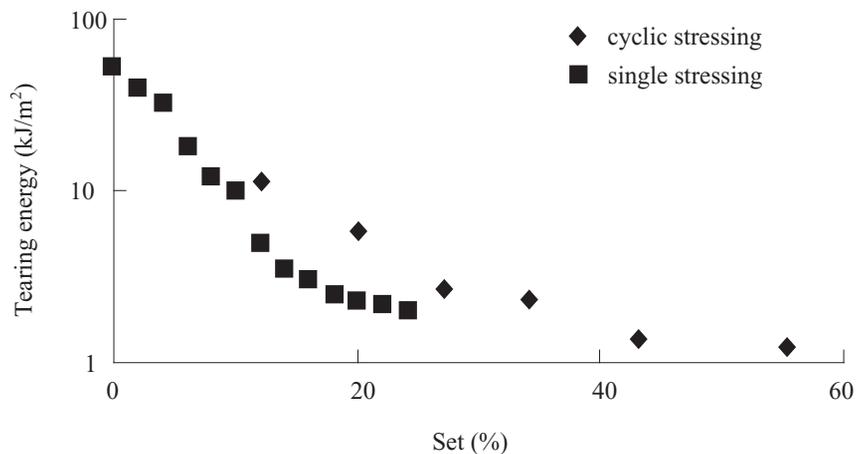


Figure 4. Effect of set on tearing energy of conventional cured black-filled NR vulcanisate at 24°C and crosshead speed 100 mm per minute.

TABLE 3. EFFECT OF SECOND STAGE VULCANISATION ON SET AND TEAR

1 st stage vulcanisation.	t_{100}	t_{80}	t_{95}	t_{95}	t_{95}	t_{95}
Cure time at 140°C (min)	50	24.5	35	35	35	35
$[X]_1 \times 10^{-2}$ mol/kg RH	7.06	6.11	6.64	6.64	6.64	6.64
2 nd stage vulcanisation at 140°C						
Time to reach t_{100} (min)	-	25	15	15	15	15
Strain imposed (%)	0	100	50	75	100	125
$[X]_2 \times 10^{-2}$ mol/kg RH	-	7.04	7.05	7.05	7.05	7.05
q_1 (%)	100	87	94	94	94	94
q_2 (%)	-	14	6	6	6	6
Set (%)	-	60	25	40	50	60
T (kJ/m ²) parallel to orientation	35	2.6	3.5	3.2	2.7	2.2
T (kJ/m ²) across the orientation	-	-	33	-	-	-
Types of tear	k	s	s	s	s	s

t_{100} = cure time to reach full state of cure

t_{80} = cure time to 80% state of cure

t_{95} = cure time to reach 95% state of cure

Percentage of crosslink concentration introduced during 1st stage vulcanisation q_1 .

$q_1 = [X]_1/[X]_2 \times 100\%$

Percentage of crosslink concentration introduced during 2nd stage vulcanisation q_2 .

$q_2 = 100\% - q_1$

$[X]_1$ = crosslink concentration measured after completion of 1st stage vulcanisation

$[X]_2$ = crosslink concentration measured after completion of 2nd stage vulcanisation

k = knotty tearing

s = smooth (steady) tearing

Test speed = 100 mm per min

Temperature = 24°C

transverse to molecular orientation, in accord with the hypothesis put forward by Rivlin and Thomas^{13,14}.

Imposing high mechanical stress on EV black-filled NR did not produce high set necessary for the anisotropy to produce smooth tear in the direction of pre-stressing. This might be attributed to the higher bond strength and stability of the monosulphidic crosslink than polysulphidic crosslinks. However, it is possible to introduce high amount of set in EV black-filled NR vulcanisate by the two-stage vulcanisation method discussed above. The results are shown in *Figure 5* below where tearing energy is plotted against set. The amount of set introduced into the EV black-filled NR vulcanisate ranged from 23% to 40%. The tearing energy was very low comparable

with that of pre-stressed CV black-filled NR vulcanisate.

The results obtained from this work indicated that the tearing energy to propagate tear in the direction parallel to applied pre-stressing is low provided that the amount of set is relatively high. The tearing energy is not dependent on the method of introducing the set, but relies on the magnitude of the set produced.

Effect of Rate and Temperature on Tearing Energy of Pre-stressed NR Black-filled Vulcanisate

This section of the paper discusses the effects of rate and temperature of tear

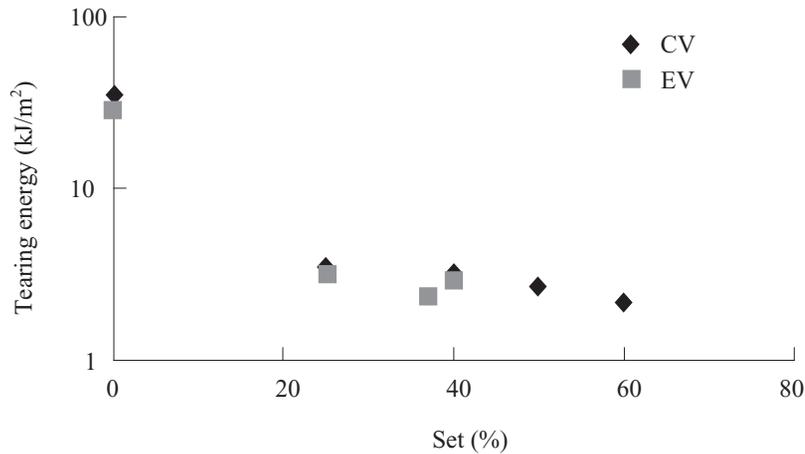


Figure 5. Tearing energy vs. set introduced during second stage vulcanisation.

measurement on the tearing energy of pre-stressed black-filled NR vulcanisate. All the samples were pre-stressed to 23 MPa in order to get high set. The samples were swollen, deswollen and dried to constant weights before carrying out tear measurements.

Figure 6 shows the tearing energy versus rate at four different test temperatures. All test-pieces produced smooth tearing. The tearing energy increased with increasing tear rate at each test temperature. At any tear rate, the tearing energy also increased as the temperature was decreased. This is a clear manifestation of the viscoelastic behaviour of the rubber. At low temperatures and high tear rates, tearing energy increased because energy dissipations were higher than either at low tear rates or high temperatures. An attempt was made to construct a mastercurve of the data shown in Figure 6 using the WLF Equation 6 shown below.

$$\log a_{\theta} = -8.86(\theta - \theta_s)/(101.6 + \theta - \theta_s) \quad \dots 6$$

where a_{θ} is the shift factor by which the rate must be multiplied to shift the points

to a mastercurve, θ is the temperature of measurement, θ_s is a reference temperature ($\theta_s = \theta_g + 50^{\circ}\text{C}$) where θ_g is the glass-transition temperature of the vulcanisate. The θ_g of the vulcanisate was determined from DSC measurements and was found to be -68°C for black-filled NR and -56.5°C for gum SBR. The two temperatures (θ_s and θ) were expressed in degrees Kelvin. Figure 7 shows the tearing energy mastercurve obtained by plotting tearing energy against reduced rate. The former is on a linear scale since the range of tearing energy values were small. In contrast, the latter is on a log scale because of the wide range of tear rates covered. All the points lay satisfactorily around the mastercurve. The results show that tearing energy increased progressively with rate, implying that energy dissipation is an important factor in affecting the strength.

The tearing energy reduced rate relationship at a very low rate of $10^{-6} \mu\text{m/s}$ was obtained from constant load measurement. This method of tear measurement is suitable only for non-strain crystallising rubbers which exhibit time dependent tearing. Indeed, pre-stressed black-filled NR vulcanisate showed time dependent

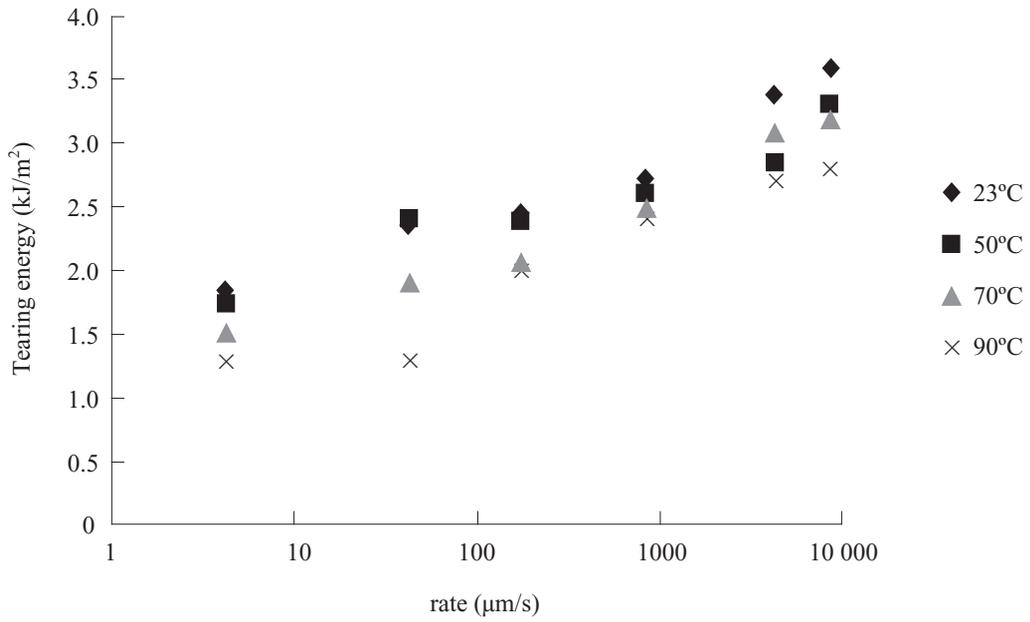


Figure 6. Tearing energy vs. rate at four different temperatures.

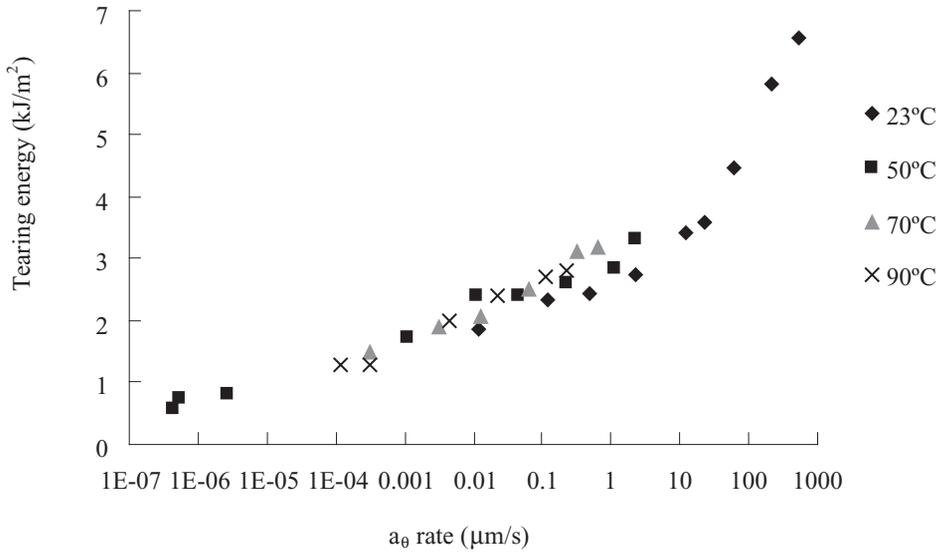


Figure 7. Tearing energy mastercurve of pre-stressed black-filled NR vulcanisate.

tearing where the crack length increased with time when subjected to constant load. Time dependent tearing under constant load is not normally observed in both unfilled and black-filled NR in the absence of pre-strain history¹⁹ because crystallisation and alignment of the black filler around the crack tip prevents time dependent crack-growth. It therefore appears as if the set (strictly speaking the second network) formed during pre-stressing interferes with strain-crystallisation at the tear tip perhaps by discouraging the chain segments from adopting the regular configuration which are necessary to induce crystallisation. Otherwise, time-dependent tearing will not occur. This is another clear evidence indicating that the tearing process involved was controlled by the viscous behaviour of the material. Indeed, as suggested by Gent *et al.*, for all rubbery materials, a direct relation is known to hold between tear strength and internal viscosity^{6,22}. However, the mechanism by which high internal viscosity is translated into high strength is not entirely clear⁶. Further insight of the phenomenon of time-dependent tearing of elastomers have been published by Lake *et al.*¹⁹ and Busfield *et al.*²⁰ respectively.

It is of interest to see whether pre-stressed black-filled NR vulcanisate shows similar behaviour with that of the unfilled SBR vulcanisate. *Figure 8* shows the tearing energy versus tear rate plot of the unfilled SBR vulcanisate. Indeed, the tearing energy-rate relationship follows the same trend as that shown in *Figure 6* above for the pre-stressed black-filled NR vulcanisate. The tearing energy increased either when the rate was increased or when the test temperature was decreased which is in accord with the time-temperature superposition principle. Tearing energy mastercurve for the unfilled SBR vulcanisate was obtained by the same method discussed above for the pre-stressed black-filled NR vulcanisate. *Figure 9* shows the tearing energy mastercurve for unfilled SBR where tearing

energy was plotted against reduced rate. The result is very similar to that of the pre-stressed black-filled NR. It is interesting to compare the two tearing energy mastercurves, *i.e.* *Figure 7* with that of *Figure 9*. At reduced rates from 0.01 $\mu\text{m/s}$ to 100 $\mu\text{m/s}$, the tearing energy of pre-stressed black-filled NR vulcanisate produced tearing energy ranging from 2.0 kJ/m^2 to 4.5 kJ/m^2 , while that of unfilled SBR gave tearing energy ranging from 1.0 kJ/m^2 to 7.0 kJ/m^2 . At very low reduce rates, the tearing of pre-stressed black-filled NR gave marginally higher tearing energy than unfilled SBR. However, at moderate and high rates, the unfilled SBR vulcanisate gave significantly higher tearing energy than pre-stressed black-filled NR vulcanisate. This result indicates that, at high rates unfilled SBR vulcanisate gave higher energy dissipation than pre-stressed black-filled NR. The tear strength increased in the ascending order of the glass transition temperature Θ_g of the rubber. SBR has higher Θ_g than NR, and dissipated more energy than NR. It appears that the carbon black in the black-filled NR vulcanisate, after being pre-stressed did not contribute much energy dissipation. However, it should be noted that tearing energy is also affected by the crosslink concentration^{4,11,21}. Although both black-filled NR and gum SBR vulcanisates contained the same amount of sulfur (2.5 p.p.h.r.) and accelerator (0.5 p.p.h.r.) but the crosslink concentration might not necessarily be the same because the kinetics of sulfur vulcanisation for each rubber is different. This factor has not been taken into consideration when comparing data in *Figure 7* and *Figure 9*.

The effect of sulfur content on tearing energy of unfilled SBR was also investigated as shown in *Figure 10*. The tearing energy increased as the tear rate increased at each sulfur content. At any tear rate, the tearing energy decreased as the sulfur content was increased. This might be attributed to lower energy dissipation at high sulfur content

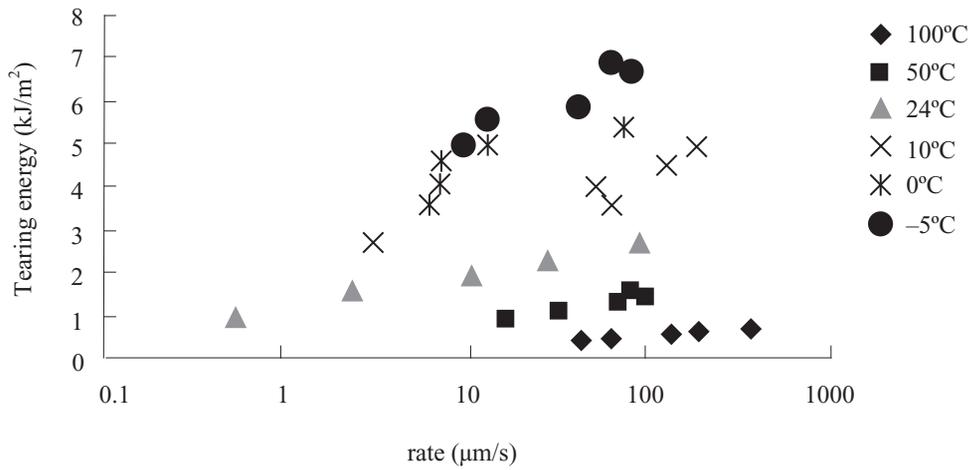


Figure 8. Effect of temperature on tearing energy of unfilled SBR.

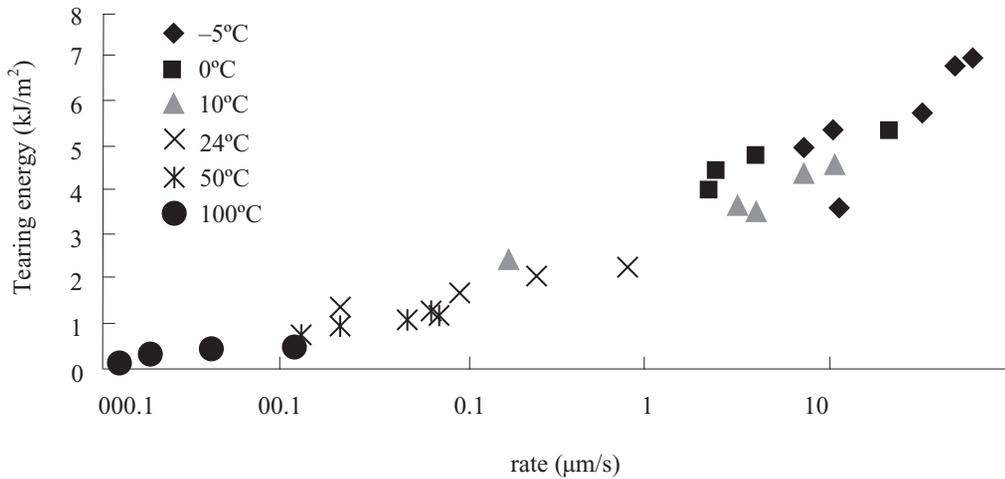


Figure 9. Tearing energy mastercurve of unfilled SBR with sulfur content of 2.5 p.p.h.r.

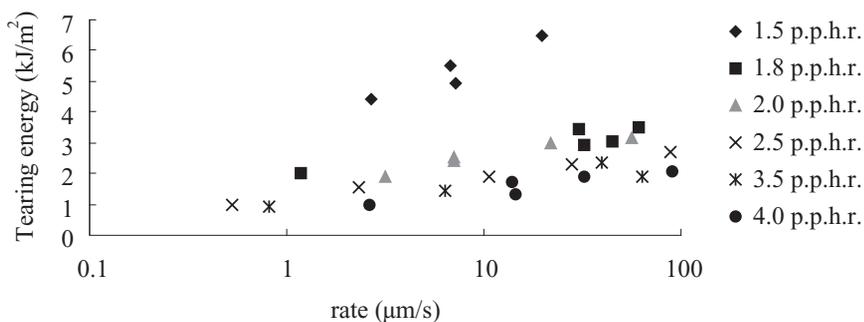


Figure 10. Effect of sulfur content on the tearing energy of unfilled SBR at 24°C.

than at low sulfur content, since the former gave higher crosslink concentration than the latter.

CONCLUSIONS

The pre-stressed black-filled NR vulcanisates showed the following tear characteristics:

- Knotty tear was suppressed and smooth tearing occurred.
- Time-dependent tearing took place (in the direction of previously applied pre-stressing) when subjected to constant load.
- Tearing energy decreased as the amount of set increased.
- Tearing energy was not affected by the method of introducing the set, but affected by the magnitude of the set.
- Repeated stressing at low stress level has similar effect like single stressing at high stress level.
- Tearing energy – tear rate relationship is similar to that of unfilled SBR.

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