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Tearing of Unvulcanised Black-filled Natural Rubber

AZEMI BIN SAMSURI*

Tear behaviour of unvulcanised black-filled natural rubber (NR) was investigated by using trouser tear test-pieces. Although the unvulcanised rubber is easily deformable and flows under large deformation, it was found that tearing was not greatly affected by the lack of perfect elasticity of the rubber

Tearing energy of unvulcanised black-filled NR increases with tear rate; this might indicate that tear behaviour is predominantly controlled by viscoelastic effects Mooney viscosity of black-filled masterbatches affect both the tearing energy and type of tear failures. High Mooney viscosity black masterbatches produce higher tearing energy than low Mooney viscosity masterbatches. The effect is more pronounced at low rates than at high rates of tearing. High Mooney viscosity masterbatches also produce small scale stick-slip tearing. The degree of stick-slip tearing is more pronounced at high rates than at low rates of tearing. Low Mooney viscosity black masterbatches produce steady tearing over all the range of tear rates investigated here.

Three properties of unvulcanised rubbers which are important to rubber technologists are flow behaviour, greenstrength and tack. Rheological study of flow and deformation can provide information on the processability of the rubber, for example in mixing, calendering and extrusion. For rubber stocks that are intended for use in tyre manufacture, the unvulcanised rubber should also possess high greenstrength and tack.

Rheological properties of unvulcanised NR have been characterised[1]. However, there is a lack of information regarding the greenstrength of unvulcanised black-filled NR. Greenstrength of rubber can be defined as resistance to deformation and fracture before vulcanisation[2]. The tack of a rubber can be defined as the ability to resist separation of surfaces after being brought into contact for a short time under light pressure[2]. While tack is certainly essential to hold the many components of a green tyre together until the moulding stage, a high greenstrength is equally essential for the green tyre, to avoid tearing during expansion in the second stage of the construction of a radial tyre.

Greenstrength of unvulcanised rubber is usually reflected by its tensile strength. However, in the present study, greenstrength of unvulcanised rubber is measured in terms of the tearing energy based on fracture mechanics which has been successfully used in various studies of the fracture of vulcanised rubbers[3,4].

Kadir and Thomas[3] have carried out work on the tearing of unvulcanised unfilled NR by

*Rubber Research Institute of Malaysia, P.O Box 10150, Kuala Lumpur, Malaysia

using trouser and pure shear test-pieces. They found that the tearing energy concept which had been used successfully to describe fracture of vulcanised rubber is equally applicable in describing the fracture of unvulcanised rubber, provided that considerations are taken into account for the poor elasticity of unvulcanised rubber.

The present work is concerned with the tearing of unvulcanised black-filled NR which is more relevant to practical situation than unfilled rubbers. The effects of mastication of raw NR and black-filled masterbatch on tear behaviour and strength were investigated.

EXPERIMENTAL

Materials

Commercially available SMR 20 and the normal structured HAF N330 carbon black were used throughout the investigation.

Mixing

All mixing and premastication work were carried out by using 2-roll mill (size 30.5 cm × 15.2 cm) at a temperature of 50°C unless stated otherwise. The quantity of HAF black used for each mix was 50 p.p.h.r. No other compounding ingredients were used in the mix. Three different methods of mixing were employed as described below.

Method 1. In *Method 1*, four portions of raw NR (each weighing 500 g) were taken from SMR 20 bale. Each portion was masticated to a different degree of breakdown to produce four different values of Mooney viscosity of raw NR, M_L (1 + 4) 100°C, (denoted as V_R). Mixing was carried out by adding carbon black into the rubber once a coherent band of rubber formed on the mill. Cutting and folding of the rubber band were carried out in the usual way to improve carbon black dispersions and uniformity of the mix. Mixing was completed after 15 min, after which the mix was sheeted out and stored in a dark cool place (23°C). No further mastication was carried out. Mooney viscosity of the masterbatch, M_L (1 + 4) 100°C, (denoted as V_B) was determined 48 h later by means of a Mooney viscometer.

Method 2. A black-filled NR masterbatch was prepared in an OOC Banbury at 80°C for 3 min at rotor speed of 80 r.p.m. Three portions (each weighing 500 g) were taken out of the masterbatch. Each portion was masticated to a different extent of breakdown to produce three different values of Mooney viscosity of masterbatch (V_B). No further mastication was carried out after this operation. V_B was determined 48 h later.

Method 3. Raw NR taken from SMR 20 bale was divided into four equal portions (each weighing 500 g) and masticated to different degrees of breakdown to produce different values of V_R. Mixing with HAF black was carried out for 15 min. V_B of each masterbatch was determined 48 h later. After knowing the V_B, post-mastication was carried out on each masterbatch to a standardised V_B of 57 Mooney units. No further mastication was carried out after this post-mastication.

Moulding

Sheets of unvulcanised black-filled masterbatch (15.2 cm × 12.7 cm × 0.2 cm) were pre-pared by moulding using a Hirahara electrical press, under a pressure of 13 MPa at 120°C for 10 min. Moulinex sheets were used to facilitate stripping the moulded sheets from the mould. Precaution was also taken to prevent any entrapped air in the mix by venting the mould three or four times at the start of the moulding.

Preparation of Trouser Tear Test-pieces

Rubber sheets carefully stripped off from the moulinex sheets were talced to avoid sticking. The talced rubber sheets were left at least 24 h (at room temperature) to allow the rubbers to recover their unstrained dimensions. Trouser test-pieces were prepared by stamping a die on the rubber sheet. Some trouser test-pieces with cotton fabric bonded on the surface (using a proprietory bonding agent) to prevent extension in the legs of the test-piece were also prepared. Using a sharp blade in a holder running on guides, accurately aligned scoring cuts could be made on the fabric backing surface to a controlled depth (*ca* one fourth of the total thickness) to enable the crack to propagate along the intended path[5].

Tear Measurement

Tearing was carried out by separating the legs of the trouser test-pieces at various uniform crosshead speeds by using the Instron tensile machine. All tear measurements were carried out 24°C unless stated otherwise. In the fabric backed trouser test-pieces, to facilitate the measurement of the torn zone, talc was sprinkled and coated along the scored line so that the freshly torn zone surfaces could be easily distinguished from the talced surface. The width of the torn zone was measured by means of an eye-piece lens scale.

The extension ratio, (denoted by λ), in the legs of the test-piece was determined by measuring the distance between the two bench marks on the legs of the test-piece. Alternatively, λ could also be determined from the stress-strain curve. Greensmith and Thomas[3,6] have shown that when tearing occurs steadily, the average rate of crack propagation, *r*, is half the speed of the cross-head separating the legs of the trouser test-piece. This approach was also adopted in this investigation.

Determination of Stored Energy Density

The stored energy density (*i.e.* work done/unit volume) denoted by *U*, was determined by carrying out stress-strain measurement on dumb-bell test-pieces using an Instron tensile machine at crosshead speed of 100 mm/min at

TABLE 1. TEARING ENERGY OF UNVULCANISED BLACK-FILLED NR PRODUCED FROM *METHOD 1* OF MIXING

*V_R	*V_B	*r = 8.30	r = 42	r = 83	r = 170	r = 420
90.5	88.5	*T = 3.28	T = 4.51	T = 5.34	T = 7.37	T = 7.66
70.5	82.0	T = 3.09	T = 3.89	T = 5.01	T = 6.52	T = 8.51
60.0	80.0	T = 2.50	T = 3.64	T = 4.11	T = 4.25	T = 7.30
45.0	70.5	T = 2.34	T = 3.88	T = 3.98	T = 3.72	T = 7.18

*V_R - Mooney viscosity of raw NR, M_L (1 + 4), 100°C – Mooney units
V_B - Mooney viscosity of black-filled NR masterbatch, M_L (1 + 4), 100°C – Mooney units
Tear rate (r) µm s^{-1}
Tearing energy (T) kJ m^{-2}

24°C. The value of U was calculated from the area under the extension stress-strain curve[3,7,8].

RESULTS AND DISCUSSIONS

Effects of Mastication of Raw NR on the Mooney Viscosity of Black-filled Masterbatch (V_B) and Tearing Energy

It is quite a common practice for raw NR to be premasticated first before mixing is carried out. Premastication is necessary in order to reduce the molecular weight and viscosity of the rubber to improve flow and facilitate the subsequent mixing and other shaping processes. Kadir and Thomas[3] have found that tearing energy of unvulcanised unfilled NR increased with increasing V_R. It is of interest to check whether or not the tearing energy of unvulcanised black-filled NR is affected by V_R. *Table 1* shows the tearing energy data of unvulcanised black-filled NR prepared by *Method 1* of mixing. The four different values of V_B shown in the table were a direct consequence of premasticating the raw NR to different values of V_R (ranging from 90 to 45 Mooney units). *Method 1* did not appear to be an effective means of producing a wide range of V_B. This is clearly reflected in the results where for a wide range of V_R only produced a narrow range of V_B (ranging from 88.5 to 70.5 Mooney units) for the corresponding masterbatches. The V_B values were still considerably high. The effects of V_B and tear rate on tearing energy are discussed below.

The effects of V_B on tearing energy can still be observed inspite of the narrow range of V_B. The results show that tearing energy increases with V_B; this trend being more pronounced at tear rates lower than 420 μm s^{-1}. At a low tear rate (8.3 μm s^{-1}), the tearing energy of high Mooney viscosity masterbatch (V_B 88.5) is 1.4 times higher than the tearing energy of low Mooney materbatch ($V_B = 70.5$). It appears that the increase is predominantly affected by the final Mooney viscosity of the black-filled masterbatch (V_B), rather than by the Mooney viscosity of raw NR (V_R), since the increase in tearing energy is consistent with the small increase in the V_B (by about 1.3 times from V_B 70.5 to 88.5) compared with the large increase *in* V_R *(by a factor of 2 from* V_R *45 to 90.5)*. At high tear rates, the effect of V_B on tearing energy was not very significant at this particular narrow range of V_B.

Effects of Tear Rate on Tearing Energy

For each masterbatch, tearing energy increases with the tear rates. However, the effects are more pronounced with low V_B than with high V_B masterbatches. The tearing energy increases by a factor of about 3 for low V_B (70.5 Mooney units) compared with an increase by a factor of about 2 for high V_B (88.5 Mooney units) masterbatch as the tear rate increases from 8.3 μm s^{-1} to 420 μm s^{-1}.

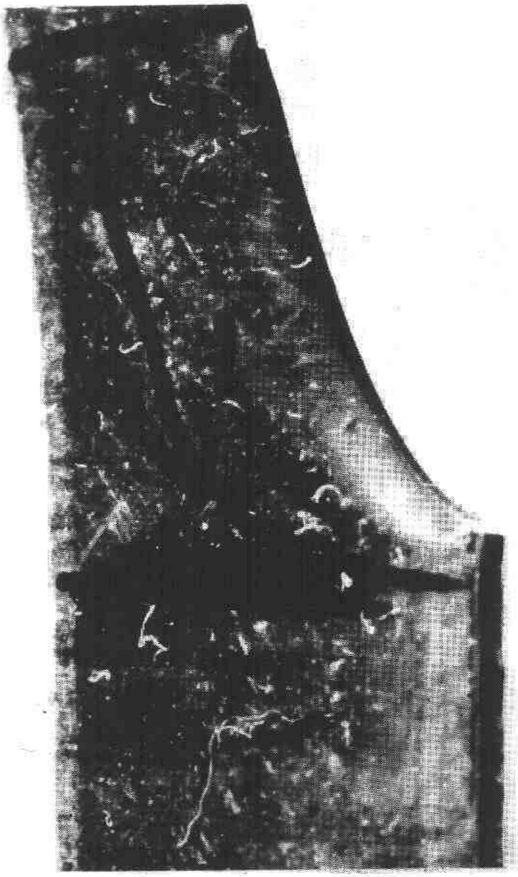
Type of Tearing

The Mooney viscosity of the masterbatch also affect the type of tearing. Small scale stick-slip tearing was observed with high Mooney viscosity masterbatches. The fractured surface was rough as shown in *Figure 1a*. The degree of stick-slip tearing became very marked at high tear rate. Smooth or steady tearing was observed with low V_B masterbatches. Low tear rates also favoured steady tearing. The fractured surface is relatively smooth as shown in *Figure 1b*.

Effects of Post-mastication of Black-filled Masterbatch

Table 2 shows the tearing energy data of unvulcanised black-filled NR prepared by *Method 2*. In this method, black-filled NR

(a) Stick-slip tearing (V_B = 88.5 Mooney units)
T = 15 kJ m^{-2} r = 8300 μm s^{-1}



(b) Smooth tearing (V_B=70.5)
T = 14 kJ m^{-2}
r = 8300 μm s^{-1}

Figure 1. Photographs showing fractured surface of unvulcanised black-filled NR.

masterbatch was first prepared in the Banbury and further mastication was carried out on the 2-roll mill to a varying degree of breakdown. This method produces low V_B masterbatches. The results show that the tearing energy increases both with increasing V_B and increasing tear rates.

Figure 2 shows the plot of tearing energy *versus* V_B based on the data shown in *Tables 1* and *2*. Generally, tearing energy increases progressively with increasing V_B. However, the effect of V_B on tearing energy was not very large as reflected by a small change in the tearing energy for a large change in V_B. Results also indicate that the tearing energy was not affected by different routes of mastication (*i.e. Method 1* or *Method 2* of mixing) but only by the final V_B of the masterbatch.

Table 3 shows the tearing energy data of unvulcanised black-filled NR produced by

TABLE 2. TEARING ENERGY OF UNVULCANISED BLACK-FILLED NR PRODUCED BY *METHOD 2* OF MIXING

Initial V_B	Final V_B	r = 42	r = 170	r = 420
80.0	66.5	T = 4.88	T = 6.44	T = 6.42
80.0	39.0	T = 4.11	T = 6.35	T = 6.41
80.0	20.5	T = 2.90	T = 4.58	T = 5.47

V_B, *r and* T *carry the same meaning and units as described in Table 1.*

TABLE 3. TEARING ENERGY OF UNVULCANISED BLACK-FILLED NR PRODUCED FROM *METHOD 3* OF MIXING

Sample	V_R	V_B	Equalised V_B	T (kJ m^{-2})
A	79.0	90.0	57.0	5.10
B	75.0	87.0	56.5	5.80
C	55.0	84.5	56.5	5.90
D	21.0	57.0	57.0	6.46

r = 170 μm s^{-1} at 23°C

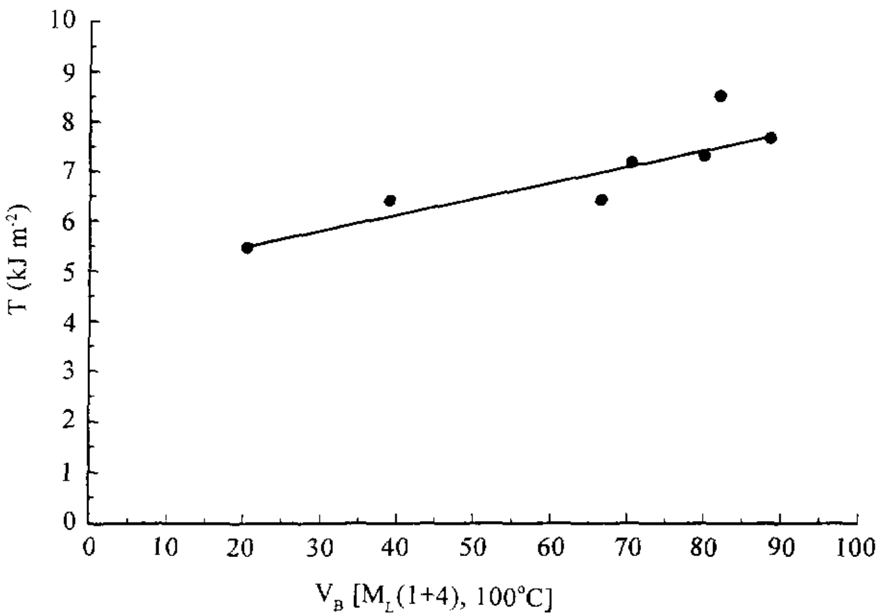


Figure 2. Tearing energy (T) versus V_B *: rate 420 μm s^{-1}; Temp. 24°C.*

Method 3. In this method, raw NR was premasticated to different V_R and later mixed with the HAF black (similar to *Method 1*) to produce black masterbatches with different values of V_B. Each masterbatch was then post-masticated to a single Mooney value of 57 Mooney units (corresponding to the lowest V_B in one of the masterbatches). These particular mixes were prepared to see whether the history of premastication of the raw NR still persisted or not after the black-filled masterbatch obtained was post-masticated to a single masterbatch Mooney viscosity.

Figure 3 shows a plot of tearing energy *versus* V_B of unvulcanised black filled NR. Points indicated by *a* are the tearing energies —V_B relationship based on data shown in *Table 3*, and line *b* shows the tearing energy — V_B relationship based on data shown in *Table 1*. Points *a* indicate a variation in the tearing energy although the V_B of the black masterbatches had been equalised to about 57 Mooney units. This variation might be associated with the degree of breakdown to bring the V_B to 57 Mooney units rather than due to the initial variations in V_R. *Sample A* which had an initial V_B of 90 Mooney units underwent heaviest post-mastication to bring the V_B to 57 Mooney units. During post-mastication it was inevitable that some of the bound rubber network formed prior to post-mastication operation was destroyed. Work has been published to show that both the tearing energy and V_B increased with storage time as a consequence of the percentage increase in bound rubber with storage time[7]. In contrast, *Sample D* was not post-masticated and hence the bound rubber network that could develop was not destroyed and thus enhanced the tear strength. Line *b* shows that the tearing energy increases with increasing V_B indicating that the effects of premastication of raw NR still persisted if there is no post-mastication carried out on the masterbatch. However, the results (points *a*) also indicate that the history of premastication of raw NR does not persist once further breakdown is carried out on the black-filled masterbatch.

Comparison Between the Tear Behaviour of Unvulcanised Black-filled NR and Unvulcanised Unfilled NR

Figure 4 shows tearing energy *versus* tear rate based on the tearing energy data of unvulcanised black-filled NR (V_B = 88.5) shown in *Table 4*. The tearing energy-tear rate relationship of unvulcanised unfilled NR (V_R = 88) was reproduced from the work of Kadir and Thomas[3]. Incorporation of carbon black has resulted in the masterbatches having tearing energies higher than that of unvulcanised unfilled NR especially if tear measurements are made at low tear rates. At tear rate of 100 $\mu m\ s^{-1}$, the tearing energy of unvulcanised black-filled NR was a factor of about 2 higher than unvulcanised unfilled NR. This enhance-ment in tear strength is probably due to the interaction between carbon black particles and the rubber which then helps to reduce the flow of rubber and increase its tendency to strain-crystallise.

However, both unfilled and black-filled unvulcanised NR show a similar trend where the tearing energy increases with tear rates. Like unvulcanised unfilled NR, the tear behaviour of unvulcanised black-filled NR is also predominantly controlled by the viscoelastic effects.

Effect of Bonding Cotton Fabric onto the Legs of the Trouser Test-pieces

The reason for bonding the cotton fabric onto the legs of the trouser test-pieces is to prevent flow and extension in the legs of the test-pieces. For normal trouser test-pieces, the

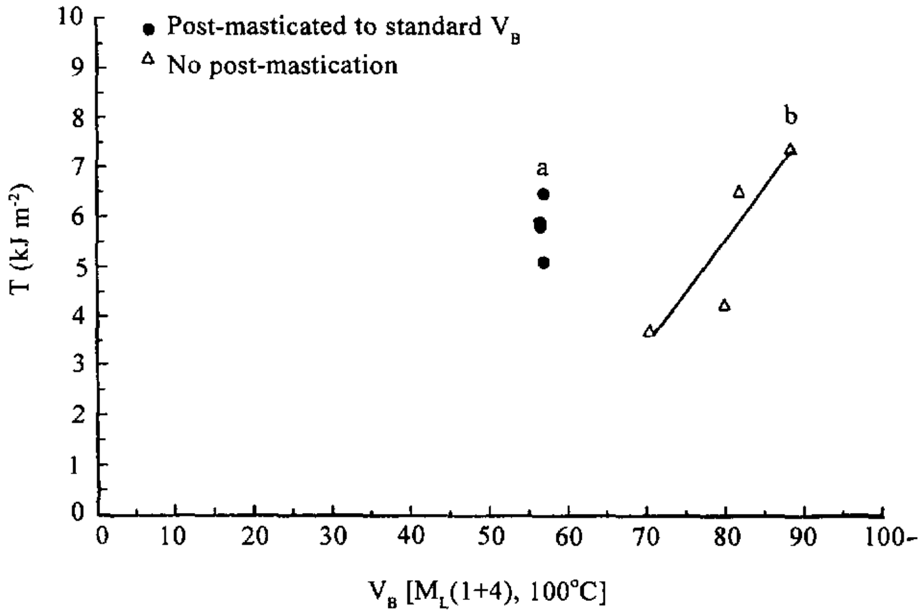


Figure 3. Tearing energy (T) versus *V_B: rate 170 μm s^{-1}; Temp. 24°C.*

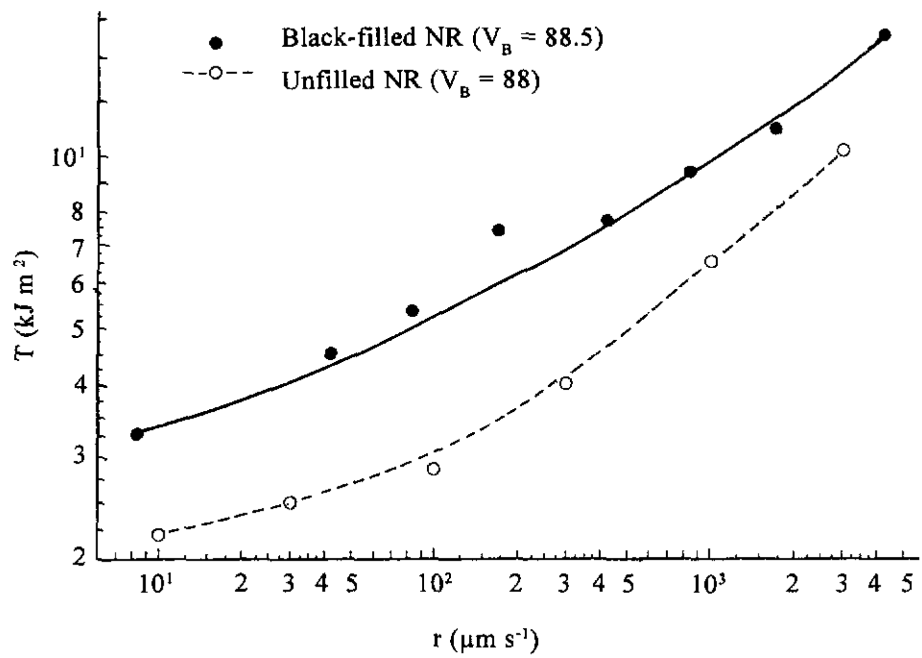


Figure 4. Tearing energy (T) versus *rate (r) at 24°C: Tearing of unvulcanised NR.*

TABLE 4. TEARING ENERGY OF UNVULCANISED BLACK-FILLED NR AT VARIOUS TEAR RATES (23°C)

Tear rate ($\mu m\ s^{-1}$)	Tearing energy ($kJ\ m^{-2}$)
8.3	3.28
42	4.51
83	5.34
170	7.37
420	7.66
830	9.33
1700	11.12
4200	16.33

Mooney viscosity of black-filled master-batch = 88.5 Mooney units

tearing energy was calculated using *Equation 1* and for bonded test-pieces *Equation 2* was used.

Both equations[8,9] are given below:

$$T = F(\lambda + 1)h^{-1} \quad \ldots 1$$

$$T = 2Fh^{-1} \quad \ldots 2$$

where T is the tearing energy, λ is the average extension ratio in the legs of the test-piece and h is the average nominal thickness.

Two 40 mm wide test-pieces and two 15 mm wide test-pieces were used both for fabric bonded and non-bonded test-pieces to see the effect of the width of test-piece on the extension ratio of the legs of the test-piece (for non-bonded test-piece). *Tables 5A* and *5B* show the tearing energy data for fabric bonded and non-bonded trouser test-pieces, respectively. In the case of fabric bonded test-pieces, as expected, the width of test-piece did not affect tearing energy. Bonding the legs of the test-piece with cotton fabric prevented extension in the legs of the test-piece. In the case of the normal test-piece (non bonded), extension in the legs of the test-piece was affected by the width of the test-piece. Wider widthed test-pieces produced lower extension ratio than narrow widthed test-pieces. Tearing energy of the former test-pieces (wider width) was comparable with tearing energy produced by fabric bonded test-piece. Narrow widthed trouser test-pieces produced tearing energy slightly lower than fabric bonded test-pieces. On the whole, the average tearing energy between bonded and non-bonded test-pieces (wider width) was also comparable.

Table 6 shows the comparison of tearing energy of unvulcanised black-filled NR (V_B = 80 Mooney units) computed using *Equations 1* and *3*, respectively. *Equation 3* is given by[3]:

$$T = (2F\lambda)h^{-1} - wU \quad \ldots 3$$

where w is the width of the test-piece and U is the stored energy density. *Figure 5* shows the density of stored energy plotted against extension ratio from which the value of U was determined. The results show that tearing energy computed using *Equation 1* was comparable with the tearing energy computed using *Equation 3*. For this reason, *Equation 1* was preferred to *Equation 3* since the former does not require the knowledge of U.

CONCLUSIONS

The following general conclusions can be made on the tearing of unvulcanised black-filled NR:

- Unvulcanised black-filled NR produced steady or occasionally small scale stick-slip tearing particularly at high tear rates. The degree of stick-slip tearing was more pronounced with high V_B black-filled masterbatches than with low V_B master-batches.

TABLE 5. TEARING ENERGY OF UNVULCANISED BLACK-FILLED NR MASTERBATCH AT CROSSHEAD SPEED OF 100 MM/MIN AT 23°C

A. Fabric bonded trouser test-pieces (V_B = 36.5 Mooney units)

h (mm)	w (mm)	F(N)	λ	$T=F(\lambda + 1)h^{-1}$ (kJ m^{-2})
1.5	40	3.9	1.0	5.20
1.2	40	3.2	1.0	5.33
1.2	15	3.55	1.0	5.92
2.0	15	5.4	1.0	5.40
				Mean = 5.46

B. Unbonded (conventional) trouser test-pieces (V_B = 36.5 Mooney units)

h (mm)	*w (mm)*	*F(N)*	λ	$T=F(\lambda + 1)h^{-1}$ *(kJ m^{-2})*
2.06	40	4.4	2.2	6.83
2.09	40	3.8	1.8	5.09
2.00	15	2.4	2.7	4.44
2.03	15	2.6	2.6	4.59
				Mean = 5.24

TABLE 6. TEARING ENERGY OF UNVULCANISED BLACK-FILLED NR COMPUTED USING *EQUATIONS 1* AND *3*

h (mm)	F(N)	λ	U(MJ m^{-3})	[a]T (kJ m^{-2})	[b]T (kJ m^{-2})
2.28	5.3	1.7	0.150	5.65	6.28
2.39	5.6	1.6	0.125	5.62	6.09
2.36	5.0	1.5	0.100	4.86	5.30
				Mean = 5.38	Mean = 5.89

[a]*Equation 2*: $T = (2F\lambda)h^{-1} - wU$
[b]*Equation 1*: $T = F(\lambda + 1)h^{-1}$
Width of test-piece (w) = 15 mm
V_B = 80 Mooney units
Crosshead speed = 100 mm/min
Temperature = 23°C

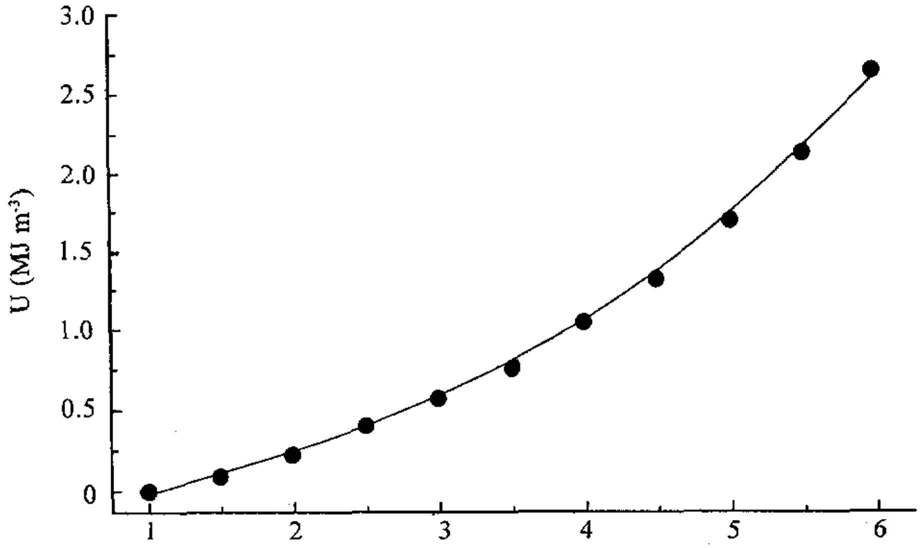


Figure 5. Stored energy (U) versus *extension ratio: unvulcanised black-filled NR (V_B = 80.0 MU)*

- The Mooney viscosity of the black-filled masterbatch, V_B, affected the tearing energy. Black masterbatches with high V_B produce higher tearing energy than black masterbatches with low V_B.

- The tearing energy of an unvulcanised black-filled NR increased as the tear rate was increased indicating that the viscoelastic effect was more predominant than the strain-crystallisation effect in affecting the tearing energy-tear rate relationship.

- The average tearing energy of unvulcanised black-filled NR using fabric bonded trouser test-pieces was comparable with the average tearing energy produced by the normal (not bonded) trouser test-pieces indicating that:

  (a) the strain energy release rate was not substantially affected by the imperfect elasticity of the rubber which is in accord with the view of Kadir and Thomas[3].

  (b) no significant macroscale tear diversion occurred in unvulcanised black-filled NR.

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