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The Effects of Isomerisation and Vulcanisation Temperature on the Tear Strength of Natural Rubber Latex Film

AZEMI SAMSURI*

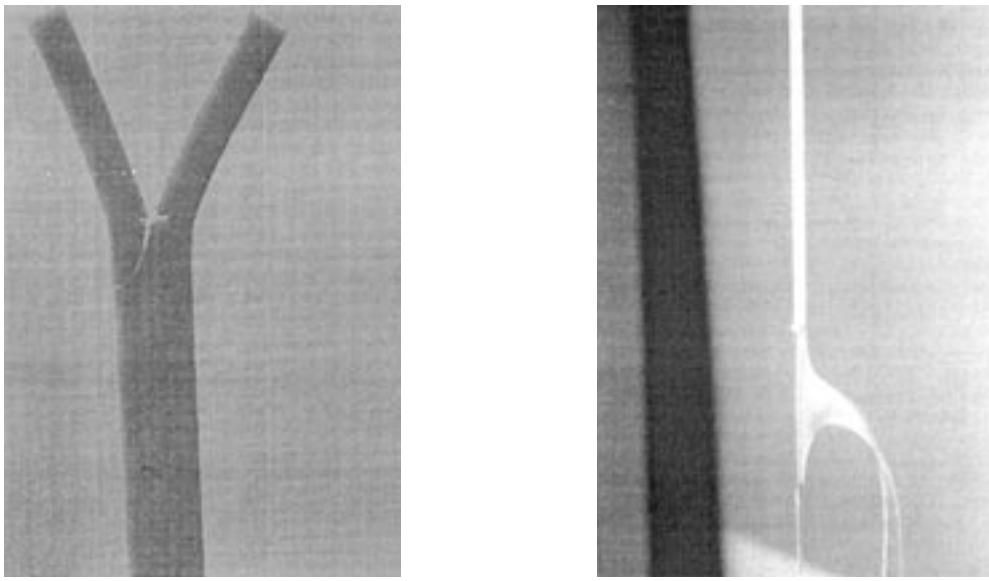
Natural rubber (NR) is predominantly (100%) cis *1,4 polyisoprene. As a consequence of its regular microstructure, vulcanised NR can undergo strain-crystallisation. In the case of NR latex film, strain-crystallisation promotes knotty tearing, a peculiar feature which is commonly observed in reinforcing black-filled NR vulcanisate but not in NR unfilled (gum) vulcanisate prepared from dry rubber. Knotty tearing enhances the tear strength of NR latex film, where its tearing energy can reach 100 kJm^{-2}. The effects of isomerisation, and temperature of vulcanisation on the tear strength of NR latex film were investigated. Isomerisation of NR latex disturbs the regularity of the microstructure and thus inhibits strain-crystallisation. In the absence of strain-crystallisation, NR latex film did not produce knotty tearing. Consequently its tearing energy was relatively low (1.0 kJm^{-2} – 12 kJm^{-2}) depending on the speed of the test. The tearing energy of NR latex film was also found to decrease as the temperature of vulcanisation was increased which might be attributed to lower concentration of polysulphidic type of crosslinks at high vulcanisation temperature than that produced at low temperature vulcanisation.*

Key words: Isomerisation; temperature; tear; strength; natural rubber; latex film; black-filled; vulcanisate; unfilled; microstructure; strain-crystallisation; energy

Strain-crystallisation enhances the mechanical properties of vulcanised NR. The crystals act as a reinforcing filler which increases tensile and tear strengths, increases crack-growth resistance and fatigue life. In the case of NR latex film, strain-crystallisation promotes knotty tearing (*Figure 1*) which enhances its tear strength. Latex products such as gloves and condoms are made from very thin latex film. The thickness is about 0.02 mm in case of condom, and about 0.1 mm – 0.4 mm in the case of surgical gloves. Such thin films are susceptible to tearing during stripping from the former. Thus the ability of NR latex film to produce knotty tearing is a highly desirable feature to minimise rejects associated with tearing during stripping of the gloves from the former. The phenomenon of knotty tearing in NR latex film is not new but has been reported by Kirchhof and Talalay as far back as 1933[1,2]. It is well established that knotty tearing occurs in filled vulcanised rubber containing appre-

*Department of Polymer Technology, Faculty of Applied Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

#Corresponding author (e-mail: azemi@salam.uitm.edu.my)



A B

Figure 1. Knotty tearing of NR latex film: A shows the crack of the torn sample which approximates to a semi-circular arc. B shows the deviation of the crack from the intended path during tearing.

ciable amount of reinforcing filler such as carbon black or precipitated silica[3–5].

The reinforcing filler introduces anisotropy around the tip of the tear and causes the propagating tear to deviate from the intended tear path. Recently, Gent and co-researchers developed model cracks and used finite element analysis (FEA) to calculate the strain energy release rate to propagate tear both forward and sideways[6]. They found that a crack will turn or split sideways if the strength in that direction is about 40% less than that of the forward direction. However, detail investigation to explain why NR latex film produces knotty tearing is still not up-dated as far as the author is concerned.

Azemi[7] has conducted some preliminary investigations on the tear behaviour of NR latex film in 1993 and suggested that the anisotropy in NR latex film necessary for the occurrence of knotty tearing might be attributed to one or the combinations of these factors:

- Ability of NR latex to strain-crystallise
- Hard protein domains which may act as reinforcing fillers[8]
- High concentration of polysulphidic crosslinks, and
- Presence of weak zones between the rubber particles inherited in the latex film.

In order to elucidate further on the factors contributing the strength anisotropy that leads to knotty tearing in NR latex film, work was conducted to investigate the effect of suppressing strain-crystallisation and the effect of vulcanisation temperature on the tear

strength of NR latex film. It is well established that NR is 100% *cis* 1,4 polyisoprene and thus possesses a regular structure, a feature which is necessary for crystallisation. On straining, the rubber molecules are able to arrange and orientate in a closely pack regular pattern to produce crystals. These crystals act as a reinforcing filler to produce the necessary strength anisotropy for the occurrence of knotty tearing. This paper is concerned with the work to eliminate strain-crystallisation by the method of isomerisation to introduce *cis*- and *trans*-isomers into NR latex. The *cis* and *trans* isomerisation disturb the stereo-regularity of the microstructure of the molecular chains and inhibit strain-crystallisation.

In this investigation, NR latex film was isomerised by using acidified sodium nitrite solution and hydrogen peroxide as described by Farley[10]. Under well controlled conditions, Farley[10] obtained isomerised NR (INR) latex containing about 14 mole% – 16 mole% *trans* content. The quantitative estimation of *trans* 1,4 polyisoprene content was determined from ^{1}H-NMR. The aim of doing tear measurement on INR latex film is to see whether it will produce knotty tear or not. If it does produce knotty tear, it indicates that strain-crystallisation does not play a predominant role, but there may be other dominating factors which need investigation.

It is also well established that polysulphidic type of crosslinks give higher tensile and tear strengths than either monosulphidic or carbon-carbon crosslinks because of the ability of the former to relieve stress since polysuphidic crosslinks are labile[9]. Polysulphidic crosslinks are known to give high permanent-set due to the ability of the broken crosslinks to recombine during deformation. Azemi and Thomas[5] indicated that the high permanent-set might contribute to the anisotropy when they found that the tearing energy of a pre-stressed vulcanisate correlated strongly with the permanent-set. In the present investigation, work was also conducted to study the role of polysulphidic crosslinks in NR latex film to promote knotty tearing. In order to attempt to reduce the concentration of polysulphidic crosslinks, high temperature vulcanisation was carried out.

Tear measurements were conducted at various speeds by separating the legs of the trouser test-piece at a uniform rate by using an Instron tensile machine. The temperature of the test was at 23ºC unless stated otherwise. The tearing energy[4,5] was computed by using the equation given below:

$$T = F(\lambda + 1)/h \qquad \ldots 1$$

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

EXPERIMENTAL

Preparation of Isomerised NR Latex (INR)

INR was prepared by using the method described by Farley[10]. HA NR latex was diluted with deionised water and stabilised with a suitable stabiliser by stirring together for 30 min in a thermostated oil bath at 29ºC. The pH of the latex was lowered to 5.26 by the drop-wise addition of formic acid followed by rapid addition of freshly prepared sodium nitrite solution (0.07 M) and hydrogen peroxide (0.02 M). Upon addition of the sodium nitrite solution and hydrogen peroxide reagent mixture, the latex immediately turned into a creamy-yellow colour and a little gas evolution took place. The reaction time[10] was about

3 h in order to get trans content of 14 mole%–16 mole%. Subsequently the INR latex was stored at 23ºC.

Latex Compounding and Casting for Post-vulcanised Latex Film

The chemicals added were either in the form of fine dispersions or solutions. The diluent used was distilled water to prepare those chemicals. *Table 1* shows the formulation for post-vulcanisation of NR and INR latex. After adding the chemicals into the latex, the mixes were stirred for 30 min at ambient temperature (27ºC). The finalised compounded latex-mix was allowed to mature for 2 days at ambient temperature. The latex film was prepared by casting on the glass plate and precautions were taken to minimise air bubbles to avoid air entrapment. The latex film was allowed to dry and removed from the glass plate when it became translucent. The latex film was further dried in the air at ambient temperature for 24 h before final drying in an oven at 80ºC for 30 min. Post-vulcanisation was done in the oven at 125ºC for 20 min.

Latex Compounding and Casting for Pre-Vulcanised Latex Film

Prevulcanised latex compound was prepared base on the formulation as shown in *Table 2*. The required amount of NR latex was first weighed, placed in the stainless steel jar and then distilled water was added to dilute to 40% total solid content. Stabilizers were then added into the latex while stirring. The steel jar with the latex mix was placed in a water bath set at 70ºC ± 2ºC. The latex mix was stirred and the compounding ingredients were added when the mixture registered temperature of 70ºC. The latex mixture was stirred at 70ºC for 6 h to 7 h. The duration for prevulcanisation was timed at the point when the mixture reached the vulcanising temperature. The same procedure was applied for SBR and NBR lattices.

High Temperature Vulcanisation Latex Film

The compounded latex film is the same as that shown in *Table 1*, except that ZDEC was replaced with N-cyclohexylbenzo-thiazole-2-sulphenamide (CBS) – 0.5 p.p.h.r. dry weight. Although there is no risk of scorching in latex processing, but ZDEC is a very fast accelerator and the cure time at high temperature may be too short and inconvenient to handle. For this reason ZDEC was replaced with CBS since the latter has a longer induction period than the former. The latex film was prepared in the same manner described above. About 12 g of the dried latex film was taken and the cure characteristics of the NR latex film at 120ºC, 140ºC and 160ºC were determined from the Swinging Die Rheometer. The unvulcanised dried latex film was vulcanised at 120ºC, 140ºC and 160ºC respectively, to its optimum cure t_{90} in accord with the recorded time on the rheometer chart. The cure time at 120ºC was 17 min, at 140ºC was 4 min and at 160ºC was 2 min, respectively. The vulcanisation was done in an electrical oven. In order to minimize the possibility of the latex film to get oxidised with the surrounding air in the oven, the latex film was wrapped with thin aluminum foil.

RESULTS AND DISCUSSIONS

Effect of Strain-Crystallisation on Tearing Energy of Latex Film

In this investigation, there was no attempt to determine quantitatively the actual amount of *trans*-content actually present in the INR to

compare with the result obtained by Farley[10]. However, the stress-strain measurement was conducted in accord with the *ISO 37* to determine the tensile strength of the INR latex film. The tensile strength for this particular INR latex film was 0.4 MPa and its elongation at break was 795%. The tensile strength of INR latex film of the present investigation was markedly lower than that reported by Cunneen[11] who obtained tensile strength of 2.5 MPa and elongation at break of 790% (INR latex film produced by treating NR latex with thiolbenzoic acid — about 22% *trans*-form). In the case of INR prepared from dry rubber by heating the deproteinised natural rubber (DPNR) in an oven in an atmosphere of sulphur dioxide for two days at 134ºC, Brown *et al.*[7] obtained a tensile strength of 1.1 MPa. Thus the low tensile strength of INR latex film of the present investigation indicated that it did not strain-crystallise anymore since the regularity of the microstructure was disturbed. In contrast, NR latex film, both post- and prevulcanised gave a tensile strength of 27 MPa.

Figure 2 shows the plot of tearing energy *versus* crosshead speed plotted on log-log scales. Both post-vulcanised and prevulcanised NR latex films produced high tearing energy associated with the development of knotty tearing over the whole range of test speed. This finding is consistent with the previous work carried out[7]. In contrast, INR latex film produced low tearing energy over the whole range of test speed. INR latex film did not produce knotty tearing but instead produced steady (smooth) tearing. Thus it indicates clearly that strain-crystallisation plays a vital role in promoting knotty tearing. In the absence of strain-crystallisation, the INR latex film produced smooth tearing typical of a non-strain-crystallising rubber gum vulcanisate. The tearing energy of INR latex film increased with increasing test speed indicating that in the absence of strain-crystallisation, the tearing energy is markedly affected by the tear rate.

The tear behaviour of INR latex film is analogous to the tear behaviour of SBR latex film. However, at test speed of 100 mm per minute and above, the SBR latex film did not show an increase in the tearing energy with increasing rate because of the tear deviated from the intended tear path as soon as the tear started to propagate. There was no attempt to control the tear path by scoring the test-piece since the latex film produced was not thick enough to permit scoring.

TABLE 1. FORMULATION FOR SULPHUR POST-VULCANISATION OF NR AND ISOMERISED NR LATEX FILMS

Item	Dry weight (p.p.h.r.)	Wet weight (p.p.h.r.)
60% HA Latex	100	167
10% Potassium hydroxide	0.4	4.0
20% Potassium laurate	0.3	1.5
50% Sulphur	1.25	2.5
50% Zinc diethyldithiocarbamate (ZDEC)	1.0	2.0
50% Zinc oxide	1.0	2.0
30% Antioxidant (Wingstay L®)	0.6	2.0

TABLE 2. FORMULATIONS OF PREVULCANISED NR, SBR AND NBR LATTICES

Item	Dry weight (p.p.h.r.)	Wet weight (p.p.h.r.)
60% HANR latex	100	167
10% Potassium hydroxide	0.4	4
20% Potassium laurate	0.4	2
50% Zinc oxide	0.2	0.4
50% Sulphur	0.5	1
35% Arbestab Z®	1	2.9
50% Wingstay L®	1	2

TABLE 3. EFFECT OF T_g AND STRAIN-CRYSTALLISATION ON TEARING ENERGY OF NATURAL AND SYNTHETIC LATEX FILMS[a]

Item	NR	NBR	SBR	INR
T_g (°C)[b]	–70	–24	–60	–70
T (kJm^{-2})	102.0	22.0	4.3	3.0

[a] 23°C, cross-head speed 100 mm per minute
[b] Elliot D.J.[12]

Table 3 compares the tearing energy of latex films produced from NR, NBR, SBR and INR latex films. They were compared at the same temperature and test speed. The NR latex film produced very high tearing energy as a consequence of its ability to strain-crystallise. The crystals formed act self-reinforcing filler and responsible for the development of strength anisotropy necessary for the occurrence of knotty tearing. In contrast, NBR, SBR and INR latex films are all non-strain-crystallising since they do not have regular micro-structure. In the absence of strain-crystallisation, they produced steady (smooth) type of tearing and the magnitude of the tearing energy is affected by the glass-transition temperature, T_g, of the rubber. Indeed, in the absence of crystallisation the tearing energy increases as the T_g of the rubber increases, *viz*. NBR>SBR>INR. In this investigation, no attempt was made to determine the T_g of INR. It is assumed that isomerisation has little effect, if any, on the T_g and thus has the same T_g as NR.

Effect of High Temperature Vulcanisation

Azemi and Thomas[5] found that the tearing energy of a pre-stressed black-filled NR correlated strongly with the permanent set. Pre-stressing means that a sample (parallel sided test-piece) is strained to a desired stress level and maintained in the strained state for a minute before unloading the stress. The pre-stressed sample is then immersed in a suitable solvent over-night after which it is dried to a constant weight. This solvent treatment is to remove any residual crystalline

phase in the rubber and also to allow rapid elastic recovery since it eliminates both short and long term viscoelastic effects. They found that the tearing energy decreased with increasing amount of permanent set. Indeed if the amount of permanent set after pre-stressing reaches 12% or more, knotty tearing disappears and tearing proceeds in a steady (smooth) manner along the intended path parallel in the direction of pre-stressing. This permanent set gives rise to anisotropy in the vulcanisate in accord with Rivlin and Thomas[13] hypothesis.

The permanent set is affected by the types of crosslink. As far as the sulphur vulcanisation system is concerned polysulphidic crosslinks give the highest set and monosulphidic crosslinks give the lowest set. *Figure 3* shows the plot of tearing energy *versus* crosshead speed plotted on log-log scales. There is a general trend where the tearing energy decreases as the temperature of vulcanisation increases over the whole range of crosshead speed investigated here. However, knotty tearing still occurred even with NR latex film cured at 160ºC. But the degree of knottiness produced by the latex film cured at 160ºC is somewhat lower than that produced by the latex film cured at 120ºC and also those produced at 70ºC. Indeed the degree of knottiness can be estimated from the size of the arc of the torn surface (*Figure 1*) which is approximately semi-circular in shape. A large arc (1 mm – 2 mm) on the torn surface indicates high degree of knottiness, and a small arc (less than 0.5 mm) on the torn surface indicates low degree of knottiness. The difference in the degree of knottiness might be attributed to the concentration of polysulphidic crosslinks. High temperature vulcanisation produces lower concentration of polysulphidic crosslinks than low temperature vulcanisation. High concentration of polysulphidic crosslinks gives high set which promotes additional anisotropy around the tip of the tear and thus responsible for the large tear diversion.

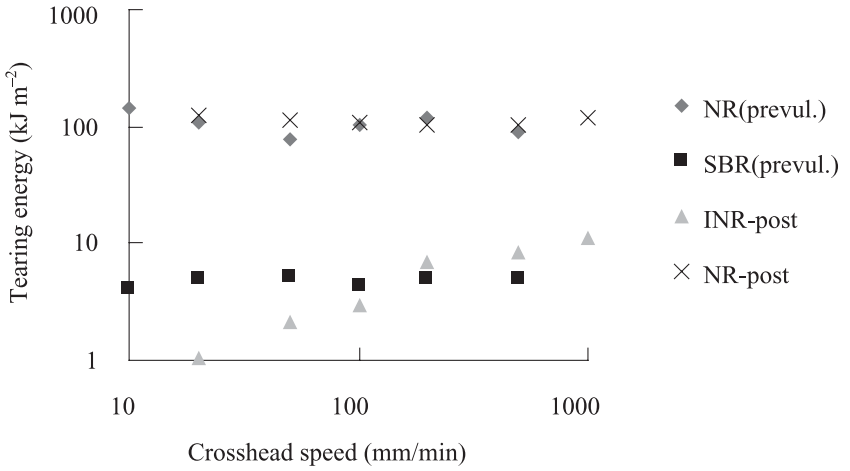


Figure 2. Tearing energy vs *crosshead speed.*

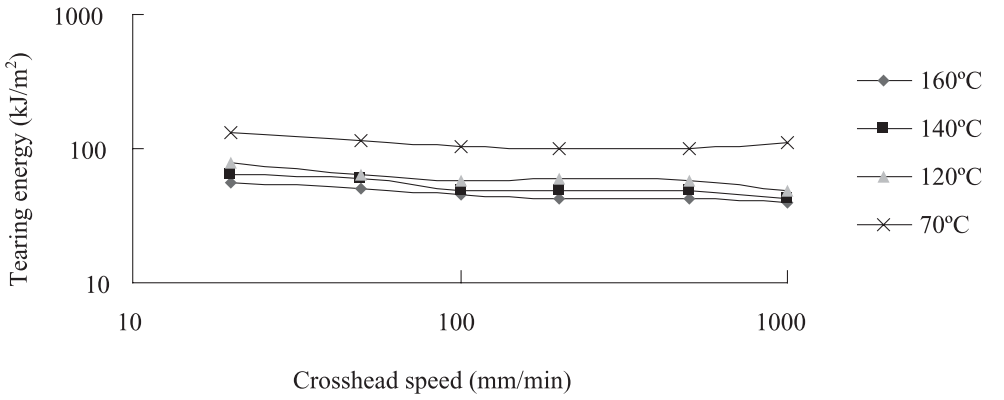


Figure 3. Tearing energy vs *crosshead speed — effect of vulcanisation temperature on tearing energy.*

CONCLUSION

In the absence of strain-crystallisation, NR latex film was unable to produce knotty tearing. It was also found that there was a higher degree of knottiness NR latex film, when cured at a low temperature than that cured at a high temperature.

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