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Knotty Tear Phenomena and Effect of Maturation Time on Knotty Tear in Filled Natural Rubber Latex Films

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Abstract: ***Knotty tearing is a phenomena normally observed in reinforced black-filled natural rubber (NR) vulcanizate but not in gum NR vulcanizate. Unfortunately the underlying cause of knotty tear is still not fully understood and need to be unraveled. Many factors contribute to knotty tear behavior which include suppression of strain-induce crystallization, protein content of latex, vulcanization temperature and pre-vulcanization and post-vulcanization of latex. In this study, we concentrate on varying the maturation time during compounding process in filled NR latex (NRL) to study knotty tear behavior. The maturation time were varied in the range (0 – 72) hrs; and the tear deviation were measured to determine the extent of knotty tear phenomena. It was found that at the optimum maturation time of 24 hrs samples show highest tearing energy and show knotty tear phenomena with the least angle of tear deviation.***

Keywords* : *Knotty tear, tearing energy, natural rubber latex, filled NRL films.

I. INTRODUCTION

In Natural Rubber Latex (NRL) films, strain-crystallization promotes knotty tearing which is related to its tear strength and tear energy. It is desirable that films of latex products such as condoms and surgical glove be thin enough (as thin as 0.02- 0.4) mm to avoid tactile insensitivity from thicker films. However, such thin films are prone to tear during the stripping of the film from the former[1]. Thus the ability of NRL films to produce knotty tearing during testing indicates its resistance to tear and therefore could be related to its strength. The phenomena of knotty tearing in the NRL film has been reported by H. Freundlich and N. Talalay since 1933[2]. Filler is usually added into NRL to modify the mechanical properties, improve processing characteristics and also to reduce the compounding cost. It is well established that knotty tearing occurs in filled vulcanized rubber containing (5 – 40) phr of reinforcing fillers such as carbon black [3].

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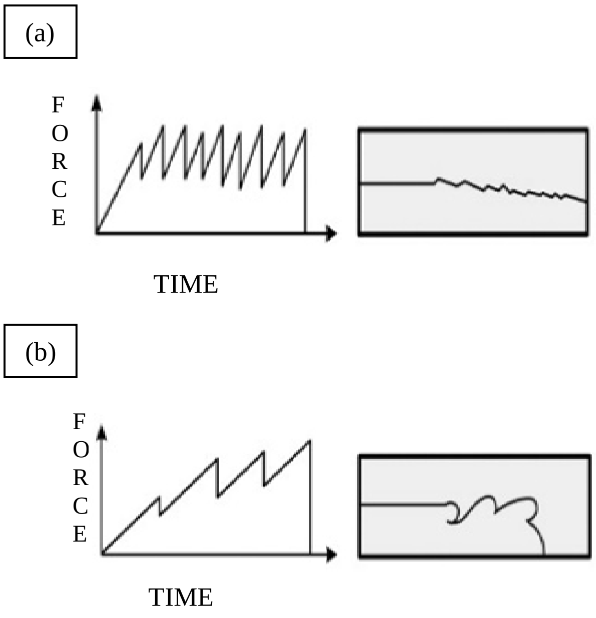

Fig.1. Schematic diagram to illustrate the tearing force-time curves and tearing path for different types of tear crack propagation obtained from the trouser test specimen in (a) knotty tearing and (b) stick-slip tearing [4].

The reinforcing filler introduced anisotropy structure around the tip of the tear which causes the tear propagate to turn aside from the intended tear path [5].

Knotty tear is one type of tear failure besides steady smooth tearing, and stick slip tearing. Knotty tear and stick slip tearing are the most observed types of tear failure in filled rubber vulcanizate. Fig. 1 shows the illustration of force-time curve and trouser test piece of two important test failures that are typically observed in rubber samples.

As shown in Fig 1, in knotty tear phenomena the tear tends to deviate from the intended tear path and circles around almost perpendicularly as compared to stick slip tearing where the tear-crack do not produce circular shape but just a straight tear and a slightly jagged shape [4]. The objective of this study is to identify the relationship between knotty tearing and tear energy from manipulation of maturation time.

Maturation time is a fundamental property and its value need to be identified first prior to latex compounding. Maturation time affect the properties of final latex products. Known properties that were affected by maturation time are tensile strength, modulus, tear strength, gel content, and cross-link density [6]. We postulated that knotty tearing would be observed at optimum maturation time and samples with high tearing energy should show knotty tearing phenomena. Furthermore we hypothesized that the extent of knotty tearing is reflected by the magnitude of tear energy.

II. METHODOLOGY

A. Chemicals and Raw Materials

All the chemicals used were of analytical grade. Carbon black (N110) was purchased from Cabot (Malaysia) Sdn. Bhd. High Ammonia Natural Rubber Latex (HA NR) was purchased from Syntomer Sdn Bhd. Zinc diethyldithiocarbamate (ZDEC) dispersion, Zinc Oxide (ZnO_2) dispersion, antioxidant dispersion (Wingstay L) Sulphur dispersion, and potassium hydroxide were purchased from Excelkos Sdn. Bhd. Anchoid - sodium salt of a naphthalene sulphuric acid/formaldehyde condensate, and potassium laurate were purchased from Malaysian Rubber Board, MRB.

B. Compounding of Filled NRL at Different Maturation Time

Table-I shows the formulation for the preparation filled-NR latex compounds. It was initially prepared according to three parts (A, B and C), before mixing them together.

Level of curative agent (50% sulphur dispersion) used in this formulation is considered high (2.5 phr) while level of accelerator (50% ZDEC dispersion) used is low (1.0 phr) for conventional sulphur cure system and economic reasons [7]. The filler loading was fixed at 10 phr.

Ingredients in part A were mixed slowly by stirring at slow speed of 45 rpm at room temperature. Part B was then added to part A to form the compounded latex. The compounded latex was stirred at 200 rpm at ambient temperature of 25°C. Dispersed filler (part C) was added into the compounded latex immediately after maturation time of (0, 24, 48 and 72) hrs. At these maturation time, required amount of sample were taken for swell test.

C. Determination of Swelling Index

The identification of swelling index is a way to determine the maturation time of NRL films. The procedure of the swell test follows British Standard (BS 1673: Part 4, 1953). Latices of unfilled compounds prepared at different maturation time were casted on a graph paper to form thin films. Films were then dried at 100°C for 1 hour to obtain 0.12 mm thickness of dry films. They were then cut into circles of 25 mm in diameter and placed in a medium sized petri dish containing toluene. Films were allowed to swell for 20 minutes (or until swelling is maximum) and the swollen diameter is measured using equation (1).

$$\textit{swelling index (percentage swell)}: \frac{z-y_0}{y_0}\times 100 \qquad (1)$$

Where z is the average swollen diameter in millimeters and y_0 is the initial diameter in millimeters.

D. Preparation of NRL Films

Latex films were prepared by casting on glass plate's mold. The compounded latex was filtered beforehand as a precaution to minimize air bubbles and to avoid air entrapment during casting process.

Table-I Filled NR latex compound formulation.

	Ingredients	Parts: Dry weight (phr)	Parts: Wet weight (phr)
Part A	60% HA NR latex	100	167
	10% Potassium Hydroxide	0.4	4
	20% Potassium Laurate	0.2	1
Part B	50% Sulphur dispersion	2.5	5
	50% ZDEC Dispersion	1.0	2
	50% Zinc Oxide dispersion	5.0	10
	50% Antioxidant dispersion	1.0	2
Part C	10% Filler dispersion	10	100

The filled NRL films was allowed to dry at 25°C; and was removed from the glass plate when it became easy to be peeled off. The latex films were further air-dried at 25°C until constant weight was achieved before final drying in an oven at 80°C for 30 mins. After drying, the latex films were post-vulcanized at 120°C for a further 30 mins [8].

E. Measurement of Crosslink Concentration of NRL Films

The filled NRL films underwent solvent-swelling procedures according to ASTM D471-97 1998. The equilibrium swelling of NRL films in toluene as a solvent was measured by allowing it to swell for 1-2 weeks in a dark condition to allow equilibrium. The swollen gel was then isolated and weighed. The weights of swelling solvent and NRL films were determined after removing the solvent by vacuum-drying.The crosslink density which are network chain per gram is calculated using Flory-Rehner equation as shown in equation (2).

$$= -\frac{[\ln(1-V_p)+(V_p)+X(V_p)^2]}{\left\{[(D_p)(V_o)[V_r^{\frac{1}{3}}]]-\frac{(V_p)}{2}\right\}} \qquad (2)$$

Where,

Vp = Volume fraction of polymer in the swollen polymer

X= Huggins polymer-solvent interaction constant

Dp = Density of polymer (g/cm^3)

Vo = Molar volume of solvent (cm^3/mol)

Do = Density of solvent (g/cm^3)

Here,

Vp = 1/(1+Q),

Where Q = [weight of solvent in the swollen polymer ×Dp]/[Weight of polymer × Do]

F. Determination of Tear Energy

The tests were carried out in accordance to ASTM D412 using Instron 5564. Tear measurement were conducted at a constant speed of 100 mm/min by separating the legs of the trouser test piece at a uniform rate. The test was carried out at 23°C. The tearing energy was calculated using equation (3) [3].

$$T = (F)\left(\frac{\lambda+1}{h}\right) \quad (3)$$

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

G. Extent of Knotty Tear Phenomena

The extent of tear deviation was estimated by measuring the angle of tear deviation by using a simple protractor. This measurement is suitable for trouser test piece type because its geometry made it the best type of test pieces to calculate the angle of deviation. Fig. 2 illustrated the technique to measure the angle of tear deviation on the trouser test piece. Fig. 3 shows the angle of deviation for T24.

III. RESULT AND DISCUSSION

A. Optimum Maturation Time

An indication of the stages and degree of vulcanization can be deduced from swell index values using information shown in Table-II [5, 6].

There are 4 stages of vulcanization which correspond to the degree of vulcanization compounded latex has reached. The degree of vulcanization is related to the crosslink concentration and hardness of the rubber. The higher the degree of vulcanization the higher would the crosslink concentration be and therefore the harder would the NR latex films become [9].

Table-III shows the results of swell percentage, crosslink density, tearing energy and angle of deviation of the various NRL films prepared at different maturation time. Both samples T0 and T24 have swell of 90% and 88% respectively which correspond to stage 3 vulcanization – i.e. moderately vulcanized compound. T48 and T72 which were allowed to mature for a longer period of time have swell percentage values below 80% indicating fully vulcanized rubber.

In general, the cross link density increases with maturation time following the stages of vulcanization.

The tearing energy of T24 is however higher than T0 by 44% although both show the same degree of vulcanization. Samples T48 and T72 which were fully vulcanized have tearing energy lower than T24. It can be concluded that the degree of vulcanization or the cross link density may not be a good indicator of strength of rubber compounds.

Tearing energy indicate the strength of the compound. Because T24 shows the highest tearing energy, it can be concluded that the optimum maturation time for producing compounds with high strength is 24 hrs.

B. Knotty Tear Behavior Versus Tearing Energy

The extent of knotty tear phenomenon observed for the various samples could be identified from the angle of deviation measured. Samples T0, T24 and T48 show knotty tear behavior. This result agreed with the early work conducted by our co-researcher Azemi [5, 10].

T72 however do not show knotty tear phenomena but showed stick slip tearing and was excluded as having high strength. Table III shows that sample T72 has the lowest tearing energy. It was related to the difficulty to strain crystallize due to very high degree of vulcanization caused the decrease in the tearing energy.

Table-II The indicator of stages and degree of vulcanization from swell index values.

Stages	Degree of vulcanization	Swell index(%)
Stage 1	Unvulcanized	>160
Stage 2	Lightly vulcanized	100-160
Stage 3	Moderately vulcanized	80 -100
Stage 4	Fully vulcanized	<80

Table- III The swelling index, crosslink concentration, angle of deviation and tearing energy of samples T0, T24, T48 and T72.

Sample	Maturation time (hrs)	% swell	Crosslink density ($\times 10^{-2}$mol/kg)	Tearing energy (kJ/m^2)	Angle of Deviation (º)
T0	0	90	1.29	98.42	77.0
T24	24	88	1.99	142.06	49.6
T48	48	77	1.34	127.13	56.8
T72	72	70	2.33	18.18	165.2

T0 which is a lightly vulcanized sample and T48 a fully vulcanized rubber have lower tearing energy and higher angle of deviation than T24. Furthermore, the angle of deviation for T24 was the smallest compared to the rest of the samples. Development of strengthening structure such as crystallization and strength anisotropy induced by the carbon black at the tear tip caused smaller angle of tear deviation during tearing. T48 which have higher tearing energy than T0 have lower angle of deviation.

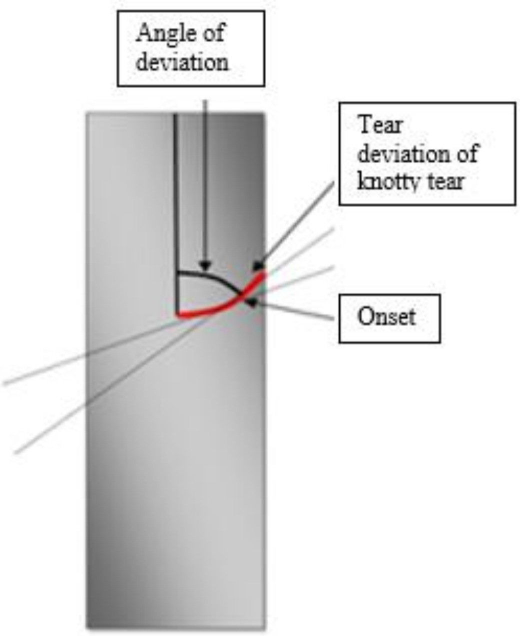

Fig. 2. Illustration of tear deviation on the trouser test piece.

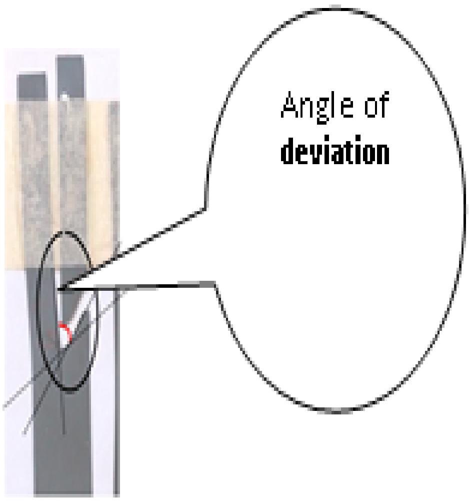

Fig. 3. The angle of tear deviation of sample *T24*

Consequently, the following order of tearing energy and angle of deviation can be assigned to the knotty tear samples.

<u>Tearing energy</u>
T24 > T48 > T0
<u>Angle of deviation</u>
T24 < T48 < T0

It seems that maturation time can be manipulated and optimized to produce high strength rubber compounds. Knotty tear phenomena has the potential to be used as an indicator of rubber compound strength but need to be exploit further.

IV. Conclusion

The samples that produced knotty tear gave higher tearing energy compared to samples that produce stick slip tearing. It was also found that the magnitude of tearing energy was affected by tear deviation from the intended path at different maturation time. The larger the angle of tear deviation the higher is the tearing energy. This is attributed to strain crystallization and strength anisotropy induced by the carbon black at the tear tip. There is a relationship between knotty tear and tear energy of the filled NRL films but further work need to be carry out. This study will contribute to the new knowledge and future research.

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Siti Aisyah Jarkasi is a PhD candidates in Science at Universiti Teknologi MARA Malaysia. She is currently completing her PhD thesis. She has published a few research papers in Scorpus indexed journal and international conference and exhibition. Recently she was co-author and published the book entitled ‘Tensile and Tear Strengths of Unfilled and Carbon-Black Filled NR’ published by LAP Lambert Academic Publishing in 2018. She is interested in rubber latex field research.

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