# AN INVESTIGATION OF THE EFFECT OF AGEING ON MECHANICAL PROPERTIES OF ELASTOMER

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# Laporan Akhir Projek Penyelidikan Jangka Pendek

# An Investigation of the Effect of Ageing on Mechanical Properties of Elastomer

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**PEJABAT PENGURUSAN & KREATIVITI PENYELIDIKAN**
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*Abstract of Research*
*(Must be prepared in 100 – 200 words in Bahasa Malaysia as well as in English. This abstract will later be included in the Annual Report of the Research and Innovation Section as a means of presenting the project findings of the researcher/s to the university and the outside community)*

## AN INVESTIGATION OF THE EFFECT OF AGEING ON MECHANICAL PROPERTIES OF ELASTOMER


### ABSTRACT

This research aims to investigate the effect of heat ageing on the mechanical properties of natural rubber (NR). The work involved the use of different curing systems to investigate the change in the strength properties of rubber after ageing at 100°C in the oven. A series of experimental tests were carried out on NR compounds with different vulcanization systems; sulfur vulcanization system and non-sulphur vulcanization system. The mechanical properties (tensile strength, catastrophic tearing energy ($T_c$) and cyclic crack growth were measured. The permanent set and crosslink density of the vulcanizates were also determined. Tensile strength showed that vulcanizates with crosslinks which are predominantly polysulphidic in conventional vulcanization system exhibit properties higher than those of the corresponding monosulphidic crosslinking vulcanizates in efficient vulcanization system and peroxide system before ageing. After ageing at 100°C, conventional vulcanization system showed the highest reduction in the tensile strength and in the catastrophic tearing energy compared than efficient vulcanization system and peroxide system because the polysulphidic crosslinks are thermally unstable and can be readily oxidized. In permanent set test, the extent of permanent set is dependent upon the extent of these processes. The higher permanent set value suggests more crosslinks have been reformed. This effect was more pronounced for conventional vulcanization system compared to efficient vulcanization system and peroxide system. The swelling test was carried out to determine the crosslink density from permanent set sample. Conventional vulcanization system showed greater increased in permanent set but small decreased in crosslink density. This may be due to scission of main chain and/or crosslink and, crosslink reformation that occur in conventional vulcanization system. The degree of main chain and/or crosslink scission, crosslink reformation and the percentage of permanent set after ageing with 100% stretch were higher compared to the efficient vulcanization system and peroxide system.


## KAJIAN MENGENAI KESAN PENUAAN HABA KE ATAS SIFAT-SIFAT MEKANIKAL BAGI ELASTOMER


### ABSTRAK

Kajian ini secara amnya adalah untuk mengkaji kesan penuaan haba ke atas sifat-sifat mekanikal bagi getah asli. Ini melibatkan beberapa teknik eksperimen untuk mengkaji perubahan sifat-sifat seperti kekuatan bagi getah asli selepas penuaan pada 100°C di dalam oven. Kajian dijalankan ke atas sistem pemvulkanan yang berbeza, iaitu sistem pemvulkanan sulfur dan sistem pemvulkanan tanpa sulfur. Sifat-sifat mekanikal (Kekuatan tensil and tenagan cabikan katastropik dan pertumbuhan retak secara berkitar) telah dilakukan. Selain itu, peratusan set kekal, kadar pembengkakkan dan ketumpatan sambung silang turut dikaji. Bagi ujian tensil, sebelum penuaan sistem pemvulkanan lazim yang mengandungi sambung silang polisulfidik menunjukan sifat yang baik berbanding sistem pemvulkanan cekap yang mengandungi sambung silang monosulphidik dan sistem peroksida. Selepas penuaan pada 100°C, sistem pemvulkanan lazim menunjukan penurunan dalam kekuatan tensil dan cabikan yang tinggi berbanding sistem pemvulkanan cekap dan peroksida disebabkan oleh sambung silang polisulfidik merupakan sambung silang yang tidak stabil terhadap suhu dan senang teroksida. Dalam ujian set kekal, pemanjangan bagi set kekal ini bergantung kepada pemanjangan semasa proses penuaan. Nilai set kekal yang tinggi mencadangkan bahawa sambung silang yang baru terbentuk. Kesan ini jelas terhadap sistem pemvulkanan lazim berbanding sistem pemvulkanan cekap dan peroksida. Ujian pembengkakkan turut dilakukan untuk mengira ketumpatan sambung silang daripada sampel set kekal. Keputusan menunjukan sistem pemvulkanan lazim mempunyai peningkatan dalam peratus set kekal tetapi pengurangan yang kecil dalam ketumpatan sambung silang. Ini mungkin disebabkan oleh pemutusan rantaian utama dan/atau rantaian sambung silang dan, pembentukan semula sambung silang berlaku. Kesan penuaan menunjukkan darjah pemutusan rantaian utama dan/atau rantaian sambung silang, pembentukan semula sambung silang dan peratus set kekal selepas penuaan dengan penarikan 100% sistem pemvulkanan lazim adalah lebih tinggi berbanding sistem pemvulkanan cekap dan peroksida.

4) Sila sediakan Laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
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*List a glosssary that explains or reflects your research:*

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| Sistem pematangan | Curing system |
| Penuaan haba | Heat ageing |
| Sifat-sifat mekanikal | Mechanical properties |
| Ketumpatan sambung-silang | Crosslink density |
| Set Kekal | Permanent set |

5) **Output Dan Faedah Projek**
*Output and Benefits of Project*

(a) * Penerbitan *(termasuk laporan/kertas seminar)*
*Publications (including reports/seminar papers)*
*(Sila nyatakan jenis, tajuk, pengarang, tahun terbitan dan di mana telah diterbit/dibentangkan).*
*(Kindly state each type, title, author/editor, publication year and journal/s containing publication)*

1. A.R.Azura and H.Ismail, Degradation behaviour of sulphur cured natural rubber vulcanisates: effect of heat ageing, Proceeding of Electron microscopy Society Malaysia, Vistana Hotel, Penang, 5-7 December 2005

2. A.R.Azura and H.Ismail, Degradation behaviour of sulphur cured natural rubber vulcanisates: effect of heat ageing, Malaysian Journal of Microscopy, Vol 2, December 2006, 188-195.

3. Juhairah Abu Bakar & Azura A.Rashid, Effect of Heat Ageing on mechanical properties of different curing systems of Natural Rubber vulcanisates, VIth National Symposium On Polymeric Materials 2006, Holiday Villa, Subang Jaya 13-14 December 2006

(b) **Faedah-Faedah Lain Seperti Perkembangan Produk, Prospek Komersialisasi Dan Pendaftaran Paten atau impak kepada dasar dan masyakarat.**
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**Tittle: Studies on the effect of heat ageing on mechaniacal properties of natural rubber compound**

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2. **Dzulhelmy Mohamad**
3. **Chew Siou Lian**
4. **Siti Rohana Yahya**
5. **Shazlin Zukifli**

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Timbalan Dekan
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P.P. Kebolehcapaian Bahan & Sumber Maklumat
Universiti Sains Malaysia

27-2-07
TARIKH
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# AN INVESTIGATION OF THE EFFECT OF AGEING ON MECHANICAL PROPERTIES OF ELASTOMER

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## FINAL REPORT

### INTRODUCTION

The properties and performance of a rubber product depend on many factors including the chemical nature of the rubber, the amount and types of ingredients incorporated into the rubber compound, processing and vulcanizing conditions, design of the product and service conditions. Optimization of rubber properties by different methods of vulcanization and tests are required for the various rubber vulcanizates so one can select the product, which will perform satisfactorily in service. Normally, rubbers are vulcanized by systems based on sulfur or peroxide.

Rubbers have hundreds of applications in nearly every industry. The hysteresis properties of natural rubber (NR) make it a particularly attractive material to use in the automotive industry. Low hysteresis rubbers are used in applications where low energy absorption is required, e.g. in tyre walls to prevent heat build up as the walls flex: high hysteresis rubbers are used for tyre treads and engine mounts where the low resilience and energy absorbing properties will reduced bouncing. In such applications the material may need to withstand mechanical stresses at temperatures cycling between −20 and 150°C. However, meeting such environmental targets is difficult, since the performance of NR is limited by its poor thermal oxidative stability (Edge *et al.*, 1999, Nagdi, 1993).

The thermal oxidation of cross-linked NR is manifested by the formation of a sticky surface layer which eventually becomes brittle followed by a rapid increase in crosslink density (Nagdi, 1993). As the crosslink density increases, the free volume decreases inhibiting bulk oxygen diffusion. Under static conditions, rapid oxidation of the rubber surface provides a sacrificial layer protecting the bulk from oxidation. However, under dynamic conditions, because the surface oxidized layer has a high crosslink density, tensile properties are high but the material has a low elongation at break. This leads to the development of surface cracks exposing more rubber to oxidation, potentially propagating the crack to a tear and catastrophic failure (Edge *et al.*, 1999).

Ageing of elastomers involves a progressive change in their physical and chemical properties, usually marked by deterioration. Factors that contribute to the deterioration of elastomers include ozone, heat, oxygen, sunlight, certain metal ions, high humidity, high energy radiation, microorganisms and atmospheric pollutants, particularly in industrial areas. Under severe conditions, the elastomer may become unserviceable after a short time (Mathew 1992 and Ahlblad, 1998). Generally, the greater the amount of unsaturation in the polymer chain, the more susceptible it is to ageing (Nagdi, 1993). Generally the loss in physical properties, associated with ageing processes, is normally caused by chain scission, crosslinking or some form of chemical alteration of polymer chains. The purpose of work undertaken here is to investigate the processes that are responsible for the modification of the mechanical properties of elastomer when subjected to an accelerated ageing test.

## LITERATURE REVIEW

### Rubber

The term 'rubber' describes a group of materials which are highly elastic: a strip of rubber can be stretched several fold without breaking and will return quickly to its original length on releasing the stretching force (Jones and Allen, 1992). There are two major categories of rubber materials-natural rubber and synthetic rubber. The structure of rubbers is similar to that of plastics in that it consists of long chain-like molecules (Crawford, 1985). Rubber can be classified under two groups which are natural rubber and synthetic rubber.

### Natural rubber (NR)

Natural rubber is a very versatile (Fuller *et al.,* 1974 and Crawford, 1985) and adaptable material which has been used successfully in engineering applications for 150 years, and remains the pre-eminent elastomer for springs and mountings. Blends of NR with synthetic rubber has been widely studied and reported as good compatible blends that provide desirable mechanical properties (Findik *et al.*, 2004). Major areas of application are in vehicles, civil engineering, railways and the offshore and aerospace industries. Natural rubber is able to withstand large strains, and it can store more elastic energy per unit volume than steel. Unlike metals, it possesses some inherent damping, which is particularly beneficial in springs when resonant vibrations are encountered. Rubber can be chemically bonded to metal or other rigid materials to provide the means for location and fixing, and for the production of units with stiffness's differing substantially in shear and compression. Installation is often simplified by the flexibility of the rubber. No maintenance is required, and natural rubber components have been found to maintain their design performance for many years (Fuller *et al.,* 1974 and Long, 1985).

### Compounding and Compounding Ingredients

Compounding is the term used to describe formulating rubber to its an appropriate end use e.g. tyres, beltings, engine, or building mounts, seals or hot water bottles. Vulcanization is the most important aspect of compounding natural rubber, and this is generally achieved by reaction with sulphur and accelerators at an elevated temperature (Metherell, 1992). In general, the materials utilized by the rubber compounder can be classified into nine major categories, which are defined as follows (Ghosh, 1990):

*Elastomers*: The basic component of all rubber compounds, it may be in the form of rubber alone, or "masterbatches" of rubber-oil, rubber-carbon black, or rubber-oil-carbon black, or reclaimed rubber. The elastomers are selected in order to obtain specific physical properties in the final product.

*Processing Aids*: Materials used to modify rubber during the mixing or processing steps, or to aid in a specific manner during extrusion, calendaring, or moulding operations.

*Vulcanization Agents*: These materials are necessary for vulcanization, since without the chemical crosslinking reactions involving these agents, no improvement in the physical properties of the rubber mixes can occur.

*Accelerators*: In combination with vulcanizing agents, these materials reduce the vulcanization time (cure time) by increasing the rate of vulcanization. In most cases, the physical properties of the product are also improved.

*Activators*: These ingredients from chemical complexes with accelerators, and thus aid in obtaining the maximum benefits from an acceleration system by increasing vulcanization rates and improving the final products properties.

*Age-Resistors*: Antioxidants, antiozonants, and other materials that are used to reduce ageing processes in vulcanizates. They function by slowing down the deterioration of rubber products. The deterioration occurs through reactions with materials that catalyze rubber failure, i.e., oxygen, ozone, light, heat, radiation, etc.

*Fillers*: These materials are used to reinforce or modify physical properties, impart certain processing properties, or reduce cost.

*Softeners*: Any material that can be added to rubber to either aid mixing, promote greater elasticity, produce tack, or extend (or replace) a portion of the rubber hydrocarbon (without a loss in physical properties), can be classified as a softener.

*Miscellaneous Ingredients*: Materials that can be used for specific purposes but are not normally required in the majority of rubber compounds can be included in this group. It includes retarders, colors, blowing aids, abrasives, dusting agents, odorants, etc.

**Rubber Processing**

Generally, the steps involved to change the raw rubber to the final product are illustrated in Figure 1. There are three main process involved to produce the final products, which are mastication and mixing, moulding and vulcanization.

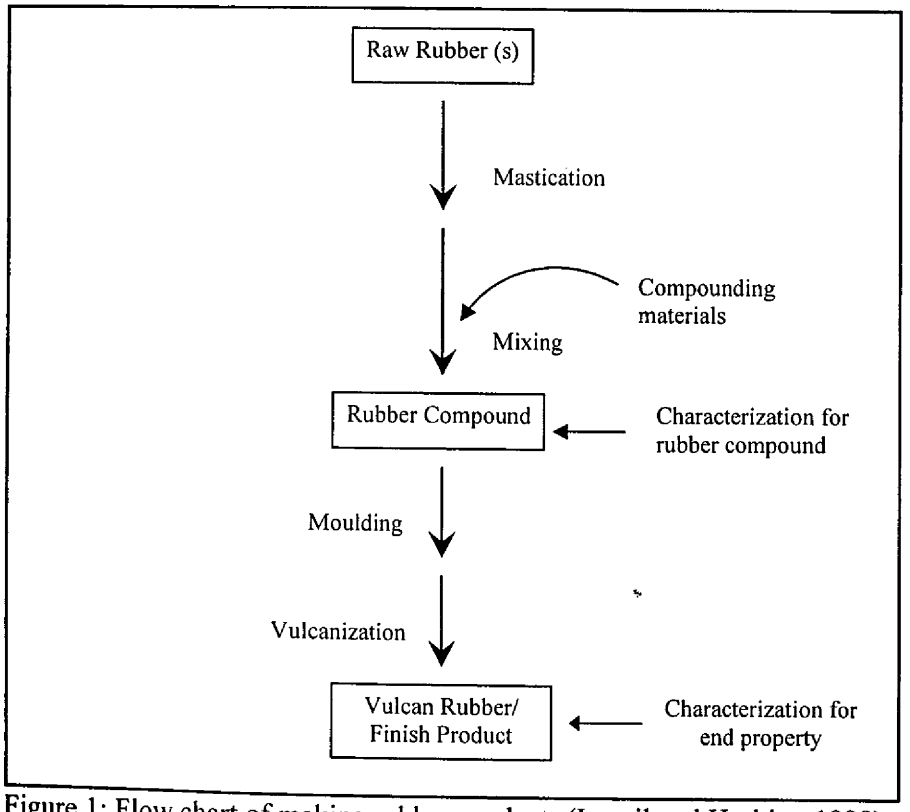



Figure 1: Flow chart of making rubber products (Ismail and Hashim, 1998)

**Mastication**

In the case of natural rubber it is necessary to 'work' the raw rubber in order to soften it before the various compounding ingredients can be incorporated. The process is variously called 'premastication', 'mastication' or 'breakdown'; at the molecular level it brings about a reduction in the molecular weight of the rubber and a change on its distribution. Mastication is effected by applying a shearing force to the rubber, in a machine of the same kind as that used for subsequent mixing: an eccentrically-shaped rotor works the rubber against the sides of the mixing chamber. Alternatively, mastication also can take place in a two-roll mill; the rolls rotate at different speeds, generating a shearing force on the rubber as it passes between the nip between the rolls (Ismail & Hashim, 1998 and Allen *et al.*, 1972).

**Mixing and moulding**

Mixing, like mastication, can be carried out either in internal mixers or on two roll mills. Considerable power is needed, and the mix becomes quite hot (Allen *et al.*, 1972). The efficiency of the process is governed by the type of mixer, the way it is used, the order of adding the ingredients, the control of times and temperature, and other parameters. The quality of the final mix is important to determine the final product properties.

There are three types of moulding: compression, transfer and injection. Compression moulding is the common and simple moulding used in many rubber industry. The transfer moulding gives better dimensional control but only for simple shape; the moulds themselves are more costly and there is more wastage of material, though these costs can be offset against lower finishing costs (Allen *et al.*, 1972). Transfer moulding may involve the heated hydraulic press used for compression moulding or a purpose built transfer moulding press. The principle is the same in both instances where the mould cavity is closed before the moulding operations starts, the rubber is then introduced into a secondary cavity adjacent to the shaped product forming cavity. It's then transferred by hydraulic ram pressure to the primary mould system two fold where the rubber receives the considerable fractional heating in transfer, shortening the vulcanization time and metals inside used in rubber to metal bonding may be positively located. The majority of engineering rubber components is produced by this method (Freakly and Payne, 1978). Injection moulding is an extension and improvement of transfer moulding, allowing more precise control of materials temperature during injection and thus allowing the further reduction of vulcanization times (Freakly and Payne, 1978). Injection moulding is economical only when very long runs of a single product are involved and especially when, in addition, extremely good dimensional control is needed (if it is not, mechanized compression moulding may well be as economical) (Allen *et al.*, 1972).

**Vulcanization**

One requisite characteristic for elastomeric behavior is that the molecular structure (long chain) become crosslinked to form three-dimensional structure (Callister, 2000). The crosslinking process in elastomers is called vulcanization, which is achieved by a non reversible chemical reaction, ordinarily carried out at an elevated temperature. In most vulcanizing reactions, sulphur compounds are added to the heated elastomers; chains of sulphur atoms bond with adjacent polymer backbone chains and crosslink them. The type of sulphur crosslink depends on the vulcanizing conditions-time and temperature and the ratio between the sulphur and accelerator contents (Fuller *et al.*, 1974).

The crosslinks are initially polysulphidic, but at normal cure temperatures further reactions occur, notably crosslink shortening, leading to cyclic sulphides, conjugated unsaturation, rearranged isolated double bonds, zinc sulphide and thiols (Chapman and Porter, 1998). These competing pathways are illustrated in the scheme in Figure 2.

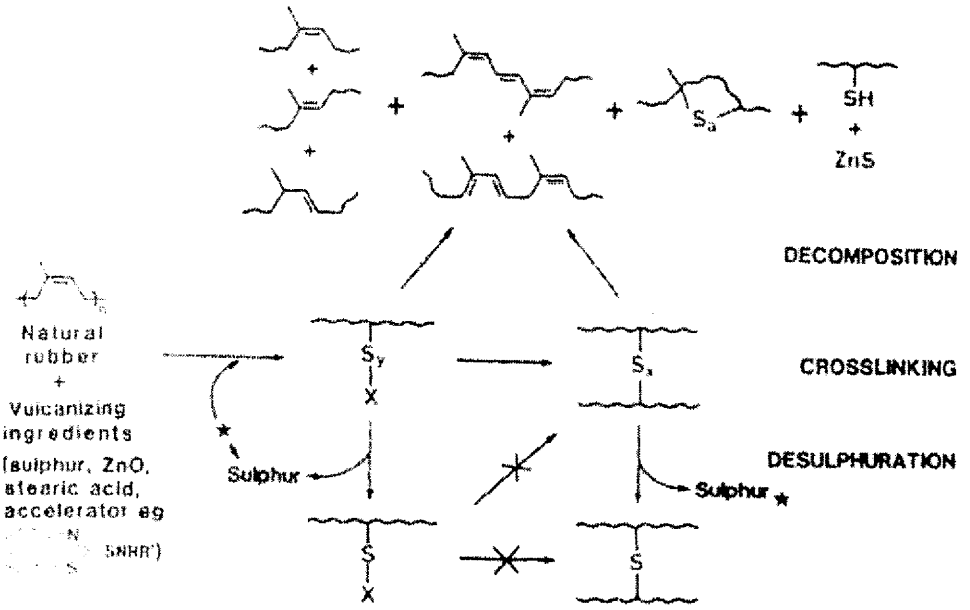



Figure 2: Reactions of vulcanization intermediates and crosslinks (Chapman and Porter, 1998)

Unvulcanized rubber is soft and tacky, and has poor resistance to abrasion. Modulus of elasticity, tensile strength (without the need for reinforcing fillers), and resistance to degradation by oxidation are enhanced by vulcanization (Brydson, 1982 and Metherell, 1992). The magnitude of the modulus of elasticity is directly proportional to the density of the crosslinks. Vulcanized natural rubber also possesses high resilience and rapid recovery from deformation (Metherell, 1992). To produce a rubber that is capable of large extensions without rupture of the primary chain bonds, there must be relatively few crosslinks, and these must be widely separated. Useful rubbers result when about 1 to 5 parts (by weight) of sulphur is added to 100 parts of rubber. Increasing the sulphur content further hardens the rubber and also reduces its extensibility. Also, since they are crosslinked, elastomeric materials are thermosetting in nature (Brydson, 1982).

Vulcanization may be carried out using substance other than sulphur, but these are far less frequently used. Non-sulphur vulcanizing systems include organic peroxides, urethanes and certain phenol-formaldehyde resins (Metherell, 1992). Two factors are very important in the vulcanization of rubber:, the density of crosslinking (the frequency with which a rubber chain is linked to others) and the nature of the crosslink.

**Vulcanization Behavior**

After the rubber has been compounded by the addition of the appropriate curing agents, processed and formed, it is then vulcanized. The vulcanization process occurs in three stages: (1) an induction period; (2) a curing or crosslinking stage; and (3) a reversion or overcure stage (Morton, 1973 and Ismail & Hashim, 1998, Gent 2000). The structural features present in the initial vulcanizate network, are summarized in Figure 3. The polysulphides crosslinks and network-bound accelerator fragments shorten at a rate which depends on the ratio of sulphur to accelerator and the cure temperature. For example if there is a high accelerator to sulphur ratio, the final network contains a high proportion of monosulphide crosslink and pendent groups, as shown in reaction A in Figure 4. However, if the ratio of accelerator to sulphur is low then polysulphidic crosslink will persist, together with some di- and mono-sulphidic crosslinks, as shown in reaction scheme B. The rubber is also modified by formation of cyclic sulphides and other reaction involving the main chain. It is evident that a considerable proportion of the sulphur

may be combined with the rubber in forms which do not contribute to the crosslink structure. Estimates of the number of sulphur atoms chemically combined with the rubber per physically effective crosslink vary between 2 and 100 (Metherell, 1992, Ghosh, 1990 and Blow, 1971).

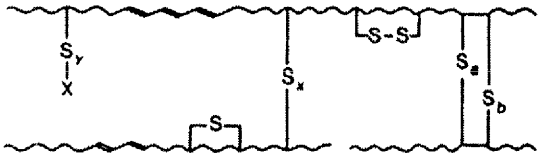


Figure 3: A diagrammatic representation of the network structure of a sulphur vulcanizate (*x, y, a* and *b* = 1-9); X = accelerator fragment (Metherell, 1992, Ghosh, 1990 and Blow, 1971).

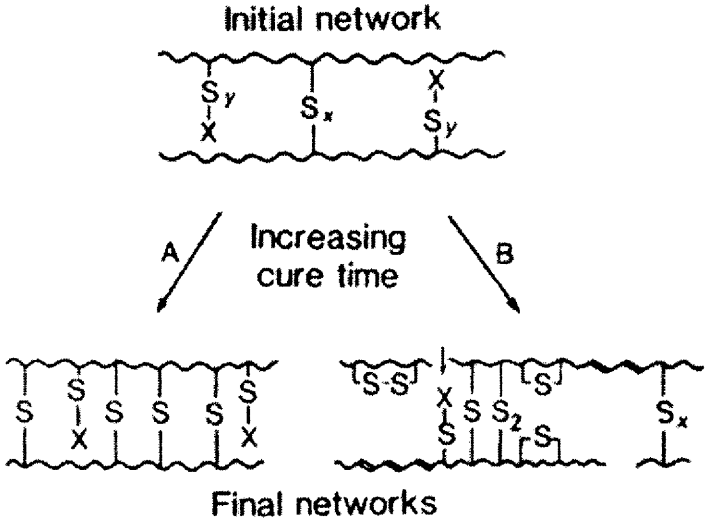



Figure 4: Dependence of network structure on vulcanizing system. A high accelerator: sulphur ratio (or sulphur donor/accelerator system) and high soluble zinc concentration; B, low accelerator : sulphur ratio or low soluble zinc concentration (Chapman and Porter, 1988 and Metherell, 1992).

The accelerated sulphur vulcanization systems can be classified into three types (Fuller *et al.*, 1974, Metherell, 1992 and, Ismail & Hashim, 1998):

1. Conventional systems (CV) containing high sulphur to accelerator ratios.
2. Efficient systems (EV) containing high accelerator to sulphur ratios.
3. Semi efficient systems (Semi-EV) that is intermediate between 1 and 2.

**Conventional Sulphur Systems**

Conventional vulcanizing systems (CV systems) have high ratio of sulphur (2-3.5 pphr by mass) to accelerator (0.5-1.0 pphr by mass). This system contains more polysulphidic crosslink (70-80%) than the disulphidic crosslink (20-30%) with a relatively high degree of polymer chain modification (Metherell, 1992 and, Ismail and Poh, 2000). This system gives vulcanisate which have excellent initial properties like resilience and resistance to fatigue and abrasion and are satisfactory for many applications (Metherell, 1992 and, Nasir and Teh, 1998). High level of polysulphidic crosslinks also gives high tensile and tear strengths particularly in unfilled vulcanizates, which has been attributed to the ability of these crosslinks to break under stress. However, they show poor heat and oxidation resistance because the polysulphidic crosslink are thermally unstable and can be readily oxidized (Metherell, 1992 and Ismail & Hashim, 1998).

**Efficiently Sulphur Systems**

This vulcanization systems using a high ratio of accelerator (2.0-6.0 pphr by mass) to sulphur (0.3-1.0 pphr by mass) which give predominately monosulphidic crosslink are called efficient vulcanizing (EV) systems. EV system shows good heat stability and oxidation resistance, but have poorer resistance to fatigue because of the presence of the monosulphidic crosslinks (Metherell, 1992 and Ismail & Hashim, 1998). This effect is attributed to the low level of main chain modifications, particularly cyclic sulphides, in EV vulcanizates.

**Semi-efficient Sulphur Systems**

Semi efficient vulcanizing systems are intermediate between CV systems and EV systems, with similar level of accelerator (1.0-2.5 pphr by mass) and sulphur (1.0-2.0 pphr by mass). This result in approximately equal amounts of monosulphidic and polysulphidic chains to be present in the rubber network. This systems are frequently used when compromises between high and low temperature properties or between fatigue life and heat resistance are required (Metherell, 1992 and Ismail & Hashim, 1998).

**Peroxide Vulcanization**

Peroxides are another type of curing agent for elastomers. Unlike sulphur curing, double bonds are not required for peroxide vulcanization, and thus, they may be used to crosslink saturated rubbers (Gent, 1992). Peroxide curing occurs by a free radical mechanism and leads to carbon-carbon crosslinks (Buzare *et al.*, 2001), which are quite stable and result in vulcanizates with good ageing and compression set resistance (Metherell, 1992, Gent, 1992 and Ismail and Hashim, 1998). Mechanism of vulcanization peroxide is illustrated in Figure 5.

The peroxide (POOP), decomposes into alkoxy radicals:

$$POOP \longrightarrow 2PO\bullet \quad (1)$$

the alkoxy radicals abstract a hydrogen atom from the rubber, RH,

$$RH + PO\bullet \longrightarrow R\bullet + POH \quad (2)$$

crosslinks are formed by combination of two rubber radicals:

$$2R\bullet \longrightarrow RR \quad (3)$$

Figure 5: Mechanism of vulcanization peroxide (Metherell, 1992)

At first stage, reaction of vulcanization of peroxide involved decomposition of peroxide into alkoxy radicals (stage 1); followed by abstract a hydrogen atom (stage 2) gives hydrocarbon radicals. Study about this model shows that this hydrocarbon radicals have combination reaction of two rubber radicals (stage 3).

**Resistance to Degradation**

Natural rubber (NR), unlike many other polymers, is highly susceptible to degradation, due to the presence of double bonds in the main chain. Degradation of NR is accelerated mainly by heat, humidity, light, ozone, radiation etc. In routine technological evaluation, rubber vulcanizates are subjected to accelerated ageing tests (heat ageing) to get information about the service life (Vinod *et al.*, 2002 and Spetz, 1995). For many years heating in air at 70°C has been used as an accelerated ageing test for natural

rubber compounds, with changes in tensile strength, elongation at break, and modulus, or more correctly stress at an arbitrary elongation, being used as a measure of deterioration (Blow, 1971).

Changes can occur in a rubber component as a result of the conditions under which it is stored or used or during heat ageing: (Blow, 1971 and Fuller *et al.*, 1974). The changes occurring during the degradation of rubber could be described in three ways (Blow, 1971, Mathew 1992, Ahlblad, 1998 and Stephen *et al.*, 2006).

1. Crosslinks and main chains scission, resulting in a reduction in chain length and average molecular weight.

2. Crosslinking resulting in a three-dimensional structure and higher molecular weight.

3. Chemical alteration of the molecules by introduction of new chemical groups and the formation of more crosslinks of the same type as those already present or of a different type which may be immune to further scission.

The degradation can occur with one or two of these three ways, or involve in all this three ways.

**Oxidative Ageing**

Oxygen is considered to be the most important degradant for natural rubber. A small amount of one to two per cent of combined oxygen in rubber serves to make it useless for most application. The oxidation of rubber is believed to take place through a free-radical chain reaction whose mechanism was proposed by Mathew (1992). In order to prevent extensive deterioration of the rubber, it is necessary to interrupt the chain reaction and stop autocatalysis. This could be accomplished by either terminating the free radicals or by decomposing the peroxides into harmless products. Antioxidants, in fact, function this way. It is established that amine antioxidants act both by reacting with free radicals and by decomposing peroxides. Phenolic antioxidants, on the other hand, react primarily as free radical sinks or chain stoppers. Phosphites react readily with free peroxides such as ROOH to give ROH and a phosphate (Mathew 1992).

The attack by oxygen on raw rubber is different from that on vulcanized rubber. In the former case, an initial induction period is followed by rapid uptake of oxygen. With vulcanized rubber, there is no induction period and the oxygen uptake is essentially linear with time. The net result of oxygen attack on natural rubber is an overall decrease in all properties. Tensile strength, elongation, flex life and abrasion resistance decrease progressively as oxidative ageing increased. Initially modulus and hardness increase slightly but then fall off (Mathew 1992 and Ismail & Hashim, 1998).

The effects of heat and oxygen on rubber, in general practice, are never separated and the practical result of heat of rubber is a combination of crosslinking and an increase in the rate of oxidation (Mathew 1992). Figure 6 show the mechanism of oxygen attack on elastomers involves an autocatalytic free radical chain propagation. The first step is creation of macroradicals R•, as a result of hydrogen abstraction from rubber chains by a proton acceptor. Oxidation continues by reaction of macroradicals with oxygen and the subsequent generation of hydroperoxides and peroxy radical as follow (Gent, 1992 and Ahlblad, 1998):

Initiation a) $RH \longrightarrow RO\bullet + H\bullet$ (4)
(rubber molecule)

Propagation b) $R\bullet + O_2 \longrightarrow RO_2\bullet$ (5)
peroxy radical

$RO_2\bullet + RH \longrightarrow ROOH + R\bullet$ (6)
hydroperoxide

Hydroperoxide can decompose unimolecularly or react bimolecularly:

$$ROOH \longrightarrow RO\bullet + \bullet OH \quad (7)$$

$$2ROOH \longrightarrow RO\bullet + RO_2\bullet + H_2O \quad (8)$$

Termination c)

$$2R\bullet \longrightarrow R\text{-}R \quad (9)$$

$$R\bullet + RO_2\bullet \longrightarrow RO_2R \quad (10)$$

$$2RO_2\bullet \longrightarrow \text{nonradical product} + O_2 \quad (11)$$

Figure 6: The basic oxidation scheme for the oxidation of polymer. (Gent, 1992 and Ahlblad, 1998)

**Fracture Mechanics**
**Tensile Properties**

Tensile properties include tensile strength, elongation and tensile modulus; these properties are determined by stretching standard test pieces at a constant rate using a tensile machine. Tensile strength is the force, or stress, required to rupture a standard test piece by stretching at a constant rate. The tensile strength of different elastomers can vary from below 7 $N/mm^2$ to above 45 $N/mm^2$, depending on the basic rubber and compounding ingredients used (Nagdi, 1993).

Elongation, or strain, is defined as the extension produced by a tension force applied to a standard specimen and is expressed as a percentage of the original length. Tensile modulus as applied to elastomers is defined as the force, required to produce a certain elongation. The test elongation is typically 100% or 300%. Tensile modulus is a measure of the stiffness and vulcanization degree of a rubber compound. It is normally determined during the course of tensile strength testing. The 100% modulus of different elastomeric materials can vary from below 1 $N/mm^2$ to above 13 $N/mm^2$, depending on the chemical composition of the rubber compound (Nagdi, 1993).

**The tearing concept**

The physical principle on which the fracture mechanics approach is founded is a consideration of the energy necessary to propagate the crack. When a crack grows, irreversible processes occur in the vicinity of the moving tip, leading to energy loses that must be made up from the available elastic energy. The magnitude of these losses is determined by the properties of the rubber and the strain in the crack tip region, and the rate of growth of the crack. In some elastomers, energy losses may occur in the bulk under the applied loading and these must also be taken into account. However, it is the losses in the crack tip region that are of prime importance, and these must be large even for rubbery materials for which the bulk losses (at much lower deformations and rates of strain) are negligible. Thus the energy necessary to propagate a crack at a particular rate is likely to be a characteristic of the rubber itself, even though it greatly exceeds the thermodynamic surface free energy, and may therefore be independent of the overall shape of the test piece (Blow, 1971 and Gent, 1992). There are many forms of tear test-piece. Current standard use is illustrates in Figure 7.

Tear measurements on a non-crystallizing styrene-butadiene rubber (SBR) have been carried out using these test pieces and the results, shown in Figure 8, are expressed in terms of $G$ and the rate of crack growth $r$. It can be seen that the results are consistent with a single relation, independent of the test piece geometry, as implied by the fracture mechanics approach (Thomas, 1960, Stevenson, 1992 and Gent, 1992)

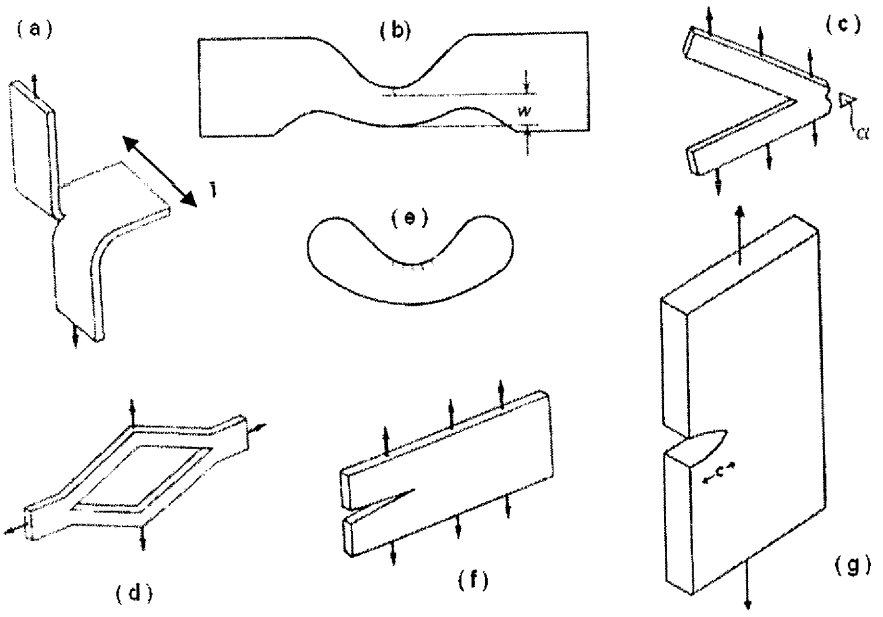



Figure 7: Tear test pieces: (a) trouser; (b) crescent (w = initial untorn width); (c) angled; (d) split; (e) crescent, original form, shown with five nicks; (f) pure shear; (g) edge crack. (Blow, 1971, Gent, 1992)

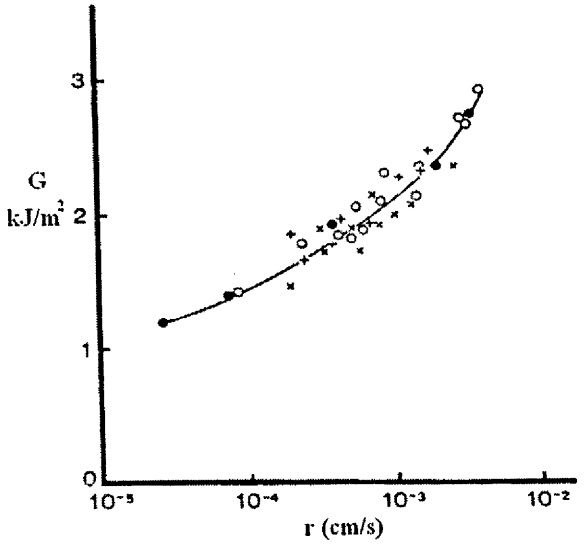



Figure 8: Strain energy release rate $G$ versus rate of tearing $r$ (logarithmic scale) for an unfilled styrene-butadiene rubber vulcanizate using the various test pieces shown in Figure 8: x, trousers; +, pure shear; O, split; ● angled (Gent, 1992)

The tear energy per unit area, T for the trouser test specimen is given (Gent, 1992)

$$T = \frac{2\lambda F}{t} - wW$$

where F is the tearing force acting on each leg of the specimen with uniform thickness $t_h$ and width $w$ as shown in Figure 7a. $W$ denotes the work done per unit volume in deforming the legs of the specimen, which is determined from the area under the uniaxial stress-strain response in tension up to an extension ratio of $\lambda$. In the above expression, the relationship between F and T is independent of the length of the initial cut. If the width of the test piece legs is sufficiently large, the deformation of the legs is very small and $\lambda$ can therefore be assumed to have a value of $\lambda \approx 1$. That is with negligible energy stored in the legs ($W \approx 0$). This assumption simplifies equation to

$$T = \frac{2F}{t_h}$$

For the pure shear test piece (Figure 7f), the tearing energy is given by:

$$T = Wh_o$$

where $W$ is strain energy density at the applied deformation level away from the crack tip and $h_o$ the height of the unstrained test piece. The pure shear test piece has the advantage that the tearing energy remains constant as the crack increases in length for a specific applied strain in this geometry.

For a tensile strip with an edge crack (Figure 7g), T is given by the equation (Gent, 1992):

$$T = 2K(\lambda)W_c$$

where $c$ is the rack length, $W$ is the strain energy density per unit volume obtained from the area under a stress-strain curve, and $K$ a slowly varying function of the strain given approximately by $K = 3/\sqrt{\lambda}$ where $\lambda$ is extension ratio in the simple extension region.

**Permanent Set**

Certain materials, including NR, do not return completely to their original dimensions after release from a deformed state which has been imposed for a finite period of time. This residual deformation is called set. If the stretching as held for a short duration at ordinary temperatures, the set that is observed is not permanent but decreases with time and largely disappears with swelling after evaporation of the swelling agent. This is attributed from secondary forces of rubber network (Tobolsky and Andrew, 1945). However, if stretching is maintained at constant extension at elevated temperatures the irreversible set called permanent set is observed. This can be attributed ossibly to the formation of crosslinks due to chemical changes that effect the structure of the rubber network (Tobolsky and Andrews, 1945 & Andrews *et al.*, 1946).

Instantly after extension all the individual molecular chains in the network are stretched fom their equilibrium configuration, which for all chains corresponds to the unstretched length of the sample. If the rubber remains at constant elongation, changes occur in both the original polymer chains and the crosslinks, and the stress relaxes. New crosslinks are formed, resulting in a second network at equilibrium in the strained state of the sample. The stress would eventually decay completely to zero if all the original network chains were cut and after reformation, all the chains in the network now are at equilibrium in the stretched state. At an intermediate stage between these two extremes, the molecular network in the rubber sample contains two types of chain:

1. Chains that are at equilibrium when the sample is at the unstretched length.
2. Chains that are at equilibrium when the sample is at the stretched length.

When the elongation or deformation is removed, chains of the first type tend to pull the sample back to its original unstretched length whereas chains of the second type tend to hold the sample at its stretched

length. The length, which the sample actually equilibrium, will be intermediate between its unstretched and stretched length such that the stresses of two types of chains are in balance which each other (Andrews *et al.*, 1946). Figure 9 shows the principle of set after loading in a state of simple extension.

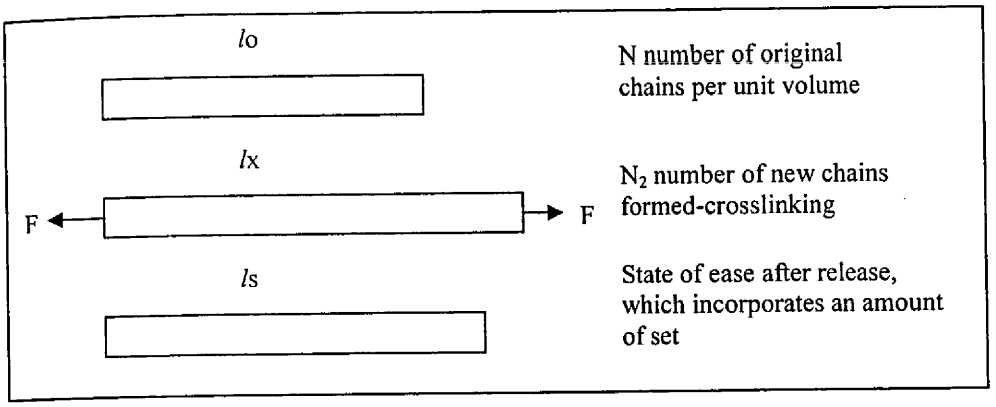



Figure 9: A schematic showing the effect of set after loading in simple extension

**Swelling**

All rubber can absorb liquids to a greater or lesser degree. The absorption of the liquid causes the rubber to increase in volume, and this is the phenomenon of swelling, a consequence of which is the deterioration in physical properties. Raw rubbers are completely soluble in certain liquids, but vulcanized rubbers are virtually insoluble. Strong bonds, such as chemical crosslinks between the rubber chains, prevent rubber molecules becoming completely surrounded by the liquid and restrict the deformation of the rubber (Blow, 1971).

The swelling of rubbers by liquids is a diffusion process. At the start of the process, the rubber at the surface of a component has a high liquid concentration while the liquid concentration in the bulk of the component is zero. Subsequently, the liquid molecules diffuse into the rubber just below the surface and eventually into the bulk of the rubbers. As the diffusion process proceeds, the dimension of the rubber component increase until the concentration of the liquid is uniform throughout the component and equilibrium swelling is achieved. The amount of a given solvent that will diffuse into the rubber until it reaches equilibrium depends upon the number of crosslinks per unit volume of rubber. The greater the number of crosslinks per unit volume, the shorter the average length the rubber chains between crosslinks and the lower the degree of swelling (Aprem *et al.*, 2003). The degree of swelling can be expressed by the percentage increase in volume or by the volume fraction of rubber in the swollen gel. Apart from crosslinking restrictions on the equilibrium swelling, the degree of swelling depends upon the compatibility of the rubber and liquid on a molecular scale. It is also depends on the amount and type of filler present in the rubber. The rate at which swelling proceeds depends upon the relative molecular size of the diffusing liquid molecule (Blow, 1971)

**Determination of Crosslink Density**

The crosslink density of an elastomer can be determined from swelling or mechanical measurements. An elastomer crosslinked above its gel point will not dissolve in a solvent but rather will absorb solvent and swell. Swelling will continue until the retractive forces in the extended chains balance the forces tending to swell the network. One expression widely used to relate the amount of swelling to the crosslink density is the Flory-Rehner equation (Gent, 1992 and Blow, 1971 Kumnuantip and Sombatsompop, 2003):

$$N = \frac{1}{V_o}\left[\frac{\ln(1-v_r) + v_r + \chi v_r^2}{v_r^{1/3} - \frac{1}{2} v_r}\right] \quad \text{or} \quad \ln(1-v_r) + v_r + N V_o v_r^{1/3} + \chi v_r^2 = 0$$

$$N = \frac{\rho}{M_c}$$

where $v$ = the crosslinks density, from swelling measurement
$V_o$ = molecular volume of the swelling solvent
$v_r$ = volume fraction of rubber in the swollen gel
$\chi$ = interaction constant- for natural rubber usually of the order of 0.4 in good solvents, and determined by the cohesive energy density of solvent and polymer and the swollen gel

Crosslink density has also been determined from equilibrium stress-strain measurement using the Mooney-Rivlin equation (Gent, 1992, Aprem, 2003 and Sombatsompop, 1998):

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + \frac{C_2}{\lambda}$$

where $\sigma$ = engineering stress, force per unit original cross sectional area
$\lambda$ = extension ratio
$C_1 + C_2$ = constant

The determination of crosslink density by equilibrium swelling measurement is a practical method for estimating the state of cure of a rubber product, and also for monitoring the degradation process including scission and crosslinking reactions. The swelling value Q is then calculated according to the equation:

$$Q = \frac{\text{swollen weight } (W_s) - \text{dried weight } (W_d)}{\text{original weight } (W_i) \times 100 / \text{Formula weight}}$$

where formula weight is the total weight of the rubber plus compounding ingredient based on 100 parts of rubber. The reciprocal swelling value 1/Q is proportional to the crosslink density (Mattson, 1993).

**Influence of Crosslink Density**

The mechanical behavior of an elastomer depends strongly on crosslink density. This is shown schematically in Figure 10, which display various physical properties as a function of crosslink density. Modulus and hardness increase monotonically with crosslink density, and at the same time, network become more elastic, or, stated alternatively, less hysteretic. Fracture properties such as tear and tensile strength, pass through a maximum as crosslinking is increased (Gent, 1992).

When an uncrosslinked elastomer is stressed, chains mat readily slide past one another and disentangle. At slow rate, fracture occurs by viscous flow without breaking chemical bonds. The effect of a few crosslinks is to increase the molecular weight-creating branched molecules and a broader molecular weight distribution. It is more difficult for these branched molecules to disentangle; hence strength increase. As crosslinking is increased further, the gel point is eventually reached, and a three-dimensional network is formed. Some chains may not be attached to the network (soluble sol phase), but the whole composition will no longer dissolved in a solvent. A gel cannot be fractured without breaking chemical

bonds. Thus, strength is higher at the gel point, since chemical bonds ruptured to create fracture surface (Gent, 1992).

However, strength does not increase indefinitely with more crosslinking. When an elastomer is deformed by an external force, part of the input energy is stored elastically in the chains and is available (will be release upon crack growth) as a driving force for fracture. The remainder of the energy is dissipated through molecular motions into heat and, in this manner, is made unavailable to break chains. At high crosslink levels, chain motions become restricted, and the 'tight' network is incapable of dissipating much energy. This result in relatively easy, brittle fracture at low elongation. Elastomers have an optimum crosslink density range for practical use. Crosslinking levels must be high enough to prevent failure by viscous flow, but low enough to avoid brittle failure (Gent, 1992).

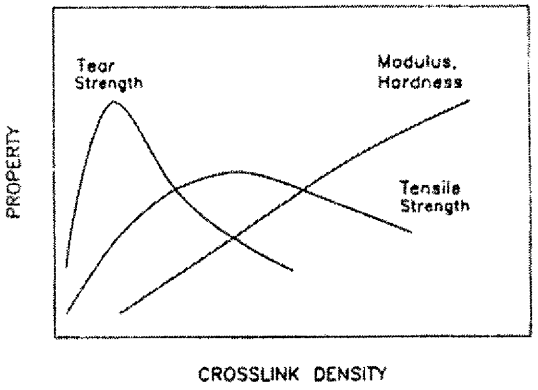



Figure 10: Effect of crosslink density in some mechanical properties of rubber (Gent, 1992).

## METHODOLOGY

### Materials

Table 1 showed the formulation used in this study. Natural rubber (SMR L) was obtained from Rubber Research Institute of Malaysia (RRIM). Other chemicals such as sulphur, zinc oxide, stearic acid, n-cyclohexyl-benthiazyl sulfonamide were purchased from Bayer (M) Ltd.

Table 1: Formulations and vulcanization conditions for NR vulcanizates.

| | **Formulation parts per hundred (pphr)** | | | | | |
|---|---|---|---|---|---|---|
| | **Conventional vulcanization systems** | | **Efficient vulcanization systems** | | **Peroxide systems** | |
| NR (SMR L) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zinc Oxide | 5.0 | 5.0 | 5.0 | 5.0 | - | - |
| Stearic Acid | 2.0 | 2.0 | 2.0 | 2.0 | - | - |
| Antioxidant | 3.0 | - | 3.0 | - | 3.0 | - |
| CBS* | 0.6 | 0.6 | 5.0 | 5.0 | - | - |
| Sulphur | 2.0 | 2.0 | 0.5 | 0.5 | - | - |
| DCP** | - | - | - | - | 2.0 | 2.0 |
| Vulcanization at 160°C, min | 4.45 | 5.33 | 7.96 | 10.15 | 21.18 | 20.89 |

* cyclohexylbenzothiazole-2-sulphenamide
** Dicumyl Peroxide

**Preparation and basic properties**

The compound formulations are given in Table 2. For sulphur vulcanizates blends have the same chemical composition, except for the amounts of Sulphur, CBS and 6PPD, which were varied to prepare the samples for CV or EV system with and without antioxidant (6PPD). But for peroxide system, only natural rubber (SMR L), dicumyl peroxide and 6PPD was used. The mixing was carried out in two-roll mill (Model XK-160) accordance to the method described by the American Society for Testing and Materials (ASTM), designation D 3184-80. The average time for one cycle mixing time must not exceeded more than 25 minutes that will caused curing occur in the rubber compounds.

**Cure Characteristics**

The respective cure time at 160°C as measure by $t_{90}$ were determined using a Monsanto Rheometer, model MDR 2000 according to ASTM D 2084-95. The cure time was the time at which the rheometer torque increased to 90% of the total torque change on the cure curve obtained from an oscillating disc rheometer. The scorch times, torque, elastic modulus, etc., can also be determined from the rheograph.

For this testing, vulcanizable rubber specimen compound (4g) was inserted into the cure meter test cavity. The cavity was maintained at cure temperature (160°C) and the torque range was 25 dNm. This testing were done for 30 minutes per sample. The force required to oscillate or rotate the disk to maximum amplitude continuously recorded as a function of time, with the force being proportional to the shear modulus (stiffness) of the test specimen at the test temperature. This stiffness first decreased as it's warm up, and then increased due to vulcanization. The test is completed when the recorded torque either rises to an equilibrium or maximum value.

**Vulcanization Process**

The testing procedure was conducted according to method described in ASTM D 1646. Compounds 2mm and 0.5mm thick sheets were compression molded at 160°C (same temperature as using to determine cure characteristic) with force of 10 MPa using hot press according to their respective cure time, $t_{90}$. Before compressed, bumping was done for 3 to 5 times to avoid bubble in the rubber sheets.

**Ageing**

The accelerated ageing tests aim to reproduce the effect of natural ageing in a shorter time. The deterioration of rubber at elevated temperature in air or at elevated oxygen pressure may provide data related to longevity during service (Azura, 2003). For the study of heat ageing resistance, tensile and tear values were determined. The test specimens were aged in a circulating air oven at 100 °C for 72 hours (3 days) and 144 hours (6 days). The aged specimens were left at room temperature before cutting and testing. Dumb-bell and trouser test pieces were then cut out.

**Mechanical Properties**

Mechanical properties such as tensile and tear properties of the specimens were measured according to ASTM D-412 and ISO 34, respectively. These properties are determined by stretching standard test pieces at a constant rate using a Instron 3366 machine.

**Tensile Test**

For tensile test, 2 mm and 0.5 mm thick dumbbell test pieces were cut from the molded sheets using a Wallace die cutter. The crosshead speed for tensile testing was 500 mm/min with an initial clamp separation of 65 mm and the test was performed at 25 ± 3°C.

**Tear Test**

The tear strength ($T_s$) determined using trouser test pieces was calculated in accordance with BS 903: Part A3 [1982], where the median force, F requires to propagate the crack is divided by the average thickness of the rubber sheet:

$$T_s = \frac{F}{t_h} \quad \text{N/mm}$$

For this measurement, the trouser test pieces of dimensions of 90 mm in length, 45 mm width, and cut of depth of 40 ± 0.5 mm were cut for 0.5 and 2 mm thickness. The last 1 mm of the cut was made using a razor blade. The crack growth for natural rubber is normally follows a tear strength measured using standard trouser test pieces as describes in BS 903: Part A3 (1995) do not properly meet the requirement for fracture mechanics interpretation. In particular, the narraw test piece described in the standard methods can result in highly strained legs, an undesirable feature made more serious by the failure of the standard methods to quantify it. For this reason, test pieces of a non-standard geometry were used in this study to measure the tearing energy.

**Measurement of fatigue properties**

Tensile strips approximately 120 mm x 25 mm and 0.5 mm thick, were cut from vulcanised sheets both for unaged and aged samples. After stress-strain measurements of the strips have been obtained, the test piece is then set up to the required maximum extension and a cut about 0.5 mm long is made in the centre of one edge with a razor blade. Samples were then cycled on fatigue machine. During the test, the cut length c, is measured with travelling microscope fitted with an eyepiece scale, the strip being slightly strained to facilitate observation. Readings are taken at intervals of cycles n corresponding to a 10-30% increased in cut length. The rate of growth dc/dn is determined from the difference in cut length divided by the number of cycles between two readings. This rate is referred to the tearing energy calculated from the average of the cut lengths and the strain energy density at the maximum strain of the cycle using equation

$$T = 2K(\lambda)Wc$$

The test is stopped when the cut reaches 20% of the test pieces width, as theory assumes this ratio to be small.

**Permanent Set**

Measurements of permanent set were made by using the metal frame. The frame consist simply of square metal bars with a fold back clip to hold the sample. There have 2 set where for set 1, samples were aged without stress and for set 2, sample were aged with strech to 100% elongation, The distance from the inside edges of the top and bottom fold back clips is 200mm (100% elongation). The frame will hold as many as four test sample.The strip test pieces used were 0.5mm thickness, 5mm width and 100mm long. Two fine ink marks were placed on the edge of each sample an appropriate distance apart (100mm). The distance between the marks was again accurately measured for each sample with a milimetre rule. The sample were then clipped to the frame, stretched to 100% extension and the distance between the marks again acurately measured.

The frame was inserted in an air-circulating oven at 100°C for 3 days and 6 days. After an appropriate period of ageing, the frame was removed from the oven and the sample quickly unclipped from the frame. After the samples were cooled for 15 minutes, the changes in length for both set and the distance between ink marks were measured. The permanent set was calculated as below:

$$\% \text{ permanent set} = \frac{I_S - I_U}{I_U} \times 100\%$$

where $I_U$ is initial length between marks
$I_S$ is set length after removing the sample from the oven and unclipping from the frame.

**Swelling**

This experiment was done according to ASTM D 471. Toluene solvent was used as swelling agent. The test pieces from permanent set (set 1 and set 2) were cut in small portion. The initial mass of each test piece was recorded. For this purpose, a laboratory balance capable of reading to ± 0.0001gm was used. The test pieces were then immersed in toluene at room temperature until a state of equilibrium swelling was obtained. On attainment of equilibrium, test pieces were taking out from swelling solvent; the surfaces were wiped and weighed.

The swelling ratio is defined as: $R = (W_1 - W_o)/ W_o$

where $W_o$ is the weight of the test piece before swelling and $W_1$ is the weight of the swollen test piece after time of immersion. The swelling ratio is a direct measurement degree of crosslinking, the smaller the ratio, the higher the degree of the crosslinking (Ismail *et al.*, 2001, Aprem *et al.*, 2003 and Nakason *et al.*, 2006).

**Crosslink Density**

The volume swelling can be used to determined the crosslink density. The volume fraction of rubber at equilibrium, $v_r$ was calculated without corrections for the presence of zinc oxide using the following relationship

$$v_r = \frac{\frac{x_r}{\rho_r}}{\frac{x_r}{\rho_r} - \frac{x_s}{\rho_s}}$$

where $\rho_s$, $\rho_r$ were the densities of swelling solvent and density of the raw rubber and $x_s$, $x_r$ were the mass fractions of solvent and rubber given by:

$$x_s = \frac{\text{Swollen equilibrium mass of test piece} - \text{Initial mass of test piece}}{\text{Swollen equilibrium mass of test piece}}$$

$$x_r = 1 - x_s$$

The higher $v_r$ indicating a lower extent of swelling and a higher crosslink density. The crosslink density was determined by the Flory-Rehner equation.

### SEM Micrograph Tensile Fracture Surface

The fracture tensile surfaces of the unaged and aged natural compounds were investigated with a Leica Cambridge S-360 scanning electron microscope. The fracture ends of specimens were mounted on aluminium stubs and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

## RESULT AND DISCUSSIONS

### Curing characteristics

Rheological behavior of polymers is one of the important factors affecting processability and the properties of final products. It has been reported that flow behavior of polymer melts depends mainly on molecular characteristics and flow geometry and processing conditions (Phewthongin *et al.*, 2005). Table 2 shows the results of cure time, $t_{90}$ and scorch time $t_2$, curing rate and maximum torque for sulphur vulcanization; conventional vulcanization (CV) and efficient vulcanization (EV) with and without the addition of antioxidant and non-sulphur vulcanization; peroxide system with and without the addition of antioxidant. Type of antioxidant that have used is N-(1,3-dimethylbutyl)-N'-phenyl (6PPD).

Generally, in natural rubber technology and processing, rubber manufacturers always prefer a vulcanization system that can give low cure time ($t_{90}$), high scorch time ($t_2$) and high cure rate as a result of processing advantages of time gained and cost reduction (Akinlabi *et al.*, 2005). It can be seen that cure time, $t_{90}$ and scorch time $t_2$ decreased with the addition of antioxidant for CV and EV. The trend observed might be due to the longer time the rubber remains on the mill during mixing. As the addition of antioxidant, the incorporation time of antioxidant into the rubber matrix also increases and, consequently, generates more heat due to additional friction, which increases the curing rate. But for peroxide system cure time, $t_{90}$ and scorch time $t_2$ are increased.

Table 2: Cure characteristics of the mixes cured at 160°C

| Vulcanization Systems | Scorch time, $t_2$ (m.m) | Cure time $t_{90}$, (m.m) | Curing Rate (CRI) | Max. Torque (dNM) |
|---|---|---|---|---|
| CV with antioxidant | 2.43 | 4.45 | 49.51 | 5.25 |
| CV without antioxidant | 2.96 | 5.33 | 42.19 | 4.94 |
| EV with antioxidant | 4.43 | 7.96 | 28.33 | 4.54 |
| EV without antioxidant | 5.76 | 10.15 | 22.78 | 4.85 |
| Peroxide with antioxidant | 9.73 | 21.18 | 8.73 | 3.47 |
| Peroxide without antioxidant | 3.00 | 20.89 | 5.59 | 6.44 |

### Mechanical Properties

There are many types of testing used in elastomeric material such as tensile, tear, compression set, hardness, fatigue and etc. However in this study, only tensile and catastrophic tearing energy test had been done to determined mechanical properties. According to Basfar et.al (2002), which have studied on influence of different curing systems of NR rubbers presented that the higher the cure temperature; the poorer are the mechanical properties of the vulcanizates.

## Tensile Properties

Tensile properties include tensile strength, elongation and tensile modulus. These properties are determined by stretching dumbbell test pieces at a constant rate using INSTRON machine. The effect of antioxidant and ageing time on the tensile strength of NR for CV and EV system, and also for non-sulphur vulcanization; peroxide for 2.0 mm and 0.5 mm thickness is presented in Figure 11 after ageing at 100°C.

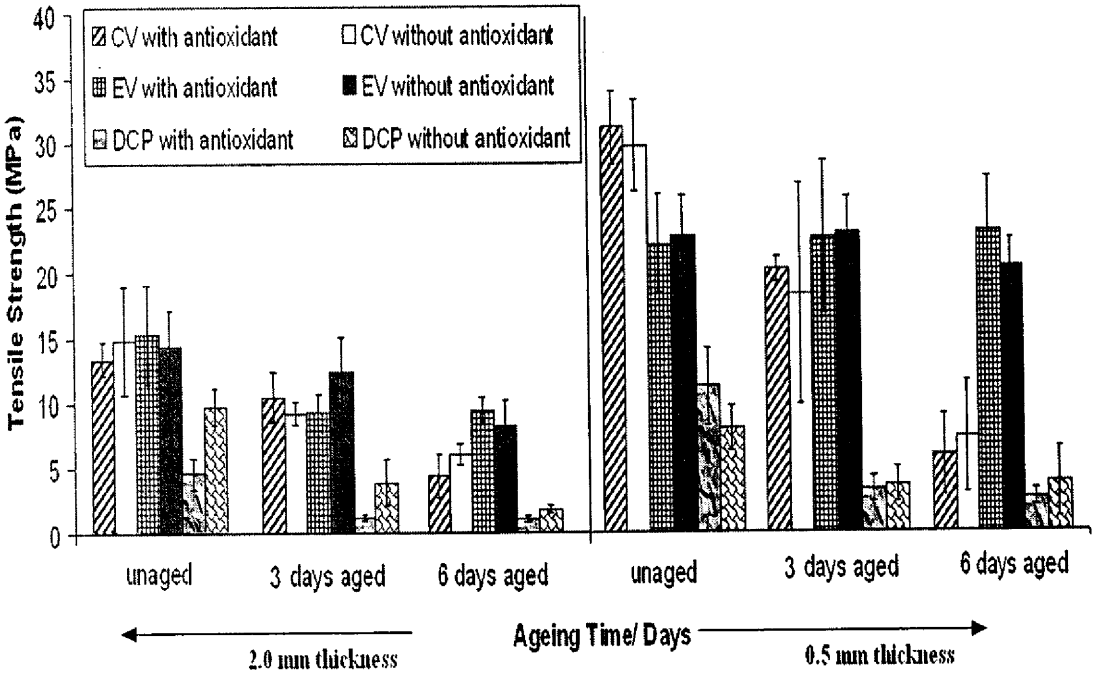



Figure 11: Tensile Strength of CV, EV vulcanizates and peroxide system as a function of ageing time for 2.0 mm and 0.5 mm thickness at 100°C.

### Effect of different vulcanization system

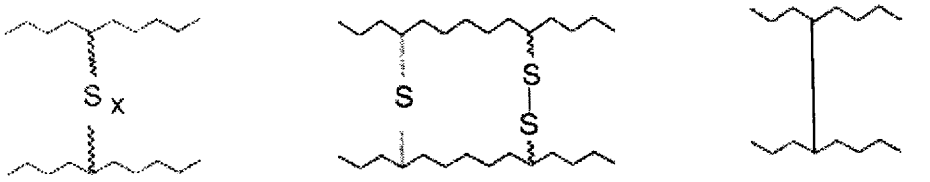
Different vulcanization systems formed different types of crosslinks. The crosslink structure and crosslink density affect the mechanical properties of NR. From Figure 11 above, unaged CV shows tensile strength slightly lower than EV for 2mm thickness. After ageing for 3 days and 6 days, tensile strength for CV system drastically drops due to ageing. Clearly evidence can be suggested that CV system has polysulphidic crosslinks which are readily oxidize and thermally unstable, compared to EV that has low level of main chain modification because of predominately monosulphidic crosslink. This type of crosslinks is more thermally stable (Metherell, 1992, Nagdi, 1993 and Ismail & Hashim, 1998).

Results for peroxide show the lowest tensile strength than sulphur-cured system; CV and EV for both thickness. This is because C – C chains in peroxide system do not have any replacing and cannot to release the inner stress when it's applied at rubber like C – $S_x$ – C chains in sulphur vulcanizates. Therefore, peroxide vulcanizates systems gives the lowest tensile strength. After ageing 3 and 6 days, this system with antioxidant shows the almost same strength but without antioxidant shows a slightly

decreasing for 2.0 mm thickness. For 0.5 mm thickness, peroxide with antioxidant shows a slightly decreased in tensile strength but peroxide without antioxidant shows almost the same strength.

Generally, tensile strength for the rubber decreases with ageing time. It's mean that ageing causes degradation of the rubber (Ghosh, 1990). The reaction of oxygen with elastomers, causes both chain scission and crosslinking. For sulphur-cured vulcanizates like CV and EV, the oxidation rate increase as sulphur content increases; it is believed that the allylic crosslink site is particularly susceptible to oxidation (Gent, 1992). As we well known, CV have a higher sulphur content than EV. So, probably this is why CV has drastically reduce in tensile strength compared than EV and peroxide.

In sulphur-cured NR, where polysulfide links are formed, while peroxide only have C – C crosslinks. A schematic representation of different types of crosslinks formed by conventional and efficient vulcanization systems is given in Figure 12 (Aprem, *et al.*, 2003).




Conventional System (CV) | Efficient System (EV) | Peroxide System

Figure 12: Different types of crosslink (Aprem, *et al.*, 2003)

For 0.5 mm thickness, CV shows a higher tensile strength, peroxide shows a lower strength and EV shows result between CV and peroxide. After ageing for 3 and 6 days, tensile strength for CV drop drastically for 0.5 mm thickness compared than 2.0 mm thickness but for EV have the almost same strength with further ageing for both thicknesses.

According to Bengt Mattson. (1993) oxidative ageing processes of natural rubber materials are dominated either by oxidative crosslinking or oxidative scission and by reaction in which different carbonyl compounds are the major product. Due to oxygen diffusion limitations, the outer layer of a 0.5 mm thickness is more oxidize than the 2.0 mm thickness.

**Effect of antioxidant**

The addition of antioxidant 6PPD in the NR and ageing time does not affect much tensile strength. NR vulcanizates for 2.0 mm thickness, in CV system, additions of antioxidant was slightly decreased the tensile strength at initial, but slightly increased for 3 days aged and decreased back for 6 days aged. For EV systems, additions of antioxidant was slightly increased the tensile strength at initial, but decreased for 3 days aged and increased back for 6 days aged.

In theoretical aspect, for sulphur vulcanizates, antioxidant functions as hydrogen donor (AH) and react with peroxy radicals (Metherell, 1992):

$$AH + RO_2\bullet \longrightarrow ROOH + A\bullet$$

The radical produced is incapable of abstraction of hydrogen from the rubber molecule. This reaction is in direct competition with the propagation reaction. Hence rubber peroxy radicals are destroyed and

oxidation of the rubber is minimized. Type of antioxidant that have used is N-(1,3-dimethylbutyl)-N'-phenyl (6PPD). 6PPD is in p-phenylenediamines group which is most effective types of antioxidant used in natural rubber (Metherell, 1992).

Peroxide for 2.0 mm thickness, addition of antioxidant causes a decreasing of the tensile strength. This is because some peroxide can trap or have some reaction with free radical and causes the reduction of efficiency crosslinking and destroy the antioxidant. Consequently, it is difficult to protect peroxide vulcanizate from ozone attack. For 0.5 mm thickness, for CV with antioxidant shows a higher reduction of tensile strength. But EV with antioxidant shows an almost same in tensile strength for unaged, 3 and 6 days aged. As discussed earlier, an EV system is a thermally stabile than EV. For peroxide with antioxidant, result shows a slightly decreased in tensile strength.

In the theoretical aspect, antioxidants are employed to slow oxidation. They fall into two classes, with different functions. The first type, called preventive antioxidants, reacts with hydroperoxides to form harmless, non-radical products. In the process, the antioxidant is oxidized. The second type, chain-breaking antioxidants, destroys peroxy-radicals that would otherwise propagate (Gent, 2000). This will lead a stability of EV after ageing.

**Effect of different thickness**

Generally, from the Figure 11, the result for 0.5 mm thickness is observed higher than results for 2.0 mm thickness. The tensile strength increases with smaller thickness. Failure occurs when the crack like defect manages to grow across the width of the specimen (Powell, 1983). For 2.0 mm thickness, which is thicker sample, possibility to have a defect like bubble or contamination with foreign material is higher. Consequently, crack propagates easily and gives a lower tensile strength. The distribution of the orientation of the chain molecules also gives the influence of tensile strength (Ghosh,1990). The thinner samples have a higher tensile strength is believed to be caused by a less of air trapped or bubble and defect in the test pieces.

According to González *et al* (2006) the tensile strength behavior of natural rubber at high strain is attributed to the capacity to crystallize on stretching. Variation of this property with the temperature and/or crosslink density was related, not only with the nature of the crosslinks, but also with their spatial distribution. After ageing, result tensile strength for CV with antioxidant for 2.0 mm thickness drop to about 21% but for 0.5 mm thickness, tensile strength drop to about 35% after 3 days aged. The higher drop in tensile strength for 0.5 mm thickness might be due to the effect of degradation. For 0.5 mm thickness sample, degradation is expected to be uniform at overall surface and centre sample than 2.0 mm thickness. This is because in 2.0 mm thickness, it's probably degrade only at the sample surface and lack of oxygen reaching the centre of the test pieces will cause a significant profile of oxidative effects through the test pieces (Azura, 2003)

**Modulus at 100% Elongation (M100)**

The effect of different vulcanization system on tensile modulus, i.e. modulus at 100% elongation (M100) with and without antioxidant is shown in Figure 14. M100 is measurement for extension at 100% elongation From Figure 13; CV system has a higher M100 than EV.

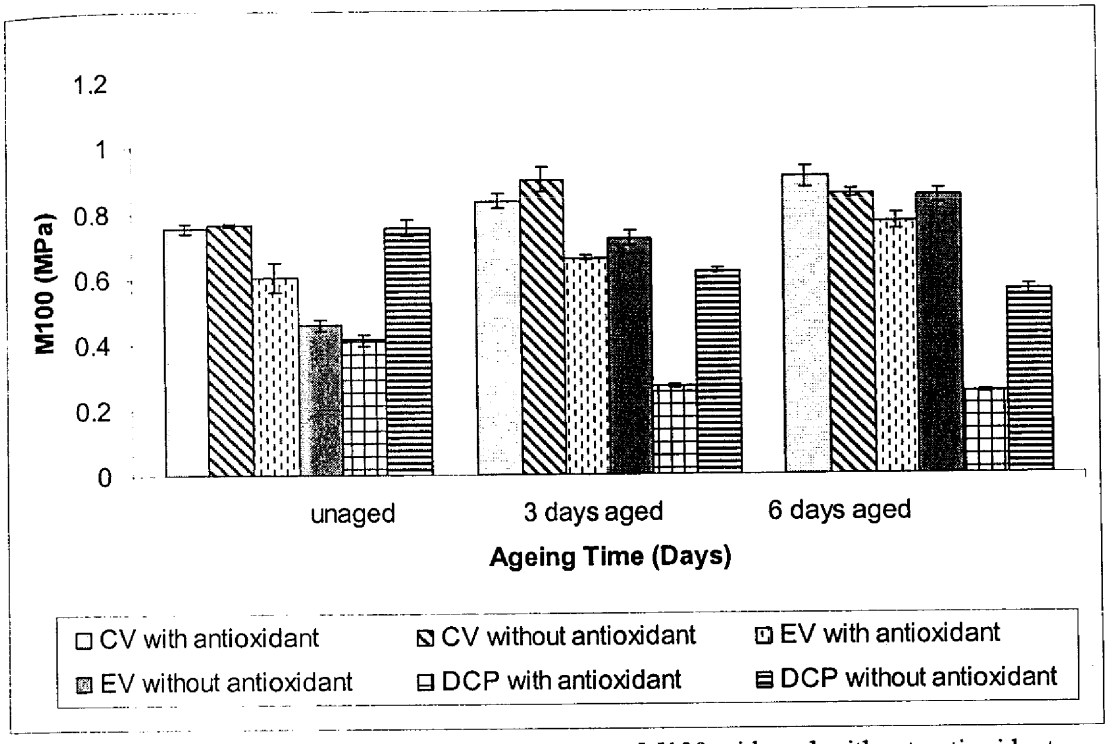


Figure 13: Effect of different vulcanization system on M100 with and without antioxidant.

According to Rattanasom et al. (2005), in their study about effect of curing system of natural rubber/tire tread reclaimed rubber blends, modulus of the samples in CV system are clearly greater than those in the EV system. They also present that the results indicate higher crosslink density of the vulcanizates in the CV system because there is more sulphur available for crosslink formation, compared to those in the EV system. As a consequence, CV vulcanizates exhibit lower breaking strain than EV. This trend can also observe in this study as shown in Figure 13.

Figure 13 above shown that M100 for peroxide is lower than sulphur vulcanizates system except peroxide without antioxidant for unaged sample. This was explained by Basfar et al. (2002) that the high strength of sulphur vulcanizate is due to an internally relaxed network. There are certain differences between vulcanization by peroxide (C-C crosslinks) in which the chains are rigidly connected and those with longer mobile crosslinks (polysulphidic crosslinks). They also proposed that the elastic behavior at room temperature improves somewhat with increasing longer crosslinks due to the increased free mobility of chain segment. In contrast, the shorter crosslinks (i.e. C-C crosslinks) restrict the orientation of the maromolecular chains of the NR when stretched. Moreover, the formed bonds because increased deformation stiffness, because less mobility of the polymer chains, and consequently lowered mechanical properties.

After ageing, M100 for sulphur vulcanizates increased. In the theoretical aspect, oxidation occurs during ageing. The attack by oxygen on raw rubber is different from that on vulcanized rubber. The net result of oxygen attack on natural rubber is an overall decrease in all properties. For modulus properties initially increase slightly but then fall off (Mathew 1992 and Ismail & Hashim, 1998). This is reason for increasing modulus in sulphur vulcanizate after ageing. Continuous ageing to longer time will decrease the modulus. For peroxide M100 decreased after ageing. Addition of antioxidant have not give a much change but still can comparable except for peroxide, addition of antioxidant cause a lower M100 than peroxide without antioxidant. This is probably having the same reason as discussed before in tensile strength.

**Elongation at Break**

The heat resistances of these formulations were followed by monitoring the percentage change in their elongation at break as presented in Figure 14. Elongation at break is the elongation at the time of rupture (Nagdi, 1993). The decreasing in elongation at break was observed when the stiffness and brittleness of the rubber compounds were increased.

Figure 14 shows the effect of different vulcanization system on elongation at break with and without antioxidant. From Figure 14 below, EV show a higher elongation at break compared than CV and peroxide. As a theory, CV system produces vulcanizates in which the combined sulphur exists predominantly in polysulphide crosslink. Such vulcanizates tend to harden excessively at elevated temperatures, possibly because suphur is released from the polysulphidic crosslink to form additional crosslink (Nagdi, 1993). Consequently, CV shows a lower elongation at break than EV. Peroxide system shows a lower elongation at break. The reason for peroxide is same as M100, where peroxide has lower mechanical properties because of C-C crosslink.

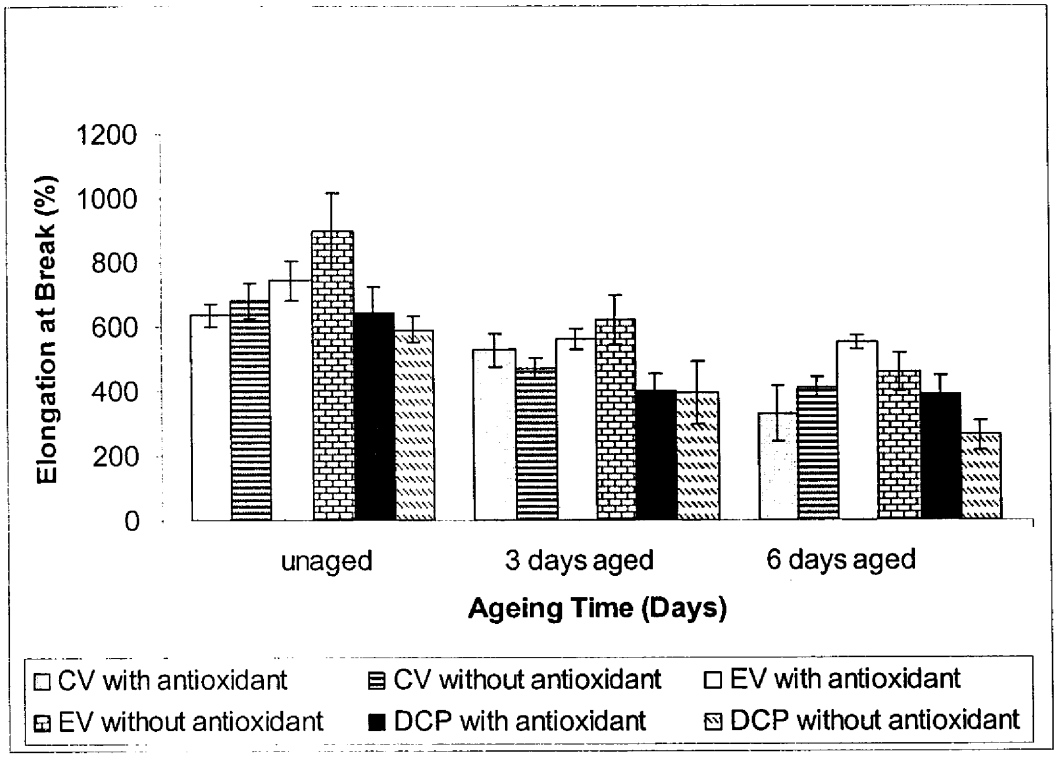



Figure 14: Effect of different vulcanization system on elongation at break with and without antioxidant

**Catastrophic Tearing Energy, $T_c$**

The tearing energy of an unfilled elastomer depends upon the nature of the molecular backbone, the molar mass of the polymer and the concentration and the nature of the crosslinks. Different curing systems can produce widely different strengths for the same polymer backbone, even when compared at a similar degree of crosslinking (Azura, 2003). Figure 15 shows the $T_c$ as a function of ageing time for the NR vulcanizates measured using trouser test pieces with different vulcanization systems with and without antioxidant for 2.0 mm and 0.5 mm thickness

**Effect of different vulcanization system**

Generally, all the vulcanizates showed a decreased in catastrophic tearing energy, $T_c$ after ageing. For 2.0 mm thickness, the reduction of $T_c$ was more pronounced for the CV when compared to the other cure systems. $T_c$ for CV system with antioxidant was decreased about 51% after ageing for 3 days at 100°C and ageing 6 days at 100°C, the $T_c$ remained only 24% of the unaged $T_c$. For CV without antioxidant, $T_c$ were decreased about 60% after ageing for 3 days at 100°C and ageing 6 days at 100°C remained only 15% of the original unaged $T_c$. The larger reduction in $T_c$ for the CV system when compared with EV system probably relates to a larger amounts of new crosslinks, scission of the main chain and crosslink and chemical modification to the main chain, all of which are believed to occur in CV system during oxidative ageing (Azura & Thomas, 2006).

$T_c$ for EV with antioxidant were decreased about 31% after ageing for 3 days at 100°C and further ageing reduced the $T_c$ to about 39% based on the unaged $T_c$. For EV without antioxidant, $T_c$ were decreased about 41% after ageing for 3 days at 100°C and further ageing reduced the $T_c$ to about 53% of the unaged $T_c$. In EV system, decreasing of $T_c$ is not drastic like the CV systems. As we know, EV system used lower amount of sulphur and higher amount of accelerator. So, this system used this sulphur efficiently to make a structure that have monosulphide chains and give lower degree of main chains modification. Using EV system in natural rubber can reduce reversion except at higher curing temperature. That's why EV system shows a higher thermally and oxidative resistance (Ismail & Hashim, 1998). For the peroxide cured NR, the effect of ageing on $T_c$ were not as severe as observed in the CV systems. The reduction of $T_c$ of peroxide with and without antioxidant was not too drastic like CV. From Figure 4.9 above, result for peroxide is much lower compared to CV and EV although for unaged sample. This is probably have a same reason like tensile strength that C – C chains in peroxide system do not have any replacing and cannot to release the inner stress when it's applied at rubber like C – $S_x$ – C chains in sulphur vulcanizates. Therefore, a peroxide vulcanizates system gives the lowest $T_c$ (Ismail & Hashim, 1998).

For 0.5 mm thickness, the trend of $T_c$ is quite similar to 2.0 mm thickness. For unaged, CV systems give high $T_c$ compared than other systems. But after ageing for 3 days, this system shows a lower $T_c$ and become much worse when ageing for 6 days. This is because of CV system show poor heat and oxidation resistance because the polysulphidic crosslink are thermally unstable and can be readily oxidized. For EV system shows a good $T_c$ after ageing compared than CV because of monosulphidic crosslink give good heat stability and oxidation resistance. For peroxide with antioxidant show a decreasing in $T_c$ but result for without antioxidant is more stabile; decreasing only about 18% from unaged.

**Effect of antioxidant**

In order to attain higher mechanical properties, antioxidant, 6PPD is added to compound. For 2.0 mm thickness, in CV, EV and peroxide system, additions of antioxidant have a slightly change in $T_c$. Addition of antioxidant, increased in $T_c$ for CV, EV and peroxide after ageing for 3 and 6 days. According to Brown et al (2000), antioxidants are added to inhibit oxidation and, clearly, if the antioxidant is used up there will be a rapid change in degradation rate. At the same time as degradation is proceeding there may be additional crosslinking taking place which again complicates interpretation of accelerated test results.

For 0.5 mm thickness, CV and peroxide system shows a similar trend like 2.0 mm thickness. CV system with antioxidant, $T_c$ is slightly lower than CV system without antioxidant except for aged 6 days. CV with antioxidant was decreased about 39% for unaged and decreasing after ageing for 3 days at 100°C is about 11% but for further ageing to 6 days the $T_c$ is slightly increased from 6.39 N/mm to 6.70 N/mm when compared to the CV system without antioxidant. For EV, addition of antioxidant increased the $T_c$ for unaged but slightly decreased for 3 days aged and 6 days aged. This is maybe because addition of

antioxidant produced marked improvements to ageing resistance (Jones and Allen, 1992) to protect it from degradation. Tc for peroxide in 0.5 mm thickness show an increased in $T_c$ with addition of antioxidant for unaged, 3 and 6 days aged.

**Effect of different thickness**

When compared with 2.0 mm and 0.5 mm thickness, the results indicate lower Tc for 0.5 mm thickness. As mention before, in 0.5 mm thickness, the degradation of the sample is expected to be uniform at overall surface and centre sample than 2.0 mm thickness. This is because in 2.0 mm thickness, it's probably degrade only at the sample surface and have some part in the centre of sample are not affected by ageing and causes higher $T_c$ for 2.0 mm thickness. The inhomogeneous nature of high temperature ageing of thick vulcanizated natural rubber has been reported. Ageing at elevated temperature affects only the outer layers causing initial softening followed by hardening to yield a resinous layer of oxidized layer (Knight and Lim, 1975). Above a temperature of about 80°C, the reaction of oxygen by an elastomer is so rapid in relation to the rate of diffusion of oxygen that it can penetrate only to a small depth before being absorbed.

The free surfaces of elastomeric components are in contact with oxygen in the air; diffusion into the rubber is a key step in oxidative ageing. Oxygen molecules diffuse into the surface, but some of them are immediately consumed by oxidation reactions to produce crosslinking, scission of the rubber chains or crosslinking and combination with molecular chains of rubber. The rate of degradation becomes slower with increasing sample thickness, because of the smaller concentration of oxygen with increasing distance from the surface. Thus, to achieve homogenous oxidative ageing the sample thickness should not exceed the value up to which the rate of oxygen uptake per unit volume is constant. Below the critical sample thickness, the oxidation may be regarded as being free from diffusion control. Azura et al (2006) have also studied the effect of thickness and she presented her result that sample thickness of 0.5 mm have relative uniform ageing throughout their thickness in the through thickness measurements.

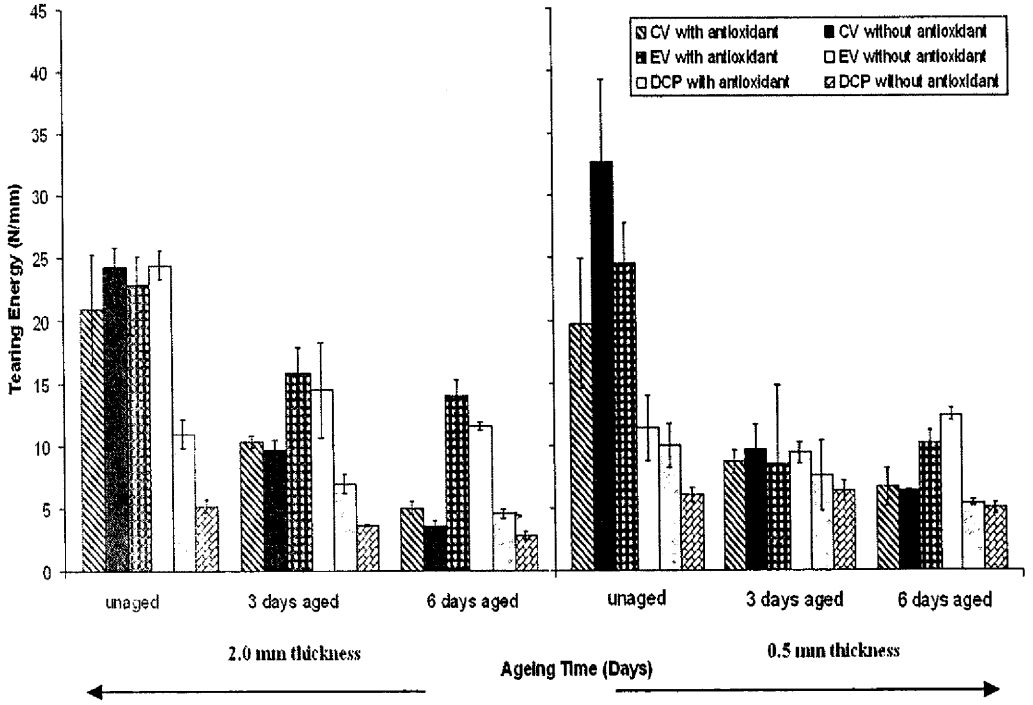


Figure 15 $T_c$ of CV, EV vulcanizates and peroxide system as a function of ageing time for 2.0 mm and 0.5 mm thickness at 100°C

**Fatigue properties (Cyclic crack growth)**

The tearing energy approach has proved to be successful in treating the fracture of elastomers (Gent et.al, 1964). However, the tearing tests presented in tensile and tear strengths only estimate the strength of elastomer under a single loading cycle producing rapid crack growth. For the majority of elastomeric components, failure is not usually due to large static load resulting in catastrophic failure but to the smaller cyclic fatigue loads. Cyclic crack growth behaviour is the most appropriate approach to predict the service life of components. Relationship between the incremental crack growth rate per cycle d*c*/d*n* and tearing energy *T* have been referred to as the "crack growth characteristics", since it represents the basic tearing property of the vulcanisates (Lake & Lindley, 1964).

The effect of accelerated ageing on the cyclic crack growth has been investigated for ageing at 100°C for efficiently cured NR and conventionally cured NR. The crack growth rate d*c*/d*n* as function of tearing energy, *T* is given in Figures 16 and 17. In general, results for different periods of ageing showed that for a given tearing energy, the rate of crack growth per cycle was increased after ageing. Figure 4 shows the tearing energy, for the conventionally cured NR vulcanisate, at a crack growth rate of 1.0 x$10^{-4}$ mm per cycle decreased by a factor 3.8 after ageing 3 days and by a factor about 10 after ageing for 6 days when compared with the unaged sample. The effects of ageing on the crack growth properties of the efficiently cured compound were not as pronounced as that for the conventionally cured NR. This may be due to the inhibition of strain crystallisation in the conventionally cured compound as a result of ageing, caused by chain modification (Bristow & Tiller, 1970).

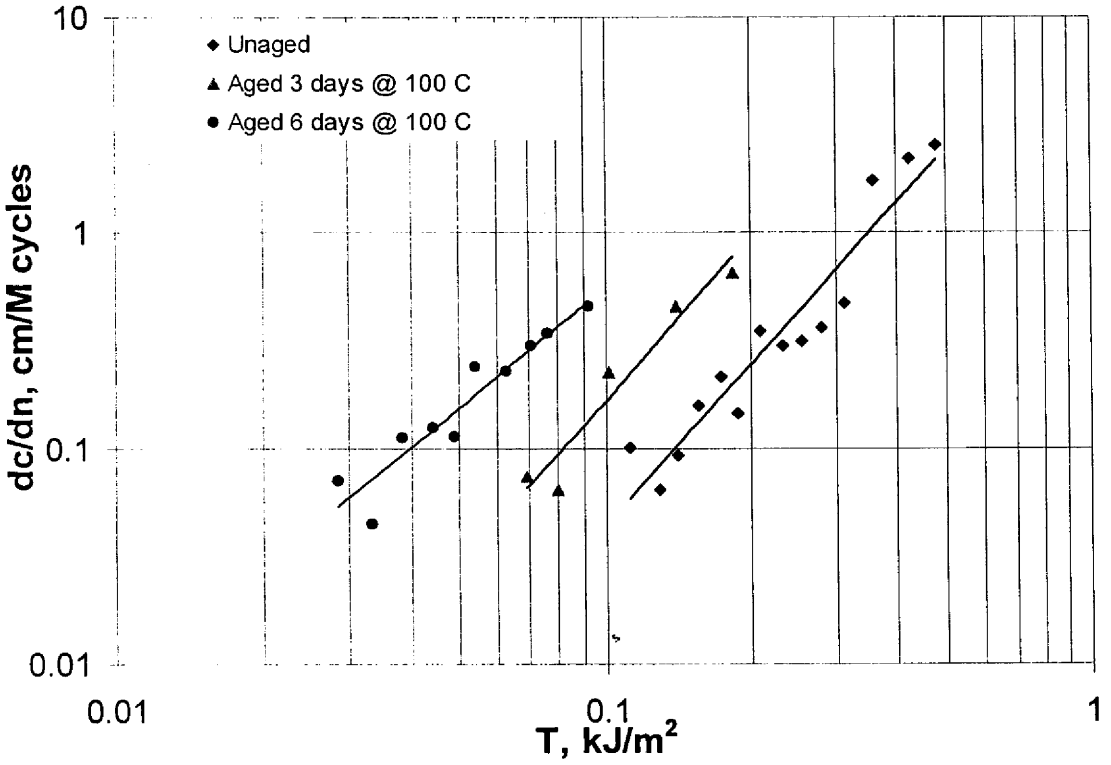



Figure 16 crack growth rate (d*c*/d*n*) as function of tearing energy (*T*) for efficiently cured NR aged at 100°C.

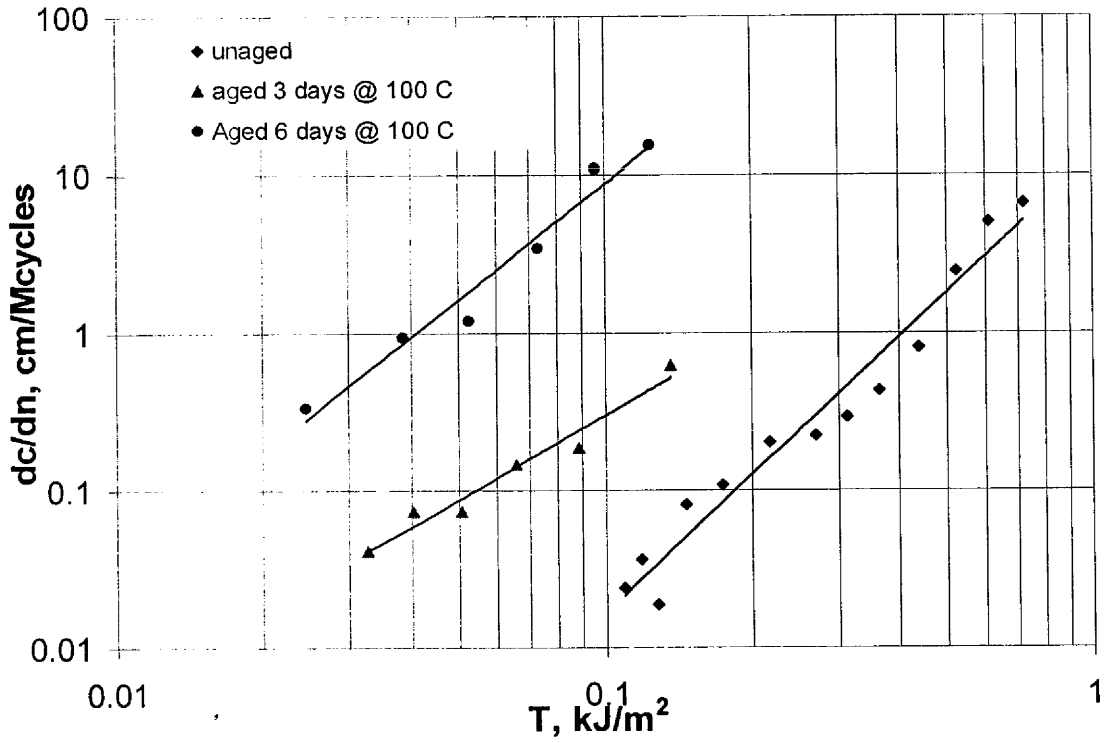



Figure 17 crack growth rate (d*c*/d*n*) as function of tearing energy (*T*) for conventionally cured NR aged at 100°C

**Permanent set**

Measurements of permanent set were made by using the metal frame shown in Figure 18. For simple experimental measurements, permanent set and equilibrium volume swelling measurements were used to investigate of the effect the main chains and/or crosslinks scission and crosslinks reformation for different ageing conditions (Azura and Thomas, 2006). Scission of main chains and/or crosslinks together with the reformation of crosslinks occurs during ageing. Scission causes softening; crosslink formation has the reverse effect, and, if ageing is carried out in the strained state causes a permanent set (Blow, 1971, Mathew 1992, Ahlblad, 1998 and Stephen *et al.*, 2006).

From the experiment that has been done, several samples broke during ageing time. These are the samples for peroxide system for 3 and 6 days ageing and sample for CV without antioxidant for 6 days ageing. For this CV sample, polysulphhidic crosslinks will break down at elevated temperatures and the material will show high permanent set if under strain (Blow, 1971).

Figure 19 show the percentage of permanent set as a function of ageing time. The higher bar means that the extended length is much longer. From graph, result show that for the CV system the degree of main chain and/or crosslink scission, crosslink reformation and the percentage of permanent set after ageing with 100% strain were higher compared to the EV system. These results are not too surprising since CV systems produced mainly polysulphidic crosslink, which are thermally unstable (Metherell, 1992 and Ismail & Hashim, 1998)

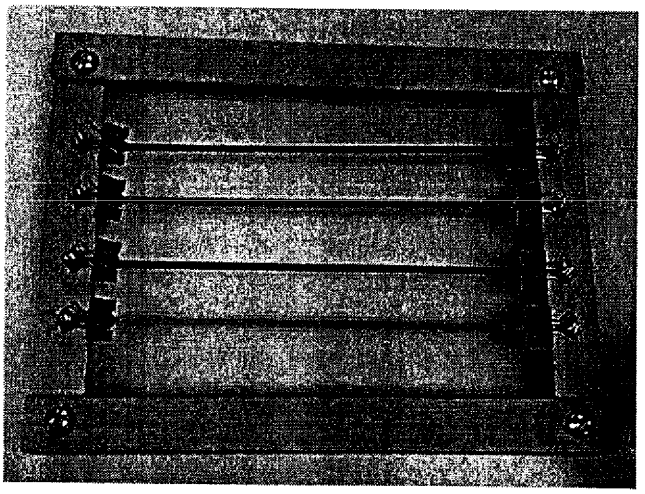


Figure 18: Rubber samples stretched to 100% strain in the permanent set frame

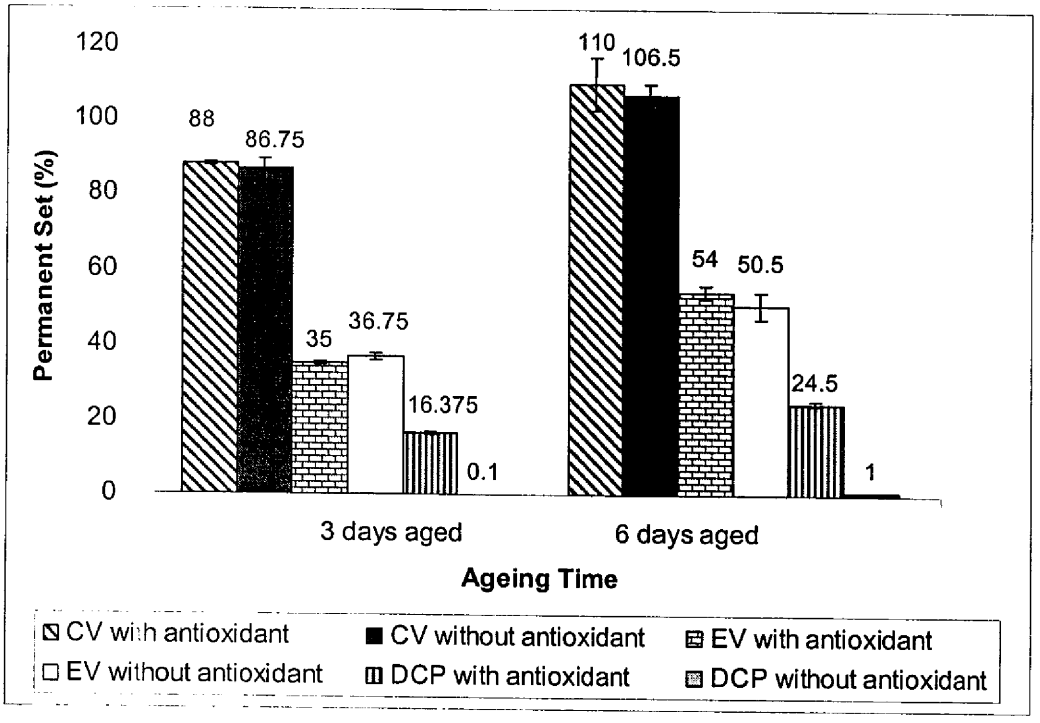



Figure 19: Percentage of permanent set of CV, EV vulcanizates and DCP system as a function of ageing time.

**Crosslink Density**

Generally, in swelling measurements, weight sample after swell at first hour are drastically increase and after that become more stable and after 48 hours, assumed that sample is in equilibrium state. This is because, in rubber have the molecules. These molecules are arranged in three-dimensional lattice of sites. When rubber immersed in toluene, each site may be occupied either by liquid (toluene) or by a single segment of a polymer chains. While a liquid molecule is free to occupy any vacant site, the successive

segments of a particular polymer molecule are restricted to adjacent sites, as illustrated in the accompanying two-dimensional diagram (Figure 20) (Treloar, 1975)

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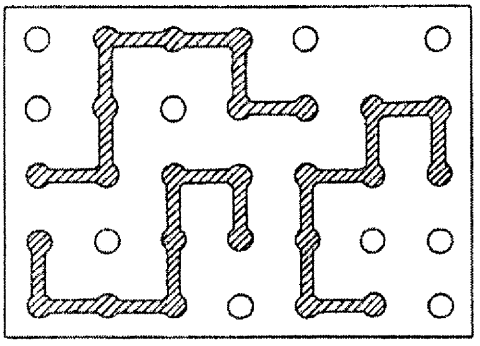


Figure 20: Schematic representation of lattice model. The circles represent toluene molecules (Treloar, 1975)

After several hours, that is no any vacancy for liquid molecule to occupied and swelling ratio become plateau if this experiment continued to several days. According to Mattson (1993), swelling measurements have been used for two different purposes. First, determination of crosslink density and second; studies on effect surface modifications (Mattson, 1993). However, in this study, swelling measurement has been used to determination of crosslink density. Determination of crosslink density by equilibrium swelling measurement is a practical method for estimating the state of cure of a rubber product, and also for monitoring the degradation process including scission and crosslinking reactions.

**Physical Crosslink Density**

Physical crosslink density can be calculated by Flory-Rehner equation (Gent, 1992 and Blow, 1971 Kumnuantip and Sombatsompop, 2003). The physical crosslink density of NR for CV, EV system, and peroxide is presented in Table.3. From Table 3 below, CV without antioxidant system for unaged sample have a lower physical crosslink density than samples 6 days aged with stretch. This is because, physical crosslink density represent only in the physical part. 6 days with stretch show a higher physical crosslink density. As mention earlier, polysulphidic crosslinks in CV system are thermally unstable have relatively high level of chain modification either scission in main and/or crosslink chain and/or reformation of crosslink. These factors may contribute to the lower crosslink density for 6 days aged. But for CV system with antioxidant, unaged sample have a higher crosslink density than 6 days aged with stretch. This is probably scission of main chain/ crosslink is more than reformation of new crosslink.

For EV with antioxidant samples show a higher in physical crosslink for unaged sample compared than samples after ageing but EV without antioxidant results indicate 3 days with stretch have a higher physical crosslink density. As discussed earlier, EV system has a monosulphidic crosslink which are thermally stable. During ageing, probably scission of main and/or crosslink chain and together with reformation of crosslink happened with caused a higher crosslink density after ageing. For peroxide system, results for without and with antioxidant shows that for unaged sample have higher physical crosslink density. In the theoretical aspect, peroxide have a C-C crosslink. Stretching to 100% elongation at 100°C caused scission of C-C chains or main chains in peroxide system. In this system, assumed that mostly C-C chain and/or main chain scission occur caused a reduction of physical crosslink density for peroxide system compared to sample after aged 3 and 6 day with and without stretched.

From Table 3, after ageing for 6 days with stretched the results show that the CV system without antioxidant has a higher crosslink density compared to others vulcanizate system without antioxidant. This is because the CV vulcanizate has mainly polysulfidic crosslinks, the EV vulcanizate has the greatest level of monosulfidic crosslinks, and the peroxide consists of a network structure carbon to carbon crosslink. But after addition of antioxidant, the density of crosslinking for CV vulcanizate for 6 days with stretched drastically decreased.

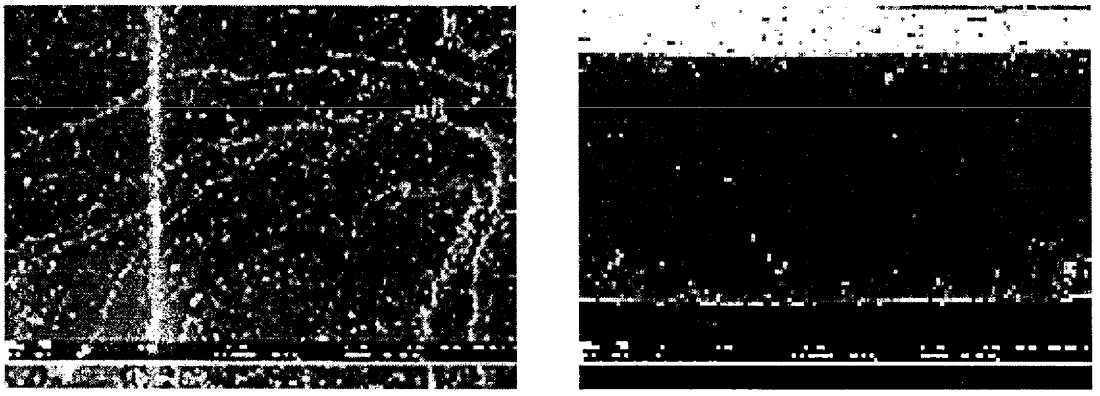
Table 3 Physical crosslink density of NR for CV, EV system, and peroxide

| System | Aged Time | Physical Crosslink Density |
|---|---|---|
| CV with antioxidant | unaged | 5.48E-05 |
| | 3 days without stretch | 4.14E-05 |
| | 3 days with stretch | 4.21E-05 |
| | 6 days without stretch | 4.42E-05 |
| | 6 days with stretch | 3.25E-05 |
| CV without antioxidant | unaged | 9.04E-05 |
| | 3 days without stretch | 1.16E-04 |
| | 3 days with stretch | 1.09E-04 |
| | 6 days without stretch | 1.09E-04 |
| | 6 days with stretch | 2.18E-04 |
| EV with antioxidant | unaged | 1.13E-04 |
| | 3 days without stretch | 9.13E-05 |
| | 3 days with stretch | 9.79E-05 |
| | 6 days without stretch | 8.56E-05 |
| | 6 days with stretch | 9.33E-05 |
| EV without antioxidant | unaged | 1.19E-04 |
| | 3 days without stretch | 1.08E-04 |
| | 3 days with stretch | 1.42E-04 |
| | 6 days without stretch | 1.06E-04 |
| | 6 days with stretch | 1.36E-04 |
| Peroxide with antioxidant | unaged | 6.94E-05 |
| | 3 days without stretch | 4.59E-05 |
| | 3 days with stretch | 4.81E-05 |
| | 6 days without stretch | 3.93E-05 |
| | 6 days with stretch | 4.35E-05 |
| Peroxide without antioxidant | unaged | 1.43E-04 |
| | 3 days without stretch | 1.26E-04 |
| | 3 days with stretch | 1.21E-04 |
| | 6 days without stretch | 1.14E-04 |
| | 6 days with stretch | 1.02E-04 |

**Morphological Observation**

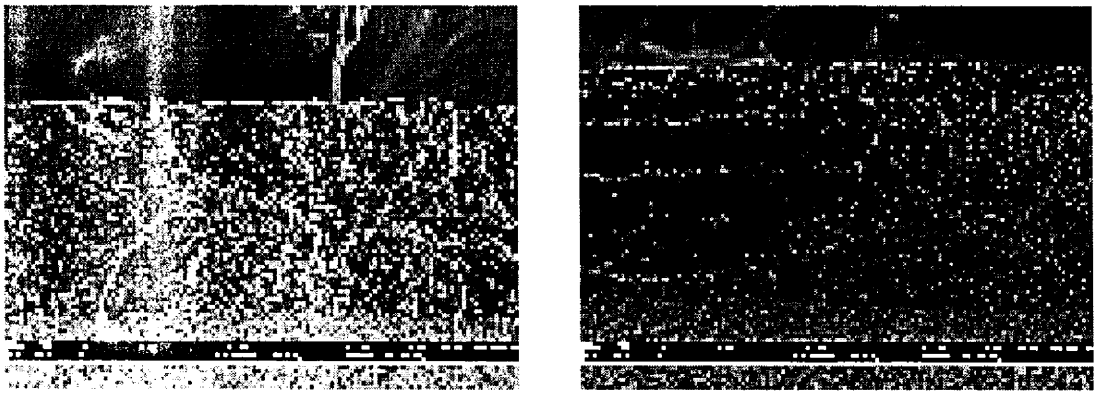
Figures 21 and 22 show the morphology of tensile fractured surface for conventionally cured NR and efficiently cured NR before and after ageing for 6 days at 100°C. It is apparent that changes of fractured surface for both systems. Figure 21 shows that conventionally cured NR gives very smooth surface after ageing. Figure 22 shows the same effect for efficiently cured NR but less pronounced compared to conventionally cured NR. The smooth fractured surface after heat ageing could be attributed from the

reduction of the ability of NR to strain crystallize hence decrease the strength properties (Azura et al, 2003).



(a) (b)

Figure 21 the SEM micrograph for conventionally cured NR (a) Unaged (b) Aged for 6 days at 100°C at 100x magnification.



(a) (b)

Figure 22 the SEM micrograph for Efficiently cured NR (a) Unaged (b) Aged for 6 days at 100°C at 100x magnification.

## CONCLUSIONS

The main conclusions drawn from this study are:

1. Cure time ($t_{90}$) and scorch time ($t_2$) properties was slightly decreased with the addition of antioxidant for CV and EV but increase for peroxide system. The trend observed might be due to the longer time the rubber remains on the mill during mixing.

2. In sulphur-cured NR, polysulfide links are formed, while peroxide only C – C. When sulfur-cured natural rubber (NR) compounds are exposed to a thermal aging environment, significant changes in tensile properties are observed. These changes are directly related to modifications of the original crosslink structure and main-chain scission.

3. Tensile strength for 0.5 mm thickness is observed higher than results for 2.0 mm thickness. For 2.0 mm thickness, which is thicker sample, possibility to have a defect like bubble or contamination with foreign material is higher. Consequently, crack propagates easily and gives a lower tensile strength. The distribution of the orientation of the chain molecules also gives the influence of tensile strength. The thinner samples have a higher tensile strength is believed to be caused by a less of air trapped or bubble and defect in the test pieces. But after ageing, result tensile strength for CV with antioxidant for 0.5 mm thickness have higher drop than 2.0 mm thickness. For 0.5 mm thickness sample, degradation is expected to be uniform at overall surface and centre sample than 2.0 mm thickness. This is because in 2.0 mm thickness, it's probably degrade only at the sample surface and lack of oxygen reaching the centre of the test pieces will cause a significant profile of oxidative effects through the test pieces

4. The tear strength for 3 days and 6 days ageing at 100°C for the conventionally cured NR decreasing drastically when compared to the efficiently cure NR and peroxide system. Addition of antioxidant have cause only a slightly change in tensile and tearing energy. Results show that samples aged for 6 days at 100°C for the conventionally cured NR exhibit higher crack growth rate when compared to the efficiently cured NR.

5. Scission of main chains and/or crosslinks together with the reformation of crosslinks occurs during ageing. Scission causes softening; crosslink formation has the reverse effect, and, if ageing is carried out in the strained state causes a permanent set. Permanent set and equilibrium volume swelling measurements were used for investigating of the effect of main chains and/or crosslinks scission and crosslinks reformation for different ageing time.

6. For CV systems, increasing in percentage in permanent set is higher but result in physical crosslink density show a small decreasing compared to unaged sample. This means that in CV system, scission of main chain and/or crosslink and, crosslink reformation occur. The degree of main chain and/or crosslink scission, crosslink reformation and the percentage of permanent set after ageing with 100% stretch were higher compared to the EV and peroxide system. These results are not too surprising since a CV system contains polysulphidic crosslinks which are thermally unstable. For EV systems, the decreased in physical crosslink density were indicate that formation in new crosslink is too small compared to the main chain and/or crosslink scission during ageing. These results were in agreement with result from tensile and tear strength with most of the original crosslinks being destroyed for longer periods of ageing. For peroxide system, increasing in permanent set and decreasing in crosslink density are almost comparable. Permanent set causing a scission of almost main chain and/or crosslink for peroxide.

7. The SEM micrograph shows the changes of fractured surface before and after ageing. Conventionally cured NR shows very smooth surface after ageing that can be associated with the inhibition of the ability to strain crystallize after ageing.

## REFERENCES

Ahlblad Gustav (1998). *Imaging Chemiluminescence Applied to Oxidation of Rubber Materials and Polyamide.* Department of Polymer Technology Royal Institute of Technology Stockholm 1998.

Akinlabi A.K., Okieimen, F.E., Egharevba, F., and Malomo, D., (2005). *Investigation of the Effect of Mixing Schemes on Rheological and Physico-Mechanical Properties of Modified Natural Rubber Blends.* Materials & Design, Article in Press, Corrected Proof.

Allen, P. W., M. A., Phil., D., A.I.R.I., F.R.I.C. (1972). *Natural Rubber and The Synthetics*. Crosby Lockwood, London, pp 8-17

Andrews, R.d., Tobolsky, A.V. and Hanson, E.E. (1946). *The Theory of Permanent Set at Elevated Temperatures in Natural and Synthetics Rubber Vulcanizates*. Applied Physics.

Aprem, A. S., Joseph, K., Mathew, T., Altstaedt, V., Thomas S., (2003). *Studies on accelerated sulphur vulcanization of natural rubber using 1-phenyl-2, 4-dithiobiuret/ tertiary butyl benzothiazole sulphenamide*. European Polymer Journal 39, pp 1451–1460

Azura A Rashid. (2003). *An Investigation of the Effect of Ageing on the physical Properties of Natural Rubber*. PhD Thesis, Research Group, Name of institution, Country. Queen Mary, University of London, pp 220 -229

Azura, A.R., Goeritz, G., Muhr, A.H. and Thomas. A.G., (2003). "*Effect of ageing on the ability of natural rubber to strain crystallize*", in Busfield, J.J.C and Muhr, A.H (eds), Constitutive Models for Rubber III, Conference Proceeding, UK, 79-84.

Azura, A.R and Thomas, A.G. (2006), "*Effect of heat ageing on crosslinking scission and mechanical properties', Elastomer and components: Service life prediction* - progress and challenges, Woodhead publishing in materials, Chapter 2, 27-38

Azura A.R.,Muhr, A.H. and Thomas, A.G. (2006), *Diffussion and reactions of oxygen during ageing for conventionally cured natural rubber vulcanisate*, Polymer-Plastics Technology & Engineering, Vol 45, 893-896

Basfar, A.A., Abdel-Aziz, M.M., Mofti, S. (2002). *Influence of different curing systems on the physico-mechanical properties and stability of SBR and NR rubbers.* Radiation Physics and Chemistry 63, pp 81–87

Bengt Mattson (1993). *Thermo-Oxidative Degradation And Stabilization of Rubber Materials.* Department of Polymer Technology, Royal Institute of Technology, Stockholm.

Blow, C. M. (1971). *Rubber Technology and Manufacture*. Institution of the Rubber Industry.

Bristow, G.M. and Tiller, R.F., (1970), "*Correlation of structure and properties of natural rubber vulcanisates*," Kautshuck Gummi Kunstsoffe, 23, 2, 55

Brown, R. P., Forest, M. J. and Soulagnet, G., (2000). *Long Term And Accelerated Ageing Test on Rubbers*. References from the Rapra Abstracts Database, Volume 10.

Brydson, J.A. (1982). *Plastic Materials* (Fourth Edition). Butterworths Scientific.

Buzaré, J. Y., Silly, G., Emery, J., Boccaccio, G. and Rouault, E., (2001). *Aging Effects on Vulcanized Natural Rubber Studied by High Resolution Solid State $^{13}$C-NMR*. European Polymer Journal, Volume 37, Issue 1, pp 85-91

Chapman, A. V. and Poerter, M., (1998). Sulphur Vulcanisation Chemistry, In *Natural Rubber and Technology*, Ch 12, Roberts, A. D., [editor], Oxford University Press.

Callister William D., Jr (2000). *Material Science and Engineering An Introduction (Fifth Edition)*. John Wiley and Sons, Inc., pp 461

Crawford R. (1985). *Plastics and Rubber-engineering design and applications*. Mechanical Engineering Publications Ltd, London.

Edge, Michele; Allen, Norman S.; Gonzalez-Sanchez, Rosa; Liauw, Christopher M.; Read, Simon J. and Whitehouse, Robert B. (1999). *The influence of Cure and Carbon Black on The High Temperature Oxidation of Natural Rubber I. Correlation of Physico-Chemical Changes*. Polymer Degradation and Stability. Volume 64, Issue 2, pp 197-205

Findik, F., Yilmaz, R. and Köksal, T., (2004). *Investigation of Mechanical and Physical Properties of Several Industrial Rubbers*. Materials & Design, Volume 25, Issue 4 , pp 269-276

Freakly, P. K. & Payne A. R (1978). *Theory and Practiceof Engineering Rubber*. Applied Science Publishes Ltd, pp3-305

Fuller K. N. G., Muhr A. H., Thomas A. G., Roberts A. D., Lake G. J. and Lewis P. M. (1974). *Engineering Design with Natural Rubber*. Dr Lindley's Bulletin, pp 3-16

Gent Alan N. (1992). *Engineering with Rubber- How to Design Rubber Components*. Hanser Publishers, Munich Vienna New York Barcelona.

Gent Alan N. (2000). *Engineering with Rubber- How to Design Rubber Components (Second Ed)* . Hanser Publishers, Munich Vienna New York Barcelona.

Gent, A.N., Thomas, A.G. and Lindley, P.B., (1964), "*Cut growth and fatigue of rubbers. Part I: The relationship between cut growth and fatigue*," Journal of Applied Polymer Science, 8, 455.

Ghosh, Premamoy (1990). *Polymer Science and Technology of Plastics and Rubbers*. Tata McGraw-Hill Publishing Company Limited, New Delhi.

González, L., Valentín, J. L., Fernández-Torres, A., Rodríguez, A., Marcos-Fernández, A. *Effect of The Network Topology on The Tensile Strength of Natural Rubber Vulcanizate at Elevated Temperature*. Instituto de Ciencia y Tecnologia de Polimeros (Csic), C/Juan de la Cierva, 3. 28006 Madrid, Spain.

Ismail H. and Hashim A. S., (1998). *Pengenalan Penyebatian dan Pemprosesan Getah*. Penerbit Universiti Sains Malaysia, pp 30-32

Ismail, H. and Poh, B. T. (2000). *Cure and Tear Properties of ENR 25/SMR L and ENR 50/SMR L Blends*. European Polymer Journal, Volume 36, Issue 11, pp 2403-2408

Ismail, H., Nizam, J. M. And Abdul Khalil, H. P. S., (2001). *The Effect of a Compatibilizer on the Mechanical Properties and Mass Swell of White Rice Husk Ash Filled Natural Rubber/ Linear Low Density Polyethylene Blends*. Polymer Testing 20, pp 125-133

Jones K. P. and Allen P. W., (1992) Historical Development of The World Rubber Industry, In: *Natural Rubber: Biology, Cultivation and Technology: Developments in Crop Science 23*, Ch. 1, M. R. Sethuraj and N. M. Mathew [editors], Elsevier Science Publishers B. V.

Knight, G. J. And Lim, H.S., (1975). *Factors Inflencing High Temperature Ageing of Large Natural Rubber Components*.Proceeding International Rubber Conference, Kuala Lumpur

Kumnuantip, C. and Sombatsompop, N., (2003). *Dynamic Mechanical Properties and Swelling Behaviour of NR/Reclaimed Rubber Blends*. Materials Letters, Volume 57, Issue 21, pp 3167-3174

Lake, G.J. and Lindley, P.B., (1964), "*Cut growth and fatigue of rubbers. Part II: Experiments on a non-crystallising rubber,*" Journal Applied Polymer Science, 8, 707.

Long, Harry (editors) (1985). *Basic Compounding and Processing of Rubber.* Rubber Division.

Metherell, C., (1992). Compounding and Vulcanization, In: *Natural Rubber: Biology, Cultivation and Technology: Developments in Crop Science 23*, Ch. 19, M. R. Sethuraj and N. M. Mathew [editors], Elsevier Science Publishers B. V.

Mathew N. M., (1992) Physical and Technology Properties of Natural Rubber, In: *Natural Rubber: Biology, Cultivation and Technology: Developments in Crop Science 23*, Ch. 18, M. R. Sethuraj and N. M. Mathew [editors], Elsevier Science Publishers B. V.

Nagdi, Khairi (1993). *Rubber as Engineering Material: Giudeline for User.* Hanser Publisher.

Nakason, C., Wannavilai, P., Kaesaman, A. (2006). *Effect of vulcanization system on properties of thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends*. Polymer Testing 25, pp 34–41

Nasir, M. and Teh, G. K. (1998). *The effects of various types of crosslinks on the physical properties of natural rubber*. European Polymer Journal, Volume 24, Issue 8, pp 733-736

Phewthongin, N., Saeoui P. and Sirisinha C., (2005). *A Study of Rheological Properties in Sulfur-Vulcanized CPE/NR Blends*. Polymer Testing, Volume 24, Issue 2, pp 227-233

Powell Peter C. (1983). *Engineering with Polymers*. Chapman and Hall Ltd, New York.

Rattanasom N., Poonsuk A., Makmoon T., (2005). *Effect of curing system on the mechanical properties and heat aging resistance of natural rubber/tire tread reclaimed rubber blends*. Polymer Testing 24, pp 728–732

Sombatsompop, N. (1998). *Investigation of Swelling Behavior of NR Vulcanizates*. Polymer-Plastics Technology and Engineering, Volume 37, Issue 1, pp 19-39

Spetz, Goran., (1996). *Recent developments in heat ageing tests and equipment.* Polymer Testing Volume 15, Issue 4, pp 381-395

Stephen, R., Jose S., Joseph K., Thomas S. and Oommen Z., (2006). *Thermal Stability And Ageing Properties of Sulphur And Gamma Radiation Vulcanized Natural Rubber (Nr) And Carboxylated Styrene Butadiene Rubber (XSBR) Latices And Their Blends*. Polymer Degradation and Stability, Article in Press, Corrected Proof.

Stevenson, A., (1992). Engineering Properties and Application of Rubber, In: *Natural Rubber: Biology, Cultivation and Technology: Developments in Crop Science 23*, Ch. 21, M. R. Sethuraj and N. M. Mathew [editors], Elsevier Science Publishers B. V.

Thomas, A. G., (1960). *Rupture of Rubber. Part IV:Further Experiments on The Tear Criterion.* Applied Polymer Science

Treloar, L.R.G., (1975). *The Physics of Rubber Elasticity, (3rd edition).* Clarendon Press, Oxford

Tobolsky, A.V. and Andrews, R.D., (1945). *Systems Manifesting Superposed Elastic and Viscous Behavior.* Chemical Physics

Vinod V.S., Siby Varghese, Baby Kuriakose, (2002). *Degradation Behaviour of Natural Rubber–Aluminium Powder Composites: Effect of Heat, Ozone And High Energy Radiation.* Polymer Degradation and Stability 75, pp 405–412

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304.PBAHAN.6035117

TEMPOH BERAKHIR 31/01/2007

AN INVESTIGATION OF THE EFFECT OF AGEING ON MECHINICAL PROPERTIES OF ELASTOMER

*JUMLAH GERAN :-*

*NO PROJEK :-*

Tempoh Projek:01/09/2004 - 28/02/2007

*PANEL :-* J/PENDEK

*PENAJA :-*

| Vot | | Peruntukan (a) | Perbelanjaan sehingga 31/12/2006 (b) | Tanggungan semasa 2006 (c) | perbelanjaan Semasa 2007 (d) | Jumlah Perbelanjaan 2007 (c + d) | Jumlah perbelanjaan Terkumpul (b+c+d) | **Baki Peruntukan Semasa (a-(b+c+d)** |
|---|---|---|---|---|---|---|---|---|
| 11000 | GAJI KAKITANGAN AWAM | 4,941.60 | 4,097.15 | 0.00 | 0.00 | 0.00 | 4,097.15 | 844.45 |
| 21000 | PERBELANJAAN PERJALANAN DAN SARA | 1,810.00 | 1,243.60 | 0.00 | 618.40 | 618.40 | 1,862.00 | (52.00) |
| 23000 | PERHUBUNGAN DAN UTILITI | 400.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 400.00 |
| 27000 | BEKALAN DAN ALAT PAKAI HABIS | 9,569.40 | 9,699.60 | 0.00 | 115.10 | 115.10 | 9,814.70 | (245.30) |
| 29000 | PERKHIDMATAN IKTISAS & HOSPITALITI | 800.00 | 815.70 | 0.00 | 761.02 | 761.02 | 1,576.72 | (776.72) |
| | | 17,521.00 | 15,856.05 | 0.00 | 1,494.52 | 1,494.52 | 17,350.57 | 170.43 |
| | Jumlah Besar | 17,521.00 | 15,856.05 | 0.00 | 1,494.52 | 1,494.52 | 17,350.57 | 170.43 |

# DEGRADATION BEHAVIOUR OF SULPHUR CURED NATURAL RUBBER VULCANISATES: EFFECT OF HEAT AGEING.

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*A better understanding of the mechanical behaviour and degradation of materials under realistic service conditions is desirable in the selection of a suitable elastomer for high temperature applications. In this work, the mechanical properties (tensile, tear and fatigue test) of sulphur cured natural rubber vulcanisate after heat ageing at 100°C was investigated. After ageing, their mechanical properties were significantly reduced with different cured systems showing different ageing behavior. The efficiently cured natural rubber showed better retention of mechanical properties after heat ageing compared to conventionally cured natural rubber. The reduction in strength of aged materials probably governed by the balance between competitive oxidative (and post vulcanisation) crosslinking reactions and oxidative chain scission reactions (loss of crosslinking) and reversion that occur in the sulphur cured vulcanisate. From scanning electron microscopy (SEM) on the tensile fracture surface of aged compounds shown that the smooth surface indicating the changes during heat ageing.*

## INTRODUCTION

The use of natural rubber (NR) in engineering applications began in the 19th century. Its wide acceptance has been largely due to its excellent physical properties and unique alterable dynamic properties, in combination with its outstanding fatigue resistance making it a very versatile engineering material. Natural rubber is used in many critical service applications such as engine mounts, pipe-sealing rings, anti vibration and earthquake mountings and bridge bearings where long term performance is very important [1].

In many applications, the longevity of rubber components is of critical importance [2]. During its lifetime, a rubber component may be subject to a variety of exposure conditions leading to different types of degradation. The degradative changes resulting from interaction with molecular oxygen can manifest themselves as drastic swings in tensile strength, modulus, elongation, and other physical properties in a specific polymer system [3-4]. Degradation reactions lead to both scissions of polymer chain as well as crosslinking in various proportions [5]. This leads to the loss of physical properties. Oxidative degradation is generally considered to be the most serious problem in the use of rubber at high temperature and proceeds relatively slowly at ambient temperature [6],

One of the requirements for engineering elastomeric components nowadays is to meet demands for long guaranteed service life. However, the service temperature is tending to rise, creating a challenge for materials. As an example, current performance specifications for engine mounts often require the component to survive a large number of cycles at its maximum loading conditions after it has been subjected to accelerating ageing tests [7]. In order to achieve this requirement, the design engineer has to understand the mechanical and degradation behaviour of the material possibly under realistic

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service conditions and how this can be affected by materials formulations. This is important because the service conditions of components play a major role in determining their reliability and life. Good heat ageing properties or resistance is an important requirement where the product should be able to withstand service temperatures of 100°C or more.

This paper is concerned with the degradation behaviour of unfilled sulphur cured natural rubber with different curing systems (conventionally cured NR and Efficiently cured NR). In this work, the mechanical and morphological characterization were used to investigate the processes that were responsible for the modification of the mechanical properties of rubber when subjected to heat ageing at 100°C.

## MATERIALS AND METHODS

### Materials, Formulation and Compounding

Natural rubber (NR) was used in the present investigation. NR, mainly Standard Malaysian Rubber grade with the viscosity stabilized to 60 (SMR CV 60) was chosen. It was chosen for its cleanliness and good batch-to-batch reproducibility of viscosity. Two different curing systems (Conventional and Efficient Sulphur system) were used. Varying the ratio of accelerator (CBS) to Sulphur (S) produces different types of cross linking chemistry. This in turn affects the accelerated ageing behaviour. Table 1 show the formulation used in this study.

Table 1. Formulations used in this study

| Ingredient* | | |
|---|---|---|
| | Efficiently cured NR | Conventionally cured NR |
| SMR CV60 | 100 | 100 |
| Zinc oxide | 5 | 5 |
| Acid stearic | 2 | 2 |
| Sulphur | 0.5 | 2.0 |
| CBS** | 5 | 0.6 |
| Cure time min@150°C | 36 | 22 |

* numbers give parts per hundred of rubber

** cyclohexylbenzothiazole-2-sulphenamide

### Oven ageing

Ageing in an oven is the most common way to accelerate physical and chemical processes connected with polymer degradation. Important information regarding polymer degradation rates and processes can be obtained when material properties are examined after oven ageing. The test pieces were aged in a circulating air oven for defined (3 days and 6 days) periods at 100°C. The test pieces were allowed to stand at room temperature at least 3 hours before measurements were carried out.

### Mechanical Characterization

### Measurement of tensile properties

Rubber sheets were compression moulded at 150°C with force of 10 MPa using a hot press according to respective cure times determined with the MDR 2000. Dumb-bell shaped samples were cut from the moulded sheets according to ASTM D 412. Tensile test were performed at the the crosshead speed of 500 mm/min. Tensile testing was carried out with Monsanto Tensometer M500.

### Measurement of tear properties

Tear strength ($T_s$) using trouser test pieces were calculated in accordance with ASTM D624, Median force, F required to propagate the cut by tearing acting in a direction substantially in the plane of cut divided by the thickness of the rubber sheet:

$$T_s = \frac{F}{t}$$

(Equation 1)

The trouser test pieces, 100 mm x 50 mm with cut to a depth 40 ±5 mm in the direction indicate of test pieces length. It is important that the last 1 mm of the cut is made by a razor blade. The test was carried out using Tensometer M500 machine at rate of separation 100 ±10 mm/min. A steadily increasing traction force was applied until the test piece breaks. The force throughout the tearing process was recorded using chart plotter.

### Measurement of fatigue properties

Tensile strips approximately 120 mm x 25 mm and 0.5 mm thick, were cut from vulcanised sheets both for unaged and aged samples. After stress-strain measurements of the strips have been obtained, the test piece is then set up to the required maximum extension and a cut about 0.5 mm long is made in the centre of one edge with a razor blade. Samples were then cycled on in-house fatigue machine.

During the test, the cut length c, is measured with travelling microscope fitted with an eyepiece scale, the strip being slightly strained to facilitate observation. Readings are taken at intervals of cycles n corresponding to a 10-30% increased in cut length. The rate of growth dc/dn is determined from the difference in cut length divided by the number of cycles between two readings. This rate is referred to the tearing energy calculated from the average of the cut lengths and the strain energy density at the maximum strain of the cycle using equation

$$T = 2K(\lambda)Wc$$

(equation 2)

The test is stopped when the cut reaches 20% of the test pieces width, as theory assumes this ratio to be small.

### Scanning Electron Micrograph Tensile Fracture Surface

The fracture tensile surfaces of the unaged and aged natural compounds were investigated with a Leica Cambridge S-360 scanning electron microscope. The fracture ends of specimens were mounted on aluminium stubs and sputter coated with a thin layer of gold to avoid electrostatic charging during examination

## RESULTS AND DISCUSSION

### Mechanical Properties

When natural rubber (NR) is aged in air at elevated temperatures its strength properties are diminished. One possible mechanism for the change in strength is a diminished capability of the aged material to undergo stress-induced crystallisation, a phenomenon that is known to be responsible for the excellent strength properties of NR [8]. It has also been established that there are a number of chemical reactions that occur in rubber during ageing that lead to both molecular break down and changes to the crosslinking. Each of these reactions proceeds at its own rate which is independently influenced by temperature [9]. Barker [10] suggests that at high ageing temperatures, network break down, leading to loss of strength, tends to have the dominant influence. He found that at lower temperatures changes to the crosslinks were relatively more important and can partly compensate for the effect of degradation.

### Tensile and Tear Strength

The tensile and tear strengths of an unfilled elastomer depends upon the nature of the molecular backbone, the molar mass of the polymer and the concentration and the nature of the crosslinks. Different curing systems can produce widely different strengths for the same polymer backbone, even when compared at a

similar degree of crosslinking [8]. Figures 1 and 2 showed how the tensile and tear strengths for Efficiently cured NR and Conventionally cured NR vulcanizates. The original tensile and tear strengths of conventionally cured NR were higher compared to efficiently cured NR. However the vulcanisates shown a decreased in tensile and tear strength after ageing which the reduction of strength were more pronounced for the conventional cured NR. In this system, the tear strength, $T_c$ was decreased by about 65% after ageing for 3 days at 100°C and further ageing reduced the $T_c$ to just 11% of the original unaged $T_c$. The larger reduction in $T_c$ for the conventionally cured system when compared with efficiently cured system probably relates to a larger amounts of new crosslinks, scission of the main chain and crosslinks and chemical modification to the main chain. all of which are believed to occur in conventionally cured NR during oxidative ageing [11].

For the conventionally cured NR vulcanisates, ageing show a drastic loss of their original strength. This may due to that the system contains predominantly poly-sulphide crosslinks which are thermally unstable and undergo a number of competing reactions (crosslink shortening, crosslink destruction and main chain modification) [6] resulting in lower strength after ageing. A smooth tearing similar to that for a non-crystallising rubber was observed for conventional cured NR after ageing 6 days at 100°C. This suggests that strain-induced crystallisation is inhibited after ageing for extended periods [12] and this behaviour was not so obvious in efficiently cured NR vulcanisates.

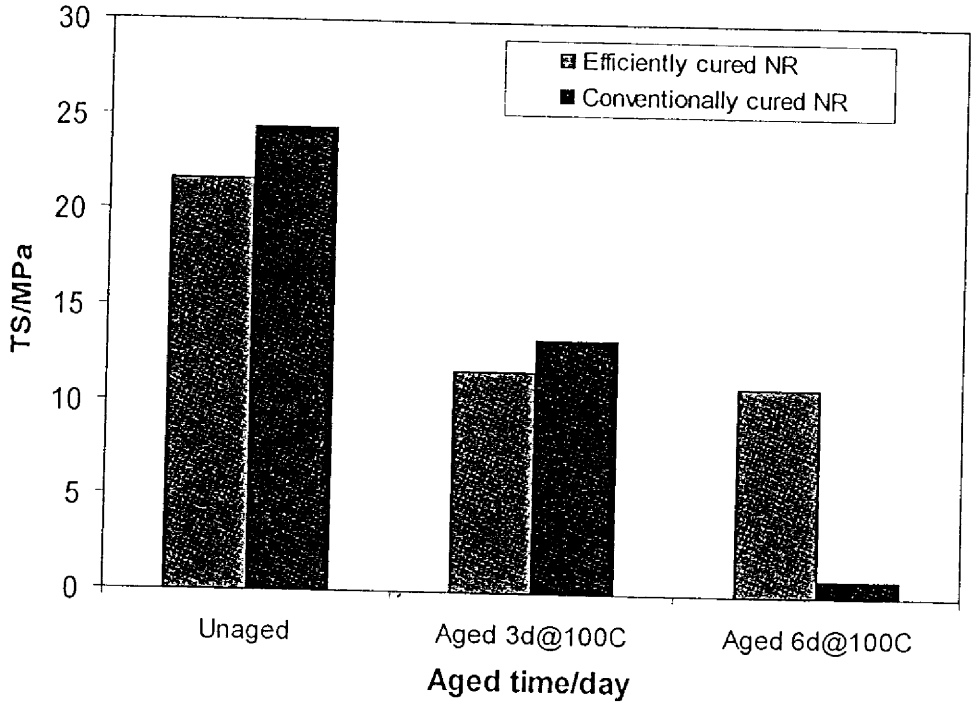



Fig. 1: Tensile Strength (TS) as function of ageing time for NR vulcanisates aged 100°C

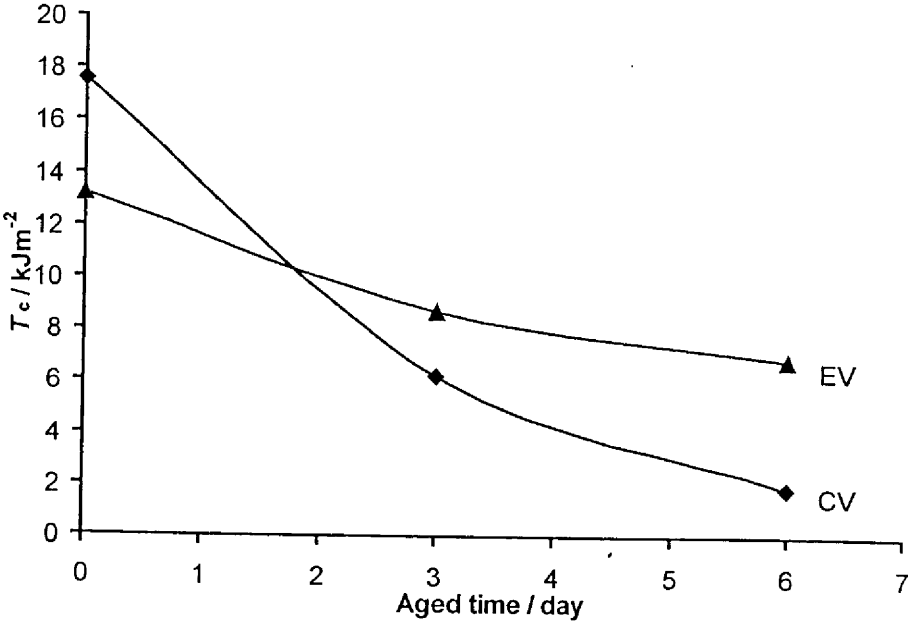



Fig. 2: Tear Strength ($T_c$) as function of ageing time for NR vulcanisates aged at 100°C

**Fatigue properties (Cyclic crack growth)**

The tearing energy approach has proved to be successful in treating the fracture of elastomers [13]. However, the tearing tests presented in tensile and tear strengths only estimate the strength of elastomer under a single loading cycle producing rapid crack growth. For the majority of elastomeric components, failure is not usually due to large static load resulting in catastrophic failure but to the smaller cyclic fatigue loads. Cyclic crack growth behaviour is the most appropriate approach to predict the service life of components. Relationship between the incremental crack growth rate per cycle $dc/dn$ and tearing energy $T$ have been referred to as the "crack growth characteristics", since it represents the basic tearing property of the vulcanisates [14].

The effect of accelerated ageing on the cyclic crack growth has been investigated for ageing at 100°C for efficiently cured NR and conventionally cured NR. The crack growth rate $dc/dn$ as function of tearing energy, $T$ is given in Figures 3 and 4. In general, results for different periods of ageing showed that for a given tearing energy, the rate of crack growth per cycle was increased after ageing. Figure 4 shows the tearing energy, for the conventionally cured NR vulcanisate, at a crack growth rate of 1.0 x$10^{-4}$ mm per cycle decreased by a factor 3.8 after ageing 3 days and by a factor about 10 after ageing for 6 days when compared with the unaged sample. The effects of ageing on the crack growth properties of the efficiently cured compound were not as pronounced as that for the conventionally cured NR. This may be due to the inhibition of strain crystallisation in the conventionally cured compound as a result of ageing, caused by chain modification [15].

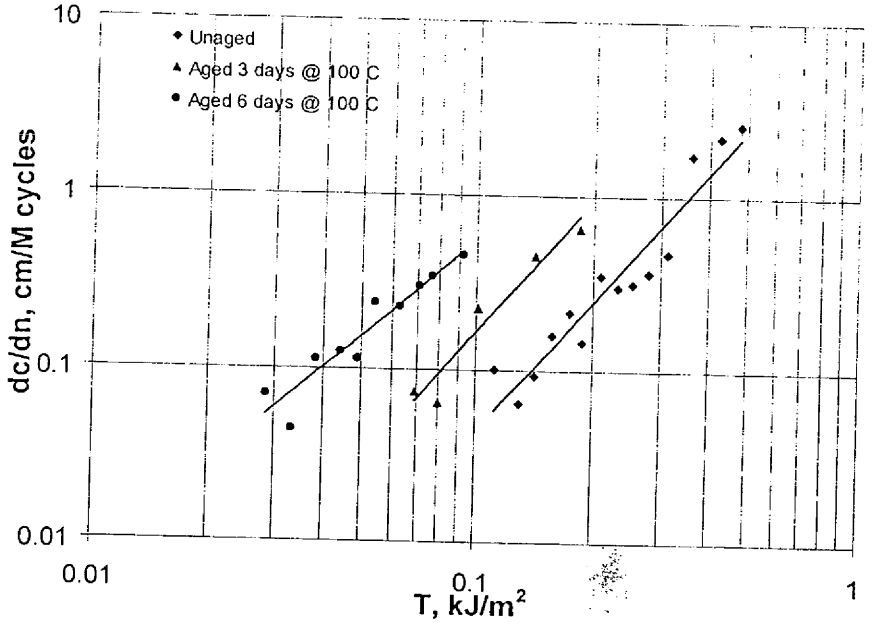



Fig. 3: Crack growth rate (d$c$/d$n$) as function of tearing energy ($T$) for efficiently cured NR aged at 100°C.

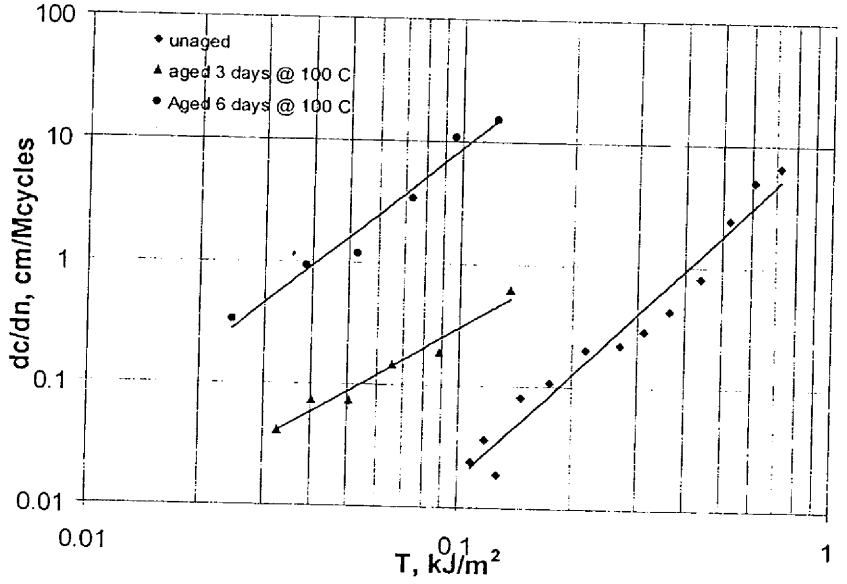
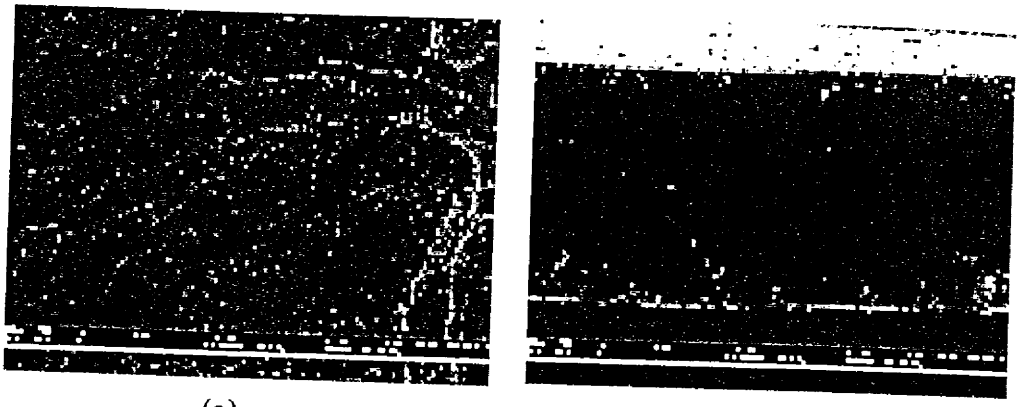



Fig. 4: Crack growth rate (d$c$/d$n$) as function of tearing energy ($T$) for conventionally cured NR aged at 100°C

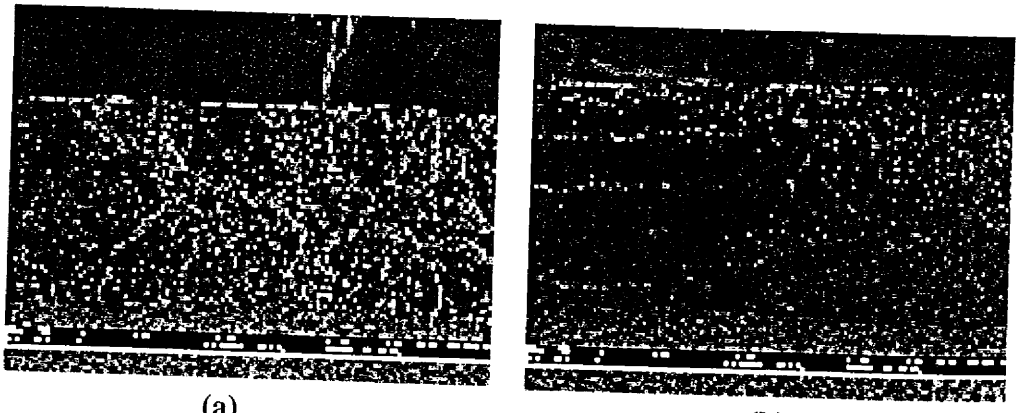
### Morphological Observation

Figures 5 and 6 show the morphology of tensile fractured surface for conventionally cured NR and efficiently cured NR before and after ageing for 6 days at 100°C. It is apparent that changes of fractured surface for both systems. Figure 5 shows that conventionally cured NR gives very smooth surface after ageing. Figure 6 shows the same effect for efficiently cured NR but less pronounced compared to conventionally cured NR. The smooth fractured surface after heat ageing could be attributed from the reduction of the ability of NR to strain crystallize hence decrease the strength properties [12].



(a) (b)

Fig. 5: The Scanning Electron Micrograph for conventionally cured NR (a) Unaged (b) Aged for 6 days at 100°C at 100x magnification



(a) (b)

Fig. 6: The Scanning Electron Micrograph for Efficiently cured NR (a) Unaged (b) Aged for 6 days at 100°C at 100x magnification

## CONCLUSIONS

Conventionally cured NR shows higher initial strength compared to efficiently cured NR. After ageing up to 6 days at 100°C, conventional cured NR lost almost 90% of it strength. The high strength of conventionally cured NR is believed to depend critically upon its ability to crystallise on stretching. For both conventionally cured NR and efficiently cured NR, tearing energy required to achieve a given crack growth rate decreased with longer time of ageing. Results show that samples aged for 6 days at 100°C for the conventionally cured NR exhibit higher crack growth rate when compared to the efficiently cured NR. The scanning electron micrograph

shows the changes of fractured surface before and after ageing. Conventionally cured NR shows very smooth surface after ageing that can be associated with the inhibition of the ability to strain crystallize after ageing.

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## REFERENCES

[1]. Gillen, K.T., (2000), "Methods for predicting more confident lifetimes of seals in air environments", *Journal of Rubber Chemistry and Technology,* **73** (2), 265.

[2]. Davies, B.J., (1988), "The longest serving polymer," *Rubber Developments*, **41**, **4**, 102.

[3]. Fuller, K.N.G. and Roberts, A.D., (1997), "Longevity of natural rubber structural bearings," *Proceeding Rubber Conference On Rubber Sciences and Technology*, Kuala Lumpur, 6-9 Oct.

[4]. Kamarudin, Ab.Malek and Stevenson, A., (1992), "A 100-year case study of the life prediction of natural rubber for an engineering application," *Journal of Natural Rubber Research*, **7**, **2**, 126.

[5]. Baba, M., Lacoste, J., Gardette, J.L., (1999), "Crosslinking on ageing of elastomers III. A new method for evaluation of crosslinking based on density measurements," *Journal Polymer Degradation and Stability*, **65**, 421-424

[6]. Chapman, A.V. and Porter, M., (1988), "Sulphur vulcanisation chemistry," in Roberts, A.D., (ed.), Natural Rubber and Technology, Oxford University Press, Chapter 12, 513.

[7]. Gruenberg, S., Blough, J., Kowalski, D. and Pistana, J., (2001), "The effects of natural aging on fleet and durability vehicle engine mounts from a dynamic characterization perspective," *Society of Automotive Engineers,* Inc. 01,1449

[8]. Gee, G., (1947), "Tensile strength of pure gum natural rubber compounds," *Journal Polymer Science,* **2**, 451.

[9]. Buist, J.M., (1956), Ageing and weathering of rubber, I.R.I, Monograph, Heffer, London, 9.
Barker, L.R., (1990), "Accelerated long-term ageing of natural rubber vulcanisates. Part 2: Results from ageing tests at 40°C," *Journal Natural Rubber Research*, **5**, **4**, 266

[10]. Cunneen, J.I., (1968), "Oxidative aging of natural rubber," *Rubber Chemistry and Technology*, **41**, **1**, 182

[11] Azura, A.R., Goeritz, G., Muhr, A.H. and Thomas. A.G., (2003 ). "Effect of ageing on the ability of natural rubber to strain crystallize", in Busfield, J.J.C and Muhr, A.H (eds), *Constitutive Models for Rubber III, Conference Proceeding, UK*, 79-84.

[12]. Gent, A.N., Thomas, A.G. and Lindley, P.B., (1964), "Cut growth and fatigue of rubbers. Part I: The relationship between cut growth and fatigue," *Journal of Applied Polymer Science*, **8**, 455.

[13]. Lake, G.J. and Lindley, P.B., (1964), "Cut growth and fatigue of rubbers. Part II: Experiments on a non-crystallising rubber," *Journal Applied Polymer Science*, **8**, 707.

[14]. Bristow, G.M. and Tiller, R.F., (1970), "Correlation of structure and properties of natural rubber vulcanisates," *Kautshuck Gummi Kunstsoffe*, **23**, 2, 55.

## PP23

## THE EFFECTS OF ACETYLATION ON PROPERTIES OF PAPER SLUDGE FILLED POLYPROPYLENE (PP) / ETHYLENE PROPYLENE DIENE TERPOLYMER (EPDM) COMPOSITES

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The effects of surface treatment of paper sludge (PS) with acetic acid (acetylation) on mechanical properties, water absorption and morphology of PP/EPDM/PS composites were investigated. The results show that the acetylation treatment increased the tensile strength, elongation at break and Young's modulus of PP/EPDM/PS composites but reduced water absorption. The scanning electron microscopy (SEM) study of acetylated composites indicates that the presence of acetic acid increased the interfacial interaction between paper sludge and PP/EPDM matrix.

## PP24

## THE EFFECT OF MALEIC ACID (MAC) ON RHEOLOGICAL PROPERTIES AND MORPHOLOGY OF RECYCLED POLY(VINYL CHLORIDE)/ACRYLONITRILE BUTADIENE-RUBBER (50/50 PVCR/NBR) BLENDS

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Blends of recycled poly(vinyl chloride)(PVCr) and acrylonitrile butadiene rubber (NBR) modified by addition of maleic acid (MAc) were prepared by using a Haake Rheomix. The effect of MAc on rheological properties and morphology of PVCr/NBR were investigated. The recorded data obtained from the Haake Rheomix were converted into values of apparent shear rate, apparent shear stress and apparent viscosity. The apparent viscosities of the blends were found decrease with increasing the shear rate and follow the pseudoplasticity behaviour. At a similar shear rate, the presence of MAc into PVCr/NBR blends exhibit higher apparent viscosity than PVCr/NBR without MAc. Activation energy, $E_a$ is found to decrease with increasing shear rate, obviously due to the strong non-Newtonian behaviour of PVCr/NBR blends. Scanning electron microscopy (SEM) examination of extracted surfaces of PVCr/NBR + MAc blends indicates the increased of the interfacial interaction between PVCr and NBR phases with the presence of MAc.

## PP25

## LOW CTE AND HIGH FLEXURAL LAMINATED WOVEN GLASS FABRIC THERMOSET COMPOSITES FOR SUBSTRATE MATERIAL IN ELECTRONIC PACKAGING APPLICATION

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In recent years, ceramic particle filled metal matrix composites have received much attention for application in microelectronic packaging. This is because of their low and tailorable coefficient of thermal expansion CTE) for reducing the thermal mismatch with device materials such as silicon. Since ceramic is expensive, semiconductor industry moved to polymeric packaging materials. Polymeric materials are found extensively used in microelectronic application. One of the major important applications is thermal property, where the thermal expansion behavior of packaging materials plays a critical role in affecting the thermomechanical reliability of devices. The objective of this study is to achieve a low CTE substrate with high flexural properties for electronic packaging application. Plain woven glass fabric was chosen as reinforcing fiber impregnated with epoxy resin using vacuum bagging process. Low CTE particulate fillers such as natural silica and quartz fused silica powders were added into woven fabric and epoxy resins to reduce the CTE of the composites. In short, it was also observed that addition of low CTE particulate filler reduces the overall CTE of the composites and increase the modulus of the composite system.

## PP26

## DEGRADATION BEHAVIOUR OF SULPHUR CURED NATURAL RUBBER VULCANISATES: EFFECT OF HEAT AGEING

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A better understanding of the mechanical behaviour and degradation of materials under realistic service conditions is desirable in the selection of a suitable elastomer for high temperature applications. In this work, the mechanical properties (tensile, tear and fatigue test) of sulphur cured natural rubber vulcanisate after heat ageing at 100°C was investigated. After ageing, their mechanical properties were significantly reduced with different cured systems show different ageing behaviour. The efficiently cured NR showed better retention of mechanical properties after heat ageing compared to conventionally cured NR. This is probably governed by the

balance between competitive oxidative (and post vulcanisation) crosslinking reactions and oxidative chain scission reactions (loss of crosslinking) and reversion that occur in the sulphur cured vulcanisate. Conventionally cured NR also showed significant main chains and/or crosslinks scission plus new formations of crosslinks after ageing during set and equilibrium swelling measurements. To further understand their degradation behaviour, the scanning electron microscopy (SEM) on the fracture surface of unaged and aged materials also being investigated.

## PP27

## ANALYSIS OF PRINTED CIRCUITS BOARD SCRAP PARTICLE AS FILLER MATERIALS IN CONDUCTING POLYMER COMPOSITES

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This study reports the results of the SEM and EDX analysis into the suitability of printed circuit board (PCB) scrap particles as conducting filler in the polymer composite materials. Due to the rapid development in the computer and electronic manufacturing technologies, the personal computer can be regarded as a short-life-cycle electronic product. PCB scraps contain some valuable materials such as copper, silver, iron, gold and other materials which make them worth recycled. According to the weight percentage analysis, printed circuit board with integrated circuit is one of the major items in a scrap computer. The typical circuit board is made of epoxy resin, fiberglass, copper and other metallic elemens. Usually, a bromine fire retardant is added to the resin to increase fire resistance. The integrated circuits and other electronic parts usually contain resin, silicon, gold, silver, nickel, iron and aluminium. In this investigation, the printed circuit boards from a computer motherboard were crushed into small particles by crusher machine. The powder particles from the crusher were filtered in order to obtained particles with diameter less than 500μm. Two different printed circuit boards were analysed using the SEM/EDX method and the results shows the composition of the elements in the board. The particles were used as a filler material in the processing of conducting polymer composites with the composition of the filler ranged from 0-30% by volume fraction. The matrix chosen were polyester and polypropylene. The mechanical and thermal properties of the composites containing the PCB particles were investigated. Fracture surfaces of the tensile specimens were captured using the scanning electron microscope. Micrograph of the fracture surfaces shown very good fibre distribution in the composites. The thermal properties improved with increasing volume fraction of PCB particles and the tensile properties does not degrade significantly.

## PP28

## THE EFFECT OF BLEND RATIO ON TENSILE PROPERTIES AND MORPHOLOGY OF ENR-50/EVA POLYMER BLEND

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Blends of epoxidized natural rubber (ENR-50) and ethylene vinyl acetate (EVA), with varying proportion of the components were prepared by melt mixing in Haake Rheometer. Tensile properties and morphology of ENR-50 / EVA blends were investigated. Tensile results revealed that, increase in EVA content in the blend will increase tensile strength and stress at 100 % strain (M100). On the other hand, it resulted in decrease in elongation at break. SEM micrograph indicated that, at all blend ratios, EVA formed a continuous phase in which a better continuous structure been formed in EVA dominant blend thus enhanced the tensile strength of the blend. ENR-50 component exist as a dispersed phases in ENR-50/EVA 20:80 and 40:60 blend ratios. At higher ENR-50 contents (50, 60 and 80 wt %) it exist as a continuous phase to form a co-continuous morphology with EVA phases.

## PP29

## TENSILE PROPERTIES AND MORPHOLOGY OF UNVULCANIZED AND DYNAMICALLY VULCANIZED ENR-50/EVA POLYMER BLENDS

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Blends of epoxidized natural rubber (ENR-50) and ethylene vinyl acetate (EVA), with varying proportion of the components, were dynamically vulcanized using different cross-linking systems, namely, sulfur and dicumyl peroxide (DCP). The blends were prepared by melt mixing in Haake Rheometer. The effect of curing systems on the tensile properties and morphology were investigated. The results revealed that, dynamic vulcanization is capable to improve tensile properties of ENR-50/EVA blends by producing a finer and homogenous dispersed phase of ENR-50 in EVA matrix. Dispersed phase is in a form of crosslink rubber particles (ENR-50) which have the ability to improve tensile properties of the blend. Overall morphology showed that, crosslink phase will become a dispersed phase at all blend ratios.

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# EFFECT OF HEAT AGEING ON MECHANICAL PROPERTIES OF DIFFERENT CURING SYSTEMS OF NATURAL RUBBER VULCANISATES

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## ABSTRACT

The heat ageing of natural rubber caused the deterioration of mechanical properties of the natural rubber vulcanizates. The effects of a sulfur vulcanization system (conventional vulcanization (CV), efficient vulcanization (EV) and peroxide vulcanization on the mechanical properties and heat aging resistance of natural rubber compounds were studied. The tensile properties and catastrophic tearing energy (Tc) of the vulcanizates were measured. The results for tensile strength showed that vulcanizates with crosslinks that predominantly poly-sulphidic in CV system exhibit properties higher than those of the corresponding mono-sulphidic crosslinking in EV system and carbon to carbon cross links in peroxide system before ageing. After ageing, CV system showed the highest reduction in the tensile strength and catastrophic tearing energy compared to EV system and peroxide system due to the behavior of the poly-sulphidic cross-links that thermally unstable and can be readily oxidized. In permanent set test, the extent of permanent set is dependent upon the extent of the main chain and/or cross-links scissions and cross link reformation processes. This effect was more pronounced for CV system compared to EV system and peroxide system.

***Keywords:*** Curing system, natural rubber, tensile strength, catastrophic tearing energy, permanent set