

## SOLUBILITY OF RUBBER ADDITIVES IN LATEX FILMS

Lim Hui Mei\*<sup>#</sup> & Ng Chiew Sum\*\*

\* Rubber Research Institute of Malaysia, Malaysian Rubber Board,

47000 Sungai Buloh, Selangor, Malaysia

\*\* JPS Partners, 15 Jalan 31/100F, 40460 Shah Alam, Selangor DE, Malaysia.

<sup>#</sup> Corresponding author: evelyn@lrm.gov.my

### ABSTRACT

*Accelerated sulfur vulcanization system is a common process used in manufacturing latex dipped products particularly gloves to achieve the desired properties. Organic accelerators are widely employed in the industry due to their fast cure rates, however a plausible scientific reason in the selection and dosage of accelerators used has not been known. Dissolution and the maximum uptake of these chemicals in polymer films could identify the true rationale behind such practical approach. In this study, cast latex films inclusive of natural rubber, nitrile and low protein latex were immersed in fine additives powder for a period of time. Films exposed to dithiocarbamate accelerators showed higher weight percentage increase as compared to the thiazole accelerator. The films immersed in sulfur powder also experienced increase in percentage of weight difference and sulfur content, suggesting solubility of additives through solid-solid interface. However FTIR spectrum and tensile strength did not indicate presence of carbon to sulfur crosslinks or strength enhancement signifying formation of such bonds require higher activation energy.*

### BACKGROUND

Latex dipped products are produced through incorporation of sulfur, accelerators and activators to transform the rubber from plastic state to elastic state. The rubber chains are crosslinked during the vulcanization process, contributing to elastic recovery when it is subjected to deformation. The chemical reaction of sulfur and other vulcanizing agents were understood through model systems, whereby low molecular weight olefins that are structurally related to rubber were used which provided the knowledge of sulfur crosslink to the users in general. Subsequently, Porter<sup>1</sup> pre-vulcanized natural rubber latex in a solid deposit of sulfur-coated flask. Sulfur was found to migrate from a continuous solid deposit into the rubber particles of natural rubber latex rather than dissolution in aqueous serum. Our present study focused on the fundamental and possible application aspects of solubility of sulfur and accelerator in latex films.

## **MATERIALS & METHODS**

### **MATERIALS**

High ammonia natural rubber latex (NR) was mixed with 1.0 phr of di-t-butyl peroxide and cast on a glass plate measuring 110 mm 300 mm. Cast films of thickness 1 mm were obtained after air dried under room temperature. Samples of 10 mm square were later cut, weighed and immersed separately in sulfur, zinc diethyl dithiocarbamate (ZDEC), zinc mercaptobenzthiazyl sulphenamide and zinc dibutyl dithiocarbamate (ZDBC) powders. The same procedure was repeated using carboxylated acrylonitrile butadiene latex (XNBR).

### **METHODS**

#### **PERCENTAGE OF WEIGHT DIFFERENCE**

The rubber piece was removed using tweezers after certain time interval and the surface was cleaned by first scraping with a blade. The remaining fine powder was removed using adhesive tape to pull off the surface material before weighing. The residual surface material was estimated by immersing a piece of rubber as the experimental samples in powdered additives, immediately withdrawing it and cleaning the surface. The corrected result was obtained by subtracting from the percentage of weight increased. The procedure is essentially that of Morris and Thomas<sup>2</sup>.

#### **MECHANICAL PROPERTIES OF FILMS**

The tensile properties of the unaged films were determined using an Instron 5565 Testing Machine according to the ASTM D412 method with a crosshead speed of 500 mm/min. The test was conducted under room temperature condition (25±1°C).

#### **INFRARED SPECTROSCOPY**

The spectra of the latex films surface were obtained using a Varian SCIMITAR 2000 FTIR spectrophotometer, US with an Attenuated Total Reflectance (ATR) flat top plate accessory (2 mm 2 mm diamond ATR crystal with an active surface of 0.6 mm 0.6 mm) and MCT (Mercury-Cadmium-Tellur) detector.

#### **BOMB COMBUSTION FOLLOWED BY ION CHROMATOGRAPH**

The rubber sample weighing from 2 mg to 200 mg was placed in a closed combustion unit purged with oxygen. The Ignition systems will combust the sample in the closed unit, and gases released during combustion were captured into water to retain the gases in the closed unit. The sulphate ions, SO<sub>4</sub> captured in water was analysed by ion chromatography. Calculation conversion from SO<sub>4</sub> to sulphur was then performed.

## **RESULTS & DISCUSSIONS**

The study evaluated the solubility of sulfur present as cyclooctasulphur (S<sub>8</sub>), and zinc diethyl dithiocarbamate in rubber films, as they are widely used as crosslinker and accelerators in dipped latex products respectively. Prior research work has proven

that both additives can migrate from a continuous solid deposit into the latex compound<sup>1, 2</sup>. For this present experiment, we examined solubility of the fine powder in cast latex films.

The percentage of weight increase for natural rubber latex films immersed in sulfur and ZDEC were determined for a period of 14 days. A gradual increase in weight percentage was observed until it plateaued off from day 9 onwards. The maximum percentage of sulfur increase approximated at 1.8 % (Figure 1). It appears that the solubility of sulfur in natural rubber films followed the conventional natural rubber cure system whereby the range of sulfur dosage is 2.0 phr to 3.5 phr.

This percentage of soluble sulphur is substantially higher than that for rubber compound containing carbon black<sup>3</sup>. Sulfur tends to crystallise out of the rubber phase and causes chemical blooming on the rubber surface when it is mixed to rubber above its supersaturation level<sup>3</sup>. The additives are soluble at vulcanization temperature but only partially soluble at ambient temperature where chemical blooming may occur. Hence sufficient and not over loading of sulfur is needed for product manufacturing. The solubility of ZDEC also plateaued off at 0.7 %, this agrees with the conventional cure system where the range of accelerator falls between 0.5 phr to 1.0 phr.

The maximum percentage of weight increase for nitrile films immersed in sulfur and ZDEC took a longer period of time to achieve as compared to the natural rubber latex films. The maximum percentage of sulfur increase approximated at 0.20 % and ZDEC at 0.13 % (Figure 2). Both rubber films showed higher percentage of weight increase of sulfur than ZDEC. The percentage of weight increase for nitrile films were much lower than natural rubber films, this could be due to the double bonds available for sulfur crosslinking were much lower than the cis-isoprene and the absence of non-rubber materials apart from the rubber hydrocarbon. Table 1 lists the solubility parameter of natural rubber and XNBR. Difference in solubility parameter may account for the differences in solubility of S and ZDEC.

Table 1: Solubility parameter for natural rubber and XNBR<sup>4</sup>.

Polymer	Solubility parameter (cal/cc) <sup>1/2</sup>
Natural rubber	8.3
XNBR (MMA: 10 %)	9.6
XNBR (MMA: 7 %)	9.4

Figure 1: Percentage of weight increase for natural rubber latex films immersed in sulfur (smooth line) and ZDEC (dotted line).

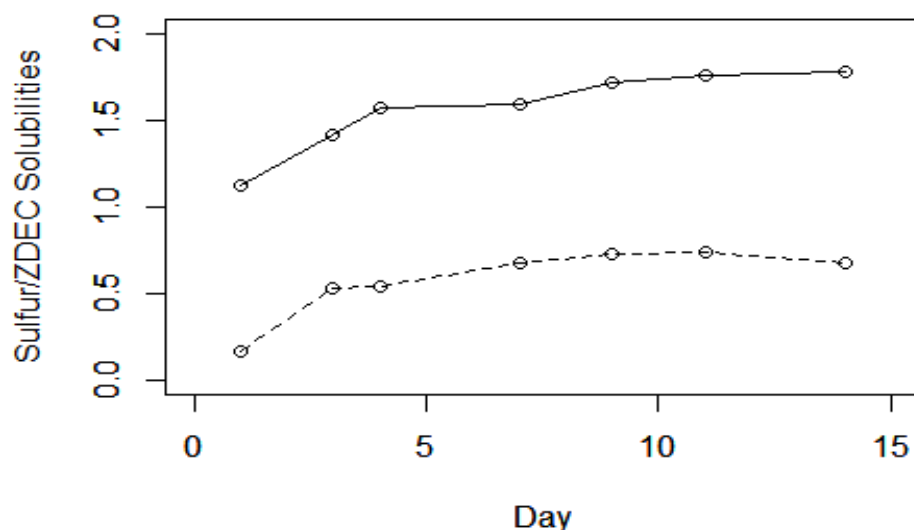
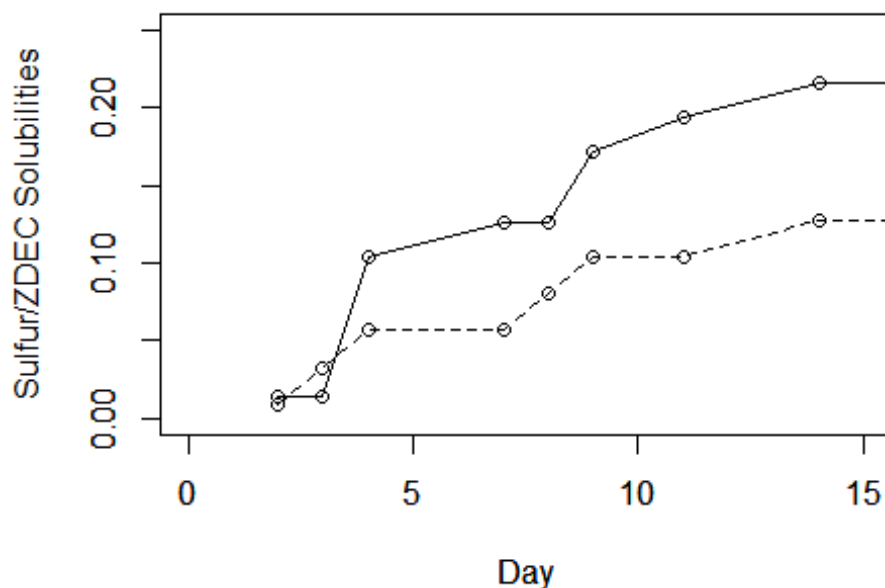
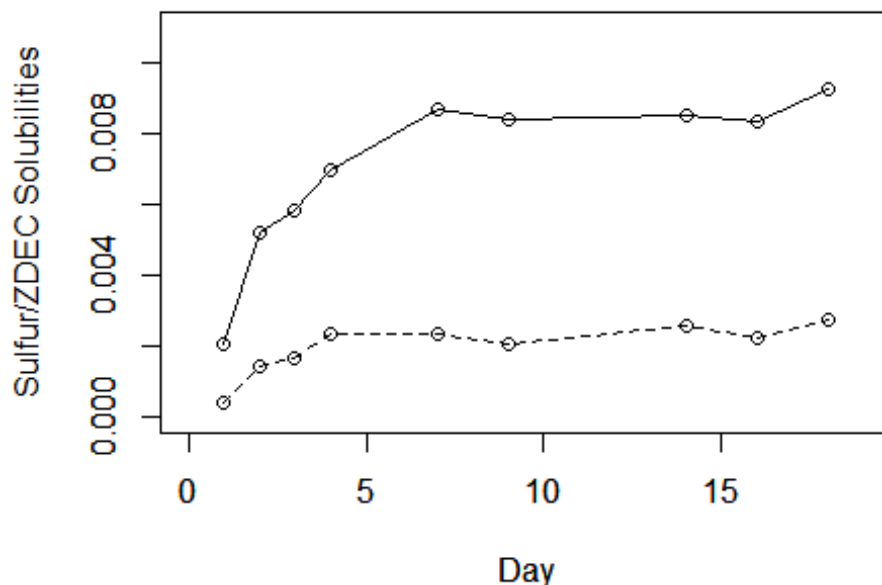


Figure 2: Percentage of weight increase for nitrile latex films immersed in sulfur (smooth line) and ZDEC (dotted line).



The effect of non-rubbers on the solubility of sulfur and ZDEC was investigated by immersing the low protein latex films in these two additives (Figure 3). A gradual increase in weight percentage was observed until it plateaued off at 0.009 % after day 6. The maximum increase in weight percentage was 0.002 % for ZDEC. The maximum increase in weight percentage for both additives was more than a hundred fold lower compared to the natural rubber latex films.

Figure 3: Percentage of weight increase for low protein latex films immersed in sulfur (smooth line) and ZDEC (dotted line).



The maximum percentage of weight increase for both natural rubber and nitrile latex films immersed in ZMBT and ZDBC increased after 6 days of immersion. The percentage of weight increase was significantly much lower compared to sulfur and ZDEC. ZMBT appeared not contributing to the weight increase for both films. While the maximum percentage of ZDBC increase approximated at 0.004 % for natural rubber films and nitrile films at 0.001 % (Figure 4 & 5). Due to substantial low difference in percentage of weight increase, error during weighing could have contributed to the fluctuation in the results.

Figure 4: Percentage of weight increase for natural rubber latex films immersed in ZMBT (smooth line) and ZDBC (dotted line).

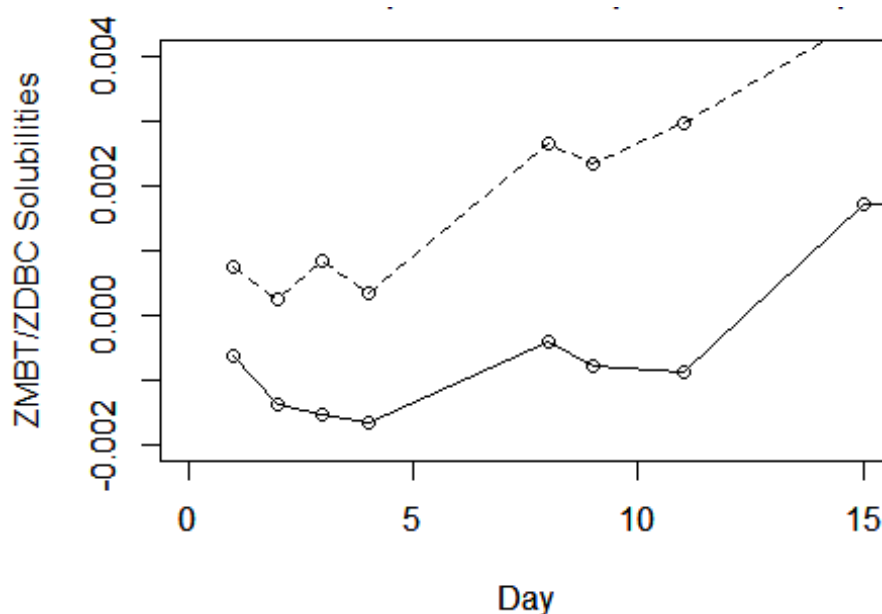


Figure 5: Percentage of weight increase for nitrile latex films immersed in ZMBT (smooth line) and ZDBC (dotted line).

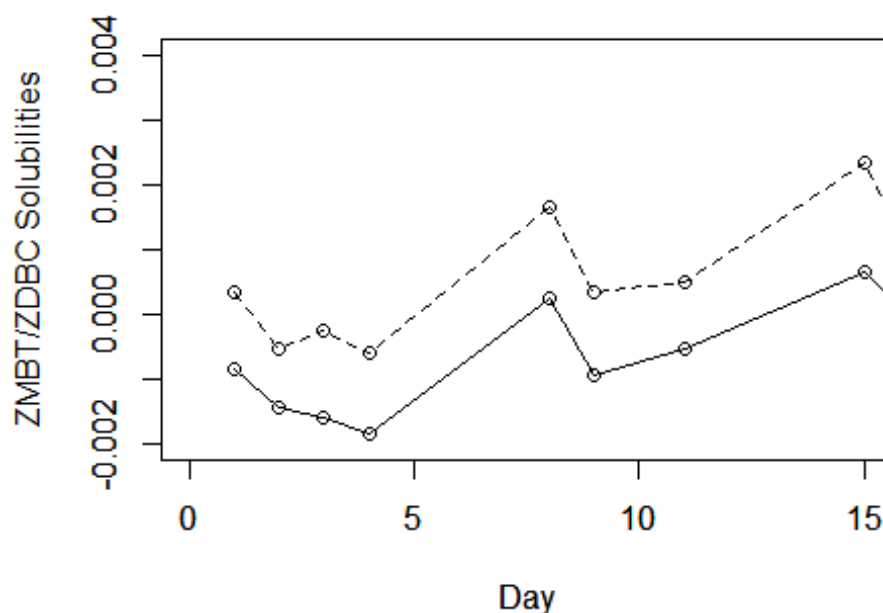
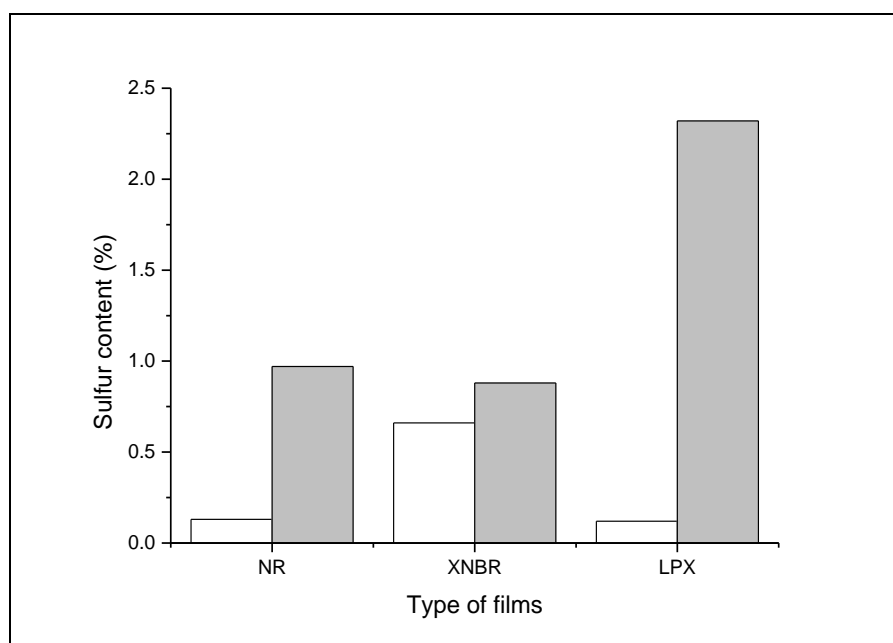


Figure 6 shows the sulfur content of the virgin latex films and films that were immersed in sulfur. Traces of sulfur content were found in natural rubber latex films. Unexpectedly, higher level content of sulfur in nitrile films were found. This could be due to the practice of nitrile latex manufacturers to pre add sulfur to the latexes as in the manufacturing of chloroprene latex. Nitrile latex users should take note of this during the formulation design, which may differ from different source of latex procured.

In the earlier result, the percentage of weight increase for nitrile films was found to be much lower than natural rubber films. It was postulated that this might be due to the double bond available for sulfur crosslinking were much lower in nitrile latex. However, the sulfur content results suggested otherwise. The solubility of sulfur in nitrile films after immersion was 0.3 % while in natural rubber latex films it was 0.9 %. The lower solubility of sulfur was due to the initial incorporation of sulfur in the latex itself thus saturated the double bonds. The increase in sulfur content in the films proves that solubility of sulfur at the solid-solid interface did occur.

The sulfur content in the virgin low protein latex was similar to the natural rubber latex films. However after immersion, the sulfur content in the low protein latex were two times higher compared to the natural rubber latex films. The result suggested higher total intake of sulfur for low protein latex film.

Figure 6: Sulfur content of virgin latex films (white) and films immersed in sulfur (gray)



The functional groups of the natural rubber, nitrile latex and low protein latex films were studied using FTIR as shown in Figure 7, 8 and 9. Generally there were no significant difference between the virgin films and films immersed in sulfur. The characteristic band of the olefinic double bond ( $-\text{CH}=\text{CH}-$ ) groups from butadiene is  $1640\text{ cm}^{-1}$ , this band was observed in natural rubber films but not in the nitrile films. The absorption band for un-ionized carboxylate band is known to be at  $1700\text{ cm}^{-1}$  and stretching of nitrile triple bonds ( $\text{C}\equiv\text{N}$ ) at weak peak of  $2237\text{ cm}^{-1}$  was evident in the FTIR spectra. The carbon-sulfur linkages could not be observed in the FTIR spectrum for both films which indicated absence of such bonds in the films.

The films were subjected to stress to evaluate its strength. Both films did not show significant increase in tensile strength (Table 2). The stress strain behaviour of the films coincided with the FTIR results. This might signifies that formation of carbon to sulfur bond requires higher activation energy.

Figure 7: Infrared spectra of natural rubber latex films (smooth line) and films immersed in sulfur (dotted line).

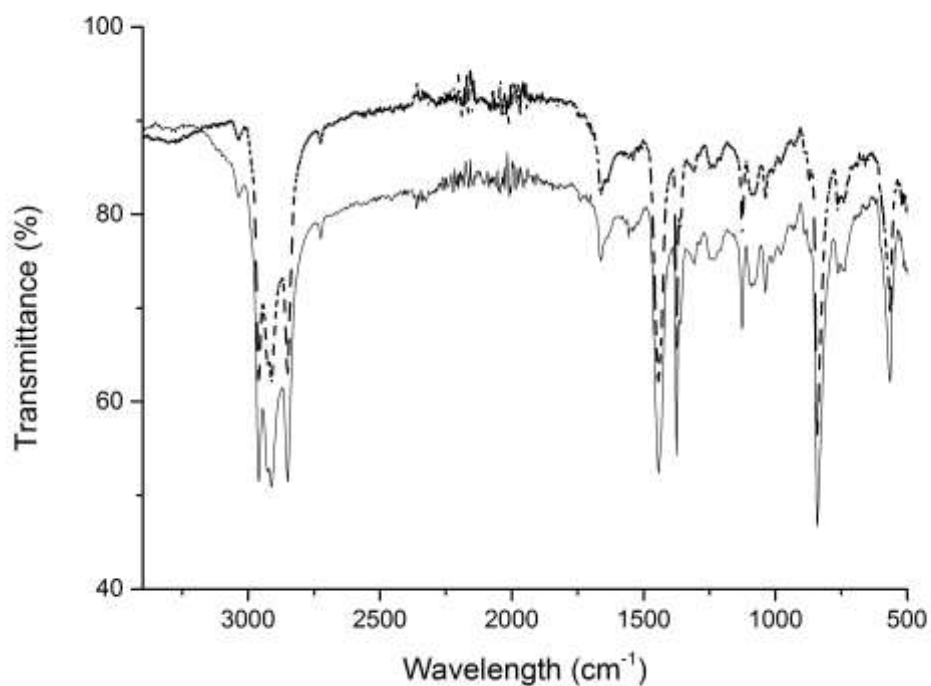


Figure 8: Infrared spectra of nitrile latex films (smooth line) and films immersed in sulfur (dotted line).

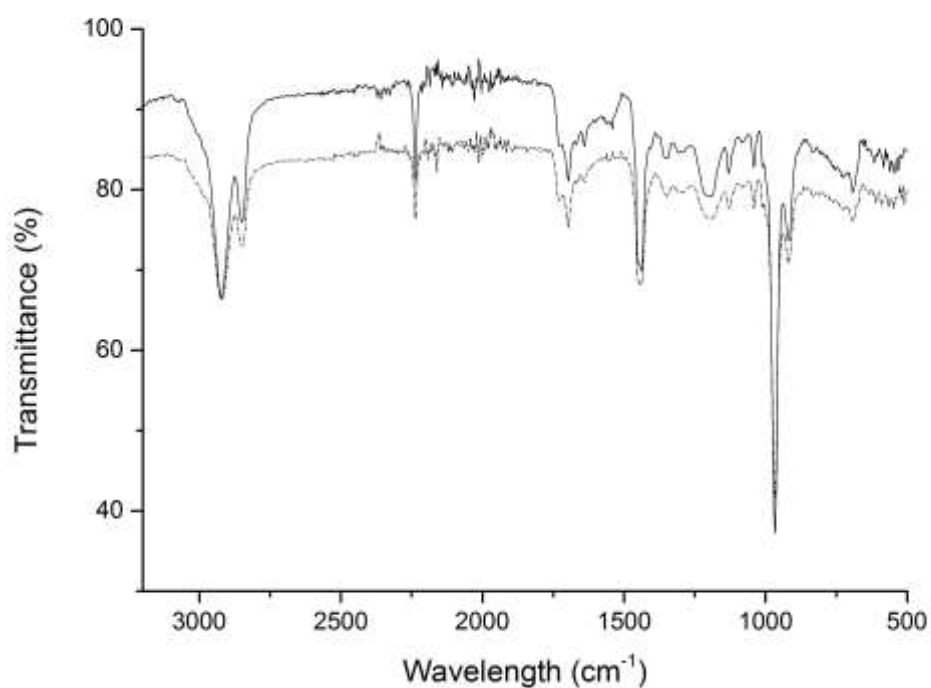




Figure 9: Infrared spectra of nitrile latex films (smooth line) and films immersed in sulfur (dotted line).

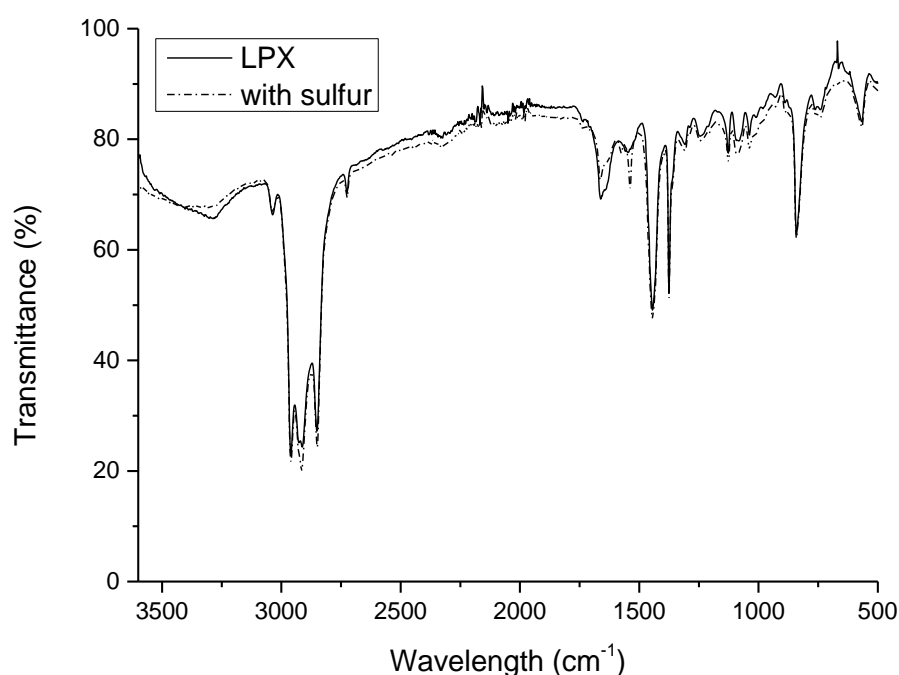
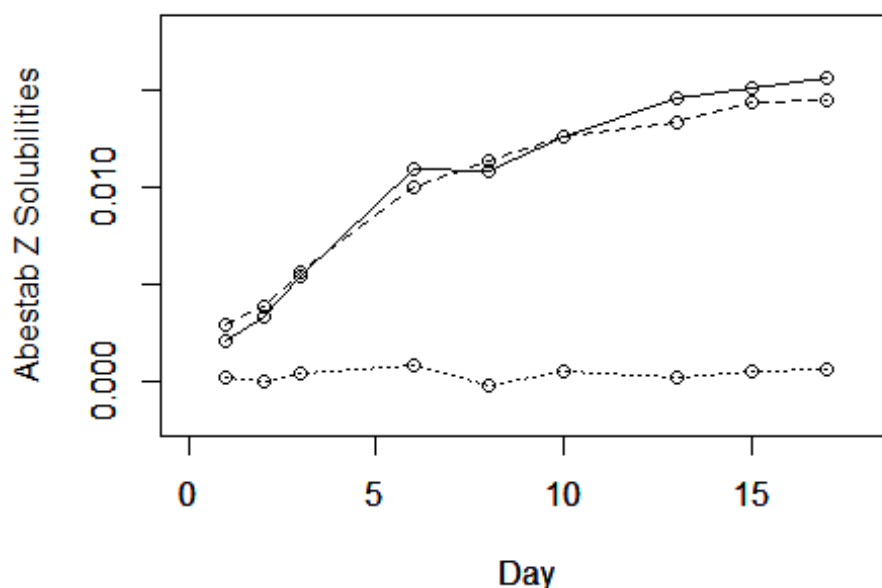


Table 2: Tensile strength of virgin latex films and films immersed in sulfur.

Type of film	Virgin	Immersed in sulfur
NR	0.549	0.551
XNBR	2.023	2.264

From the maximum increase of weight percentage for films immersed in ZDEC and ZDBC, it appears that the higher solubility was achieved with shorter alkyl chain length. To further establish this finding, the three types of film were immersed in Arbostab Z (zinc diisononyl dithiocarbamate) (Figure 10). Both natural rubber and low protein latex films have a maximum weight percentage increase that approximated at 0.015 % while the nitrile films showed minute solubility. However the earlier expectation of lower solubility with accelerator of longer alkyl chain was proven otherwise in the results. The solubility of natural rubber and low protein latex films in Arbostab Z was higher than ZDBC.

Figure 10: Percentage of weight increase for natural rubber latex (smooth line), nitrile (dotted line) and low protein latex (dash line) films immersed in Arbostab Z.



## SUMMARY

The solubility of sulfur and zinc diethyl dithiocarbamate in rubber films was studied. A gradual increase in weight percentage of films over a period of time was observed. The solubility of sulfur and ZDEC in natural rubber films was 1.8 % and 0.7 % respectively, for nitrile films it was found to be 0.20 % and 0.13 %. The low protein latex films showed a much lower maximum percentage of weight difference for sulfur and ZDEC which was 0.009 % and 0.002 % respectively. The solubility of both sulfur and ZDEC were consistently higher for natural rubber latex, followed by nitrile and lastly low protein latex films according to the weight difference method. The total sulfur content for natural rubber films was 1.0 %, 0.9 % for nitrile films and 2.2 % for low protein latex films. There were no significant difference between the virgin films and films immersed in sulfur; such observation was confirmed by the stress strain behaviour of the films. From our findings, there was no indication of solubility increased with short alkyl chain length accelerator.

## ACKNOWLEDGMENT

The authors would like to thank the Director General of the Malaysian Rubber Board for the permission to publish and present this paper. The authors are also grateful to the Director of Technology & Engineering for the support and advice to the project, the Head of Latex Science and Technology Unit for discussion and Mr Wenddy Mojuning for the laboratory assistance rendered. Special thanks to GME Chemtech Sdn. Bhd. for providing some of the chemicals needed for this project. The project is under the MRB Divisional Research Grant No. DIV2015/LP/2016(18)/626.

## REFERENCES

1. Porter, M. Rosemaze, R. & Sapi'ai, A.R. (1992). Chemistry of the Latex Pre-vulcanisation Process. Part 1. Migration of Reactants from the Solid Phase into Rubber Particles. J. Nat. Rubb. Res., 7(2), 85 - 101.
2. Morris, M.D & Thomas, A.G. (1995). Solubility of Sulfur and Dithiocarbamates in Natural rubber. Rubber Chem Tech 68(5), 794-803.
3. Yusof, A. & Hepburn, C. (1979). Problems of Bloom Experienced When Insoluble Sulphur is used in Natural Rubber J. Nat. Rubb. Res., 27(2), 57 - 67.
4. Duryodhan, M. (2002). Elastomer Blends. Rubber Chemistry and Technology., 75(3), 365-427.