

**SULPHUR VULCANIZATION OF NR LATEX – REDUCING  
CHEMICAL RESIDUES IN NR LATEX PRODUCTS- PART 1**



**INSTITUT PENYELIDIKAN, PEMBANGUNAN DAN PENGKOMERSILAN  
UNIVERSITI TEKNOLOGI MARA, SHAH ALAM  
SELANGOR, MALAYSIA**

**BY:**

**ASSOCIATE PROF HJH. ASIAH ABDULLAH**

**Dr. AMIR HASHIM B. MD. YATIM**

**ASSOCIATE PROF Dr. AZEMI B. SAMSURI**

**Dr. FAUZI B. MD. SOM**

**JANUARY 2004**

## ABSTRACT

The process of vulcanization requires chemicals such as crosslinkers, accelerators, activators and anti-oxidants. The unused chemicals during the vulcanization process may be left as residues in the final latex products. This brought about the concern of chemical residues eluting from the products while in service which can cause allergy Type IV in certain individuals. The residual thiocarbamate accelerator in the latex films was quantified using HPLC method. Results of the study indicated that the crosslink concentration and vulcanization time influenced the amount of extracted residual ZDEC. The study of the fractured surface of tensile test piece by SEM technique showed that the appearance of the surface could be correlated with the physical properties of the latex films in particular to the crosslink values. Sulphur probe experiment results showed a sulphur donor system yielded higher mono and di sulphidic crosslink than the elemental sulphur system.

## TABLE OF CONTENTS

<b>Acknowledgements</b>	i
<b>Abstract</b>	ii
<b>List of illustrations</b>	v
Tables	
Figures	
Micrographs	
Abbreviations	
<b>CHAPTER 1 – INTRODUCTION</b>	<b>1</b>
<b>CHAPTER 2 – EXPERIMENTAL</b>	
2.1 Materials	3
2.2 Preparation of the aqueous dispersions of vulcanizing ingredients	4
2.3 Formulations used in the study	6
2.4 Preparation of prevulcanized latex	7
2.5 Preparation of latex films by casting method	8
2.6 Determination of prevulcanizate relaxed modulus (PRM)	9
2.7 Determination of crosslink density of cast NR latex films by equilibrium volume swelling method	10

2.8	Determination of stress/strain properties	11
2.9	Quantification of types of crosslinks by chemical probes method	11
2.10	Quantification of accelerators residues by HPLC	14
2.11	Study of surface morphology by SEM technique	17

## **CHAPTER 3 – RESULTS AND DISCUSSION**

3.1	Optimum cure time	18
3.2	Effect of sulphur content on crosslinks formation	25
3.3	Modulus Measurement: PRM versus M300	28
3.4	Correlation between crosslink density and tensile strength values	28
3.5	Correlations between crosslink density and elongation at break (EB) / modulus (M300) values	<b>30</b>
3.6	Effect of ageing on physical properties	32
	3.6.1 Crosslink density	32
	3.6.2 Tensile strength, elongation at break and modulus	32
3.7	Assessment of the types of crosslink by chemical probe.	34
3.8	Accelerator residues	36
3.9	Study of surface morphology by SEM technique	41

<b>CHAPTER 4 – CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK</b>	<b>45</b>
---	-----------

<b>BIBLIOGRAPHY</b>	<b>47</b>
---------------------	-----------

## CHAPTER 1- INTRODUCTION

Raw rubbers have to be crosslinked or vulcanized in order to make products. This is because the vulcanization process will cause changes in the rubber physical properties, such as increase its strength, elasticity and its resistance to changes in temperature. The process of vulcanization requires chemicals such as crosslinkers, accelerators and activators. Typically, the quantities of these chemicals added into the latex are very small and about 1 – 2 per hundred part of rubber or even less, depending on the properties and applications required. Not all of the chemicals added into the compound are generally used up in the vulcanization process. Unused chemicals during the vulcanization process may be left as residues in the final latex products and this brought about the concern of chemical residues eluting from the products while in service.

Based on theoretical and experimental evidence, it was also postulated that some of the by-products of vulcanization, such as zinc sulphide and dithiocarbamic acid from the thiocarbamate accelerator may occur as by-products (Nieuwenhuizen et. Al. 1999). The carbamic acid if not removed can complicate Type IV chemical sensitivity reactions if the products are in contact with certain individuals. Burger and Hodes (1946) studied some of the organic accelerators used in the vulcanization system especially the thiocarbamic acid derivatives on their skin effects. A study on twelve rubber compounds with accelerators, activators and antioxidants for their toxicologically on the skin- irritating and skin-sensitizing properties shows that reaction from mild to severe skin irritants (Mallette and Haam 1952). Based on these data, it is emphasized that the importance of testing all new materials before they are introduced into the industry. In another study on the frequency of the Type IV allergy shows that the high incidence of allergy towards some rubber additives such as thiurams and carbamates (Conde-Salzar et.al. 1993).