

## Vulcanisation and Coagulant Dipping of Epoxidised Natural Rubber Latex

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### ABSTRACT

Epoxidised Natural Rubber (ENR) is now a commercially available polymer produced by chemical modification of natural rubber. Currently, three types of ENR are commercially available, and these are ENR 10, ENR 25, and ENR 50 with 10%, 25%, and 50% mol epoxidation, respectively. Studies on pre-vulcanisation of ENR 50 and post-vulcanisation of the latex films were carried out. The objective of this study was to develop ENR 50 that could be dipped easily in coagulant dipping solution to produce dipped products. Several attempts were made by compounding pre-vulcanised ENR 50 at various sulphur levels ranging from 0.5 to 3.0 pphr. Using suitable coagulant dipping systems, ENR 50 film could be formed despite the high contents of non-ionic surfactant. It was found that the tensile strength of pre-vulcanised ENR 50 film decreased with the increase in the sulphur level. The results show that as level of sulphur increased,  $M_{300}$  also increased to an optimum value of 1.5 pphr of sulphur. For the post-vulcanised ENR 50 film, however, the tensile strength increased and then decreased with the increasing sulphur level. Meanwhile  $M_{300}$  increased with the increasing post-vulcanization time and sulphur level. The post-vulcanisation of ENR 50 film seems to be a more effective way of increasing tensile properties than by pre-vulcanisation of ENR 50.

**Keywords:** Epoxidised natural rubber latex, pre-vulcanisation, post-vulcanisation

### INTRODUCTION

Natural rubber (NR) latex has invariably become the first choice for the production of most of latex dipped products. However, NR latex films have very poor resistance to rubber solvents and certain oxidising chemicals. As a result, chemical modifications of NR have been carried out to improve these important properties. The chemical modifications of NR were carried out either in latex or in dry phase. Basically, the chemical modifications of NR can be categorised into three main categories, namely grafting copolymerisation of NR, hydrogenation NR, and epoxidised NR (ENR). Epoxidised natural rubber (ENR) was produced by attaching the epoxy groups to NR molecule. The epoxidation reaction involves the addition of oxygen atom to the carbon-carbon double bonds of olefinically unsaturated polymer, thereby converting them to oxirane (epoxide) ring (Gelling, 1991).

Despite the fact that any desired epoxidation level can generally be achieved using this modification route, only three grades of ENR (ENR10, ENR 25, and ENR50) containing 10, 25, and 50% mol epoxidation levels, respectively are produced by the Malaysian Rubber Board (MRB) at present. These three grades of ENR should cover the range of desirable properties for most of the intended applications. ENR has been shown to exhibit beneficial properties, particularly its

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Received: 25 November 2009

Accepted: 5 March 2010

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oil and chemical resistance, air permeability, and adhesive properties (Gelling, 1991). It would be useful if these desirable properties of ENR could be exploited in latex dipped product applications. In addition, the ENR latex with a polar epoxy group could be expected to confer a certain degree of chemical resistance to products prepared from it.

However, uncompounded epoxidised natural rubber latex has been shown to be incapable of being satisfactorily processed by coagulant dipping due to its inability to gel on the former and because of the formation of a very thin latex deposit. The main reason for this observation is the stabilization of ENR latex by high level of non-ionic surfactant. Whilst the non-ionic surfactant is necessary to keep the latex stable during epoxidation reaction with acetic acid and hydrogen peroxide, it however keeps the latex chemically too stable against the calcium salt coagulant such as calcium nitrate.

ENR latex was compounded with sulphur vulcanising system in the attempts to develop ENR latex that could easily be dipped in coagulant. This process is called prevulcanisation. The prevulcanisation of NR latex, a process of chemical crosslink that takes place inside the particle, is generally performed by using sulphur, peroxide, and  $\gamma$ -radiation system. The vulcanisation of latex was proposed by Schidrowitz (1923) and subsequently by Schidrowitz and Stutchbury (1925). The production of prevulcanised (Gorton, 1979) latex involves heating of raw latex with various compounding ingredients such as accelerators and sulphur until the required degree of crosslinking is obtained as indicated by the relevant parameters. Using this system, this is not be possible and hence, ENR dipped film has to be developed.

## EXPERIMENTAL DESIGN

### *Prevulcanisation of Latex*

ENR latex and potassium hydroxide were added into stainless steel container and stirred for 10 minutes at room temperature. As shown in Table 1, sulphur at various levels, zinc dibutyl dithiocarbamate, tetra methyl thiuram disulphide, zinc oxide, and antioxidant were added into the container and stirred for 10min. After that, the latex was heated at 60°C for 3 hours. The vulcanised latex was cooled and then sieved. Later, the latex properties were tested.

TABLE 1  
Level of sulphur added to prevulcanisation epoxidised natural rubber latex (ENRL)

Formulation	A	B	C	D	E	F
Level of sulphur (pphr)	0.5	1.0	1.5	2.0	2.5	3.0

### *Coagulant Dipping Process*

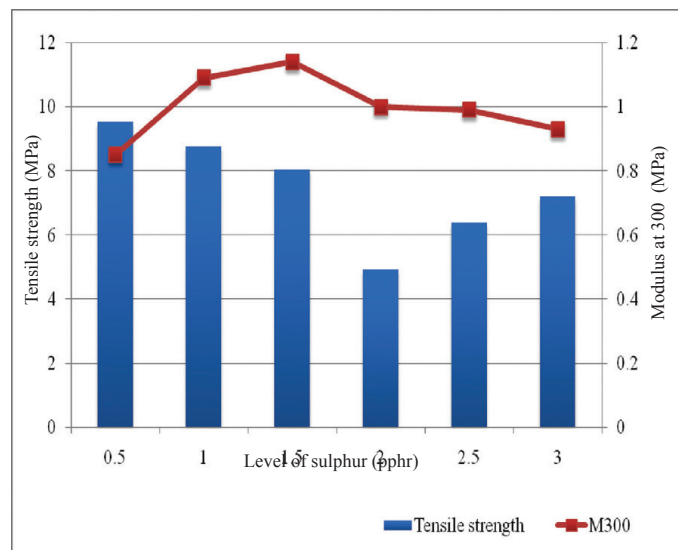
The former was first immersed in a 10% coagulant solution. After withdrawing the former from the solution, the solvent was allowed to evaporate, leaving either a very viscous concentrated solution or a dry deposit of calcium nitrate. The coated former was then immersed in the ENR latex compound and allowed to dwell for a predetermined time. This time, the coagulant migrated from the former into the latex and this resulted in the destabilization/gelation of the latex particles adjacent to the former and in the zone of the diffusing ions. The gelled deposit was vulcanized at

100°C in the oven, postvulcanised for 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 6.0, and 22.0 hours. The films were cooled and stripped-off from the former. Tensile test was carried out according to ISO 37:1998 test method. Type 2 dumbbells were cut parallel to the grain of the films. The test was carried out at room temperature (23±4°C) using the 'Instron 5565' tensile machine.

## RESULTS AND DISCUSSION

### *The Effect of Sulphur Level on the Tensile Properties of Prevulcanised ENR Latex Films*

The prevulcanisation of ENR latex with was prepared at various levels of sulphur and the effects on the tensile properties were evaluated. *Fig. 1* illustrates the increase in the level of sulphur has caused the tensile strength to slightly decrease. However, the value of tensile modulus M300 was slightly increased with 0.5, 1.0, and 1.5 pphr of sulphur levels but decreased at 2.0, 2.5, and 3.0 pphr of sulphur levels. The tensile strength of latex films is largely dependent upon the amount of sulphur added. Thus, it can be stated that increasing the amount of sulphur would theoretically increase the strength of vulcanisate. Based on the result, the abrupt decrease in the tensile strength at 2.0-3.0 pphr sulphur was observed, and this indicated that the level of sulphur had passed the optimum level of sulphur for the maximum tensile strength of vulcanised ENRL film.



*Fig. 1: Effect of the sulphur level on the tensile properties*

### *Effect of Sulphur Levels and Postvulcanisation Time on Tensile Properties of Postvulcanised ENRL Films*

The postvulcanisation studies of ENRL films were also carried out in order to improve the tensile properties of prevulcanisation. The tensile strength and modulus at 300 for the postvulcanised ENRL films prepared at various sulphur levels are shown in *Figs. 2* and *3*, respectively. The results of the tensile strength are generally in the range of 3-12 MPa. Meanwhile, the tensile strength for 1.0 pphr and 3.0 pphr of sulphur was higher as compared to the ones for 0.5, 1.5, 2.0, and 2.5 pphr of

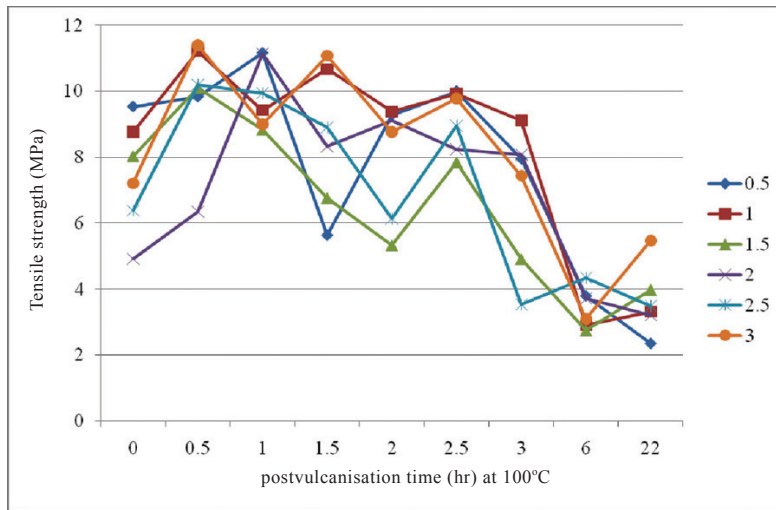


Fig. 2: The effects of postvulcanisation time on the tensile strength of ENRL films at various sulphur levels

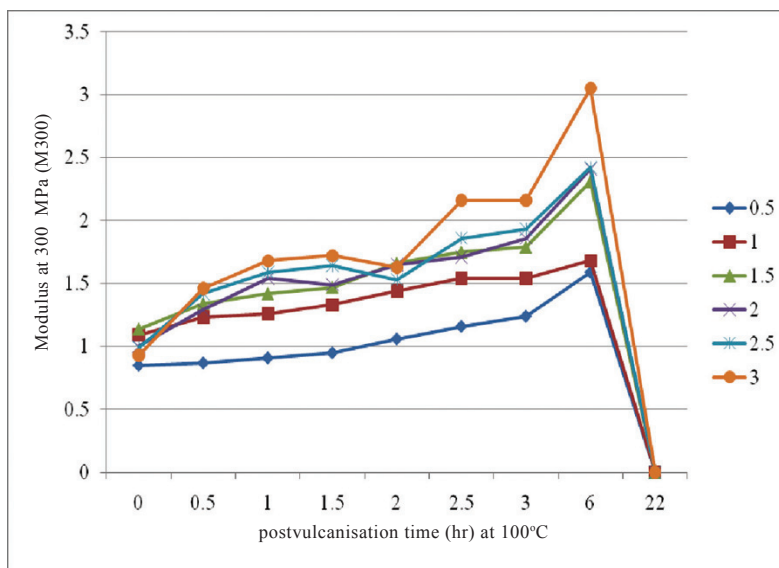


Fig. 3: The effects of postvulcanisation time on the tensile modulus of ENRL films at various sulphur levels

sulphur. When postvulcanised for 0.5 hours, the tensile strength was found to increase but it then decreased with the increasing sulphur content over the range of sulphur levels studied. However, there was a cyclical increase observed while the tensile strength was found to decrease over the range of postvulcanisation time. These results are significant as the changes in the tensile strength values were substantial in the range 2-4 MPa, and were observed for all the studied samples. Nonetheless, the reason for this phenomenon is still not clear.

An interesting feature is that the tensile modulus M300 value increased with postvulcanisation time quite significantly over a wide range of postvulcanisation times for all the compounds containing sulphur. Meanwhile, the postvulcanisation of ENR latex film is much more effective in increasing the degree of crosslinking as compared to prevulcanisation. The range of M300 values obtained for all the samples is 0.8-3.0 MPa. The modulus result showed that when the level of sulphur was increased, M300 also increased. The highest M300 value for ENRL vulcanisate was obtained using 3 phr of sulphur. The M300 value was dramatically reduced to zero after 22 hours of heating, suggesting that an extensive oxidation of the ENR had occurred.

### CONCLUSIONS

Coagulant dipped films could be formed from compounded ENRL-50 using suitable coagulant systems. The postvulcanisation of ENRL-50 films is a more effective way of increasing crosslink density as compare to using prevulcanisation of ENRL-50

### ACKNOWLEDGEMENTS

The authors wish to express their gratitude and thanks to the Malaysian Rubber Board for the financial support and to Ms. Syarintan Azima Jamaludin for the assistance rendered.

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