EFFECT OF ORGANOCLAY ON CURE KINETICS AND MECHANICAL PROPERTIES OF NATURAL RUBBER – ORGANOCLAY NANOCOMPOSITES.

Dissertation

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DECLARATION

I hereby declare that this research project was conducted by me, under the supervision of Dr. Upul N Ratnayake, Senior Research Officer, Department of Raw Rubber Processing Development and Chemical engineering, Rubber Research Institute, Rathmalana, Sri Lanka.and Dr Nilwala Kottegoda ,Senior Lecturer, Department of Chemistry, University of Sri Jayewardenepura, Sri Lanka. I also certify that, this thesis has not been submitted in whole or in part to any University or any other institute for another Degree/Diploma.

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ABSTRACT

Different types of curing systems play important roles in Curing kinetics and mechanical properties of Natural rubber-nanoclay vulcanizates. In this study organically modified nanoclay (montmorillonite clay) filled and unmodified nanoclay filled natural rubber (NR)compounds were prepared by melt mixing method and cured with conventional curing system at 150°C using compression molding machine in view of evaluating the curing behavior and reinforcing effect of nanoclay in NR vulcanizates The vulcanization of natural rubber-nanoclay by benzothiazolesulfenamide class of accelerator (TBBS) was studied based on DSC and cure curves.Organoclay/unmodified clay loadings from 2 to 10 phr were used in this research study. Characterization of vulcanizate structures with X-ray diffraction technique showed a phase separated unmodified clay structures and intercalated/exfoliated organoclay structures when NR was compounded with unmodified clay and organoclay respectively. Solid state mechanical properties of NR/organoclay nanocomposite vulcanizates have shown a significant reinforcement, especially tensile properties and strength characteristics, in comparison to equivalent NR/unmodified clay vulcanizates. Marked reinforcement achieved with organoclay in NR compounds has explained in terms of compatibility as a result of organic modification, degree of dispersion/exfoliation.

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CHAPTER 1

INTRODUCTION

1.1. Background

The vulcanization of natural rubber (NR) by sulphur in presence of organic accelerator is a complicated process. The mechanism of vulcanisation and its acceleration depends on the structure of the rubber, type and concentration of accelerators and activators (zinc oxide and stearic acid) and on the thermodynamics of each crosslinking reaction. The resulting crosslinks may be mono-, di-, tri- or higher poly-sulphides, which is determined by the vulcanisation system, the cure time and the temperature. [1] The accelerator increases the rate of cure and the efficiency with which sulphur is used in crosslinking reactions. The sulphur/accelerator ratio is particularly important in determining the type of crosslink formed. High sulphur levels, e.g., 2 to 3.5 phr, and low levels of accelerator, 0.5 to 1 phr, are called conventional systems, and at optimum cure the vulcanizate contains mostly polysulphidic crosslinks with relatively high level of chain modification.

Typically, performance of a NR product depends on the right combination of rubbers with rubber chemicals and a reinforcing filler system. Reinforcing fillers are used in rubber compounding mainly to improve mechanical properties of the final product.[2] A typical reinforcing filler for rubber compound is carbon black which causes pollution and gives a rubber a black color.[3] Other than carbon black, silica is used as a filler where the colour of the final product is important.[4] In addition, clay layered silicate such as montmorrilonite (MMT) is another type of filler that is increasingly used in rubber applications.

One of the drawbacks of using the clay mineral as filler for a rubber is the incompatibility between hydrophilic clay and hydrophobic polymer, which often causes agglomeration of the clay in the polymer matrix. Therefore, surface modification of the clay is an important parameter to achieve polymer nanocomposite. Such modified clays are commonly called organoclays [5].

MMT clays modified with long chain primary amines show much more improved mechanical properties than the unmodified MMT in a NR matrix.[6,7,8] Generally, the modification of clay surface can be done via ion exchange of the interlayer cations of clay with those of organic surfactants. Organic compounds normally used to modify clay are alkyl amine surfactants.[3] Therefore, blending NR with modified organo clay (OMMT) could improve the clay dispersion with in the polymer matrix leading to enhancement of mechanical properties of the nanocomposite. As explained by Lopez et al. natural rubber/organoclay nanocomposites prepared with long chain quaternary amine showed a significant decrease in the induction time(TS_2) and optimum cure time(T_{90}).[9] The kinetics of cure reaction showed that the organoclay was not just filler but also behaved as a cocuring agent .[10]

Current work focuses to study the effect of organically modified clay on vulcanization kinetics and reinforcement on natural rubber (NR) in comparison to unmodified clay.

1.2. Research objectives

The aims of this research are as follows:

(i) To introduce organically modified clay (montmorrilonite) as a reinforcing filler and prepare NR/clay nanocomposites

(ii) To optimize the concentration of accelerator for conventional curing systems in the presence of organically modified clay

(iii) To optimize the value of scorch delay in the presence of organoclay

(iv) To determine the effect of organoclay content on the mechanical properties and cure characteristics of NR nanocomposites

CHAPTER 2

LITERATURE REVIEW

Sri Lanka is one of the largest producers of natural rubber (NR). However, larger portion of natural rubber is exported (90%) as raw rubber while the rest is used to produce rubber products[7] for exporting and use within the country. NR has many attractive properties including low hysteresis, high resilience and excellent dynamic properties.

2.1.Natural Rubber (NR)

Latex from the trees of *Hevea Brasiliensis* is the only important commercial source of natural rubber.

Chemical structure

The empirical formula of natural rubber molecule, as C_5H_8 was found by Faraday in his early work in 1826. Later Grivelle William and other subsequent workers have shown that the rubber molecules have the following structure.

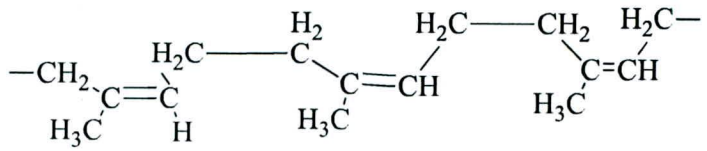

Figure 2.1 Straight chain polymer structure of *cis* – 1, 4 polyisoprene.[11]

The molecules consist of thousands of isoprene units joined end to end and all the double bonds have cis stereo chemistry. The number average molecular weight (Mn) and the weight average molecular weight (Mw) of the rubber have been found to be in the following range

Mn =2.5-27 $\times 10^5$ and Mw = 3.4-10 $\times 10^6$