

# CHAPTER I



## INTRODUCTION

### 1.1 The Statement of Problem

Rubber is the main economic plant of Thailand. Our country has become the largest rubber producer of the world since 1991. In 2007 alone, over 3 million tons of natural rubber (NR) was sourced from Thailand followed by Indonesia with 2.79 million tons, Malaysia, India and China as shown in Table 1.1. In fact, Thailand has to import technology, knowledge and finished rubber products from other countries. Thus, the scientists, rubber producers, rubber processors, rubber merchants, rubber technologists and all NR users in Thailand should emphasize on research and innovation development for supporting the market demand in commercial strategy.

Blending of rubbers is a common practice to produce vulcanized compounds containing the desirable features of each elastomer component (Soares and Oliveira, 2003). NR is well known for its excellent physical properties, but its resistance to heat, oxygen and ozone is poor. To improve the ageing resistance, the

**Table 1.1** World product of natural rubber (The Thai Rubber Association, 2008)

Year	Thailand	Indonesia	Malaysia	India	China	World Grand Total
2001	2319.5	1607.3	782.6	631.5	478.0	7328
2002	2615.1	1630.0	804.9	640.8	527.0	7332
2003	2876.0	1792.2	909.2	707.1	565.0	8033
2004	2984.3	2066.2	1097.5	742.6	573.0	8748
2005	2937.2	2271.0	1060.7	771.5	510.0	8882
2006	3137.0	2637.0	1284.0	853.3	533.0	9680
2007	3056.0	2791.0	1215.0	767.0	577.0	9685

unit : thousand tons

NR is normally blended with saturated or low unsaturated synthetic rubbers. Ethylene propylene diene rubber (EPDM) is a good partner for developing new rubber compounds with better ageing resistance because EPDM has the saturated structure providing the good thermal and oxidative resistance (Sirqueira and Soares, 2001). Since NR is a renewable resource which has high impact to the rubber market, it is worth addressing way to improve its limitations for using in the various applications (Akinlabi et al., 2007). Hydrogenation is one of chemical modifications to saturate the structure of NR to give better thermal and oxidative resistance. On comparison with EPDM, it was found that decomposition temperatures of the almost completely hydrogenated NR were close to those of EPDM (Hinchiranan, Prasassarakich and Rempel, 2005). According to the increase in the cost of petroleum which is the raw material for the polymerization of plastic and synthetic elastomers, considerable interest has arisen to use NR or modified NR as a possible substitute for synthetic rubbers (Hinchiranan et al, 2008). Thus, it is expected that the hydrogenated NR will has the potential to replace the use of EPDM in the rubber industries in the future.

Although the blend of unsaturated rubber with saturated ones could enhance the thermal and oxidative properties of blends, most of these blends are thermodynamically incompatible resulting in poor interfacial adhesion and gross-phase separated morphology. In addition, the resulting vulcanizates also display heterogeneous cross-link distribution between phase components due to the difference of unsaturation level to cause the imbalance vulcanization rate. Normally, the curatives tend to migrate into the more unsaturated phase resulting to lead an overcure phenomenon for the unsaturated rubber in the blends. All these characteristics contribute for a decrease in the mechanical performance compared to the pure rubber vulcanizate (Soares et al., 2002). For outstanding mechanical performance, the rubber blend vulcanizates should present a single network structure including cross-linked macromolecules of both polymers across the macro-domain interfaces. The process providing this ideal situation is known as co-vulcanization. Several studies have been developed vulcanization systems to produce co-vulcanized rubber blends to achieve the better performance. Moreover, the various techniques such as the addition of a third polymeric component with low molecular weight (El-Sabbagh, 2002), chemical modification of the accelerators to improve their solubility in both phases of

unsaturated and saturated rubbers (Ghosh et al., 2000) and grafting of accelerators onto the EPDM phase providing the enhancement of the crosslink density (Cook, 1998) have been reported to increase the mechanical performance of the blends.

Functionalized polymers have been employed as reactive compatibilizers containing mercapto functional group in several polymer blends. For this purpose, both ethylene vinyl acetate copolymer (EVA) and EPDM have been functionalized with mercapto group along their backbones (Barbosa, Soares and Gomes, 1993 and Oliveira et al., 1999). It was found that the reactive compatibilization was occurred and improved the interfacial adhesion and the crosslink distribution in the rubber blends. This means that the functionalized copolymer could be used as an improver agent for increasing tensile properties.

## **1.2 Objective of the Research Work**

The objective of this work was to study the preparation of thioacetate-modified HNR and mercapto-modified HNR for using as the compatibilizers for NR/HNR blends.

## **1.3 Scope of the Research Work**

This research dealt with the chemical modification of HNR via functionalization with thioacetate and mercapto. The effect of the addition of functionalized HNR as the compatibilizers on the mechanical and physical properties of HNR/NR blends was also reported.

The experimental procedures were carried out as follows:

1. To survey previous research works.
2. To prepare HNR via NR hydrogenation catalyzed by  $105.8 \mu\text{M}$  of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  at various reaction time: 2.5, 3 and 4 h to achieve 80, 90 and >95% hydrogenation, respectively.
3. To functionalize HNR by reacting with thioacetic acid in the presence of 1,1'-azobis(cyclohexanecarbonitrile) (ACCN) as an initiator at  $80^\circ\text{C}$  to produce

thioacetate-modified HNR (HNRTA). The extent of the reaction was investigated as a function of reaction time and concentrations of thioacetic acid and ACCN.

4. To prepare the mercapto-modified HNR (HNRSH) via methanolysis of HNRTA in sodium hydroxide methanolic solution. The reaction conversion was detected as a function of reaction time and the amount of sodium hydroxide/methanol (w/v).
5. To investigate the structure of both HNRTA and HNRSH using FTIR spectroscopy. To confirm FTIR results, <sup>1</sup>H-NMR spectroscopy was used to calculate the extent of conversion for both reactions.
6. To study the cure characteristics of HNR/NR blends at 50/50 wt ratio with and without the addition of functionalized-HNRs (HNRTA and HNRSH) using a moving die rheometer (MDR) at 150°C. The vulcanized sheets were prepared using a hydraulic compression mold at 150°C for the optimum cure time obtained from MDR.
7. To investigate morphology, crosslinking density and mechanical properties of such as hardness and tensile properties including dynamic mechanical properties of HNR/NR vulcanizates with and without the addition of HNRTA or HNRSH.
8. To investigate the effect of the addition of functionalized HNRs as the compatibilizers on the thermal and ozone resistance of HNR/NR vulcanizates.
9. To summarize and discuss the obtained results.