

CHAPTER I INTRODUCTION

1.1 The Statement of Problem

The increasing amount of waste tires has become a serious environmental concern because the waste tires need a very long time for natural degradation due to the crosslinked structure of rubbers and the presence of stabilizers and other additives. Recycling or reusing is the way to eliminate or reduce the amount of waste tires, for example, retreading to reduce spending of tire, burning to produce heat and material recycling (devulcanization) to regenerate new rubber for suitable applications [12]. The chemical devulcanization is a process for decomposing crosslinked structure as poly-, di- or mono-sulfidic bonds in the vulcanized rubber. Unfortunately, the devulcanization also degrades the main chain of rubber, which causes the rubber product to have lower molecular weight, shorter chain and undesired properties. Moreover, most of devulcanizing agents are expensive and the devulcanizing process requires a complex system and method. So, it was used by limitation.

Oxidation is an effective route to devulcanize the crosslinked rubber due to process simplicity, low cost and high activity. The manner, in which the different types of sulfidic bonds are reacted and the structure of devulcanizate is formed, depends on types of oxidizing agent and reaction conditions. The general oxidizing agents are hydrogen peroxide (H_2O_2) and nitric acid (HNO_3). It is known that the concentrated nitric acid is a strong oxidizing agent and can oxidize disulfide bonds according to the reaction (a) shown in Figure 1.1.

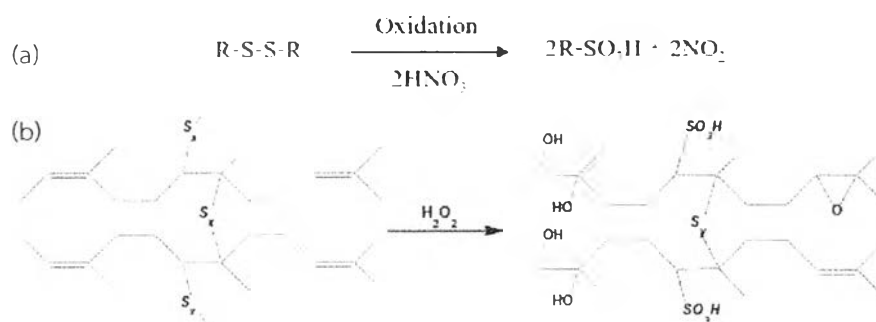


Figure 1.1 Oxidation of sulfidic bonds in the crosslinked rubber with oxidizing agents, (a) Nitric acid [1] and (b) Hydrogen peroxide [8].

Oxidation of thiol (R-SH) and disulfides (R-S-S-R) can generate sulfonic acid groups (R-SO₃H) which has high ion-exchange capacity. Also, oxidation of waste tires that contain various types of sulfur bond with H₂O₂ or HNO₃ is likely to generate sulfonic acid group in the structure. However, the oxidation of waste tires also generates oxygen-containing functional groups, such as epoxide ring and hydroxyl group [8]. Under severe conditions, the main rubber chain is oxidized, giving lower molecular weight devulcanizate as the product [1].

Due to their high ion-exchange capacity and high acidity, polymers with sulfonic acid groups have been applied to many researches, for example, adsorptive removal of heavy metals from aqueous solution [13], cation exchange membranes for separation of sodium ions and alkaline earth cations [14] and conversion of fatty acids to biodiesel via heterogeneous catalysis [15]. Amberlyst[®] series are ion exchange resins composed of copolymer polystyrene crosslinked with divinyl benzene and sulfonation with oleum (concentrated sulfuric acid). In the area of catalyst, Amberlyst-15 is a promising heterogeneous acid catalyst for reducing amount of free fatty acids in vegetable oils which are used as feedstock for biodiesel production [11]. However, its high cost limits the practical use in an industrial scale.

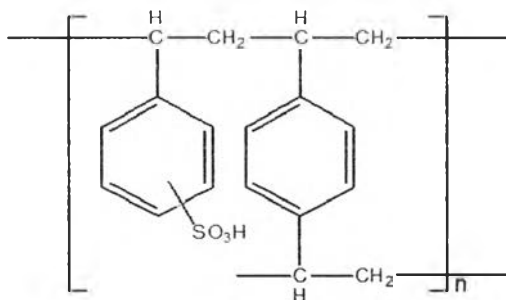


Figure 1.2 Cation exchange resins structure in Amberlyst[®] series.

Esterification is a chemical reaction for synthesis of ester compound (R₁-COO-R₂) by heating alcohol (R₁-OH) and carboxylic acid (R₂-COOH) in the presence of an acid catalyst.



Figure 1.3 Esterification of free fatty acid and methanol to produce fatty acid methyl ester and water as products [11].

In this research, waste tires as crumb rubber was converted to polymer containing sulfonic acid groups via a controlled oxidation by using HNO_3 or H_2O_2 as the oxidizing agent. The influences of oxidation conditions, including type and concentration of oxidizing agent were studied. The ion-exchange capacity of oxidized crumb rubber was evaluated by an acid-base titration. Functional groups of the oxidized rubber were characterized by Fourier transform infrared spectroscopy (FTIR) using KBr method. Thermogravimetric differential thermal analysis (TG/DTA) was applied to study degradation behaviour of crumb rubber before and after the oxidation at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ and a dry nitrogen flow ($50\text{ mL}/\text{min}$). The swelling degree of samples was measured by swelling test following ASTM D471. Scanning electron microscopy (SEM) was applied to study the morphology of crumb rubber before and after the oxidation. The catalytic performance of the oxidized rubbers was evaluated by esterification of octanoic acid with long chain alcohols.

1.2 Objectives of the Research work

1. To optimize the conditions for preparation of polymer containing sulfonic acid group from crumb rubber via controlled oxidation by using HNO_3 or H_2O_2 as the oxidizing agent.
2. To study the catalytic performance of the oxidized crumb rubber in the esterification of octanoic acid with long chain alcohols.

1.3 Scope of the Research work

1. Literature survey and study the research work
2. Preparation of polymer containing sulfonic acid groups from crumb rubber by oxidation crumb rubber with 2 different oxidizing agents
3. Study the effects of oxidation conditions following Table 1.1 on the physicochemical properties of the oxidized crumb rubber

Table 1.1 The oxidation conditions with the different oxidizing agents

Oxidizing agent	Concentration	Temperature (°C)	Time (h)
H ₂ O ₂ with HCOOH ¹	10%	50	5
H ₂ O ₂ with HCOOH ¹	20%	50	5
H ₂ O ₂ with HCOOH ¹	30%	50	5
H ₂ O ₂	20%	50	5
H ₂ O ₂	30%	50	5
HNO ₃	2 M	80	3
HNO ₃	4 M	80	3
HNO ₃	6 M	80	3
HNO ₃	8 M	80	3

¹The mole ratio of H₂O₂ with HCOOH was 1:1

4. Characterization of crumb rubber before and after the oxidation by following techniques:
 - X-ray fluorescence spectrometry (XRF)
 - Bomb calorimetry with ASTM D3177
 - Thermogravimetric/differential thermal analysis (TG/DTA)
 - Fourier transform infrared spectroscopy (FTIR)
 - Scanning electron microscopy (SEM)
 - Swelling method according to ASTM D471
 - Sol/gel method according to ASTM D3616
 - Acid-base titration for cation-exchange capacity
5. Evaluation of the catalytic activity of the oxidized rubbers in the esterification of octanoic acid with long chain alcohols following Table 1.2



Table 1.2 The esterification condition of octanoic acid with long chain alcohols

Condition of esterification	Value
Total batch size reactor	20 gram
The ratio of carboxylic acid with alcohol	1:2 by mole
Temperature	120 °C
Reaction time	8 h
Carboxylic acid	Octanoic acid
Long chain alcohols	Octanol 2-Ethyl-1-hexanol

6. Evaluation of the octanoic acid conversion after the esterification by gas chromatography (GC) using an Agilent Technology 7890A GC system
7. Evaluation of the possibility to reuse the oxidized rubber catalysts in the esterification of octanoic acid with octanol
8. Summation of the results and write thesis

