



# CHAPTER I

## GENERAL INTRODUCTION

### 1.1 Scientific Rationale

Natural rubber is a naturally occurring polymer which has been commercially available for more than a hundred years. The main constituent of this polymer is *cis*-1,4-polyisoprene, which can be obtained in a latex form by tapping the rubber tree, *Hevea Brasiliensis*. Natural rubber has excellent physical properties (e.g. high green strength) which is unmatched by most synthetic rubbers together with the fact that it is a renewable resource (1).

The development of synthetic polymer after the Second World War has made the natural rubber latex manufacturers look into alternative uses, in order to compete with synthetic rubber in the market. Various methods of chemical modification of natural rubber were explored to promote its uses. The unsaturated backbone in natural rubber facilitates various types of chemical modification, such as, grafting (2-5), crosslinking (6-8), chlorination (9-12) and also hydrogenation (13-16). These modifications yield a wide range of rubber products; e.g. high performance tyres and pressure sensitive adhesives (17-19). Each of these modifications enhances certain properties of natural rubber (e.g. chlorination of rubber gloves will harden the film

and also cause it to become non-sticky compared to the original unmodified natural rubber).

The design of novel copolymers with specific and controlled molecular architectures is both an intellectual challenge (equivalent to the synthesis of unusual molecules by organic chemists) and a procedure with considerable technical potential. Presented here is a study for the development of a new process to produce novel copolymer structures that utilizes the topology of a polymer colloid specifically for the purpose of chemically grafting hydrophilic polymer onto hydrophobic polymer backbones. It is believed that this copolymer is present as a hydrophilic polymer chain extending into the aqueous phase from the surface of a hydrophobic polymer onto which it is grafted.

Graft copolymerization has become of recent interest in modifying natural rubber. It would be desirable to carry out the modification in the latex stage rather than solution for two reasons. The first is that, natural rubber has a very high molecular weight; therefore, preparing a complete solution is impossible, and even then its viscosity would be very high even at low concentrations (20). The second reason is that there is a growing interest in environmental safety where the proposed process obviates the use of organic solvents and the resulting stress on the environment.

One of the primary targets for this chemical modification is the biomacromolecule *cis*-polyisoprene from natural rubber latex (NRL). This polymer in

its native form has many special properties (such as being essentially 100% *cis*-polyisoprene, which gives a mechanical response that makes it well suited in applications such as surgical gloves). However, it also has limitations, such as a colloidal stability which is very sensitive to pH changes, and the presence of proteins which can cause allergenic reactions. There are clearly potential advantages in being able to carry out grafting reactions using NRL in a seeded emulsion polymerization to yield a synthetically modified latex, and indeed there are a number of such modifications reported in the literature.

## 1.2 Objectives of Research Work

The objectives of this research work were as follows:

- 1.2.1 To synthesize the polyisoprene seed latex by conventional free-radical emulsion polymerization. Effects of such influential parameters namely surfactant, initiator, and monomer concentration, reaction temperature and time on the percentage of conversion and particle size of the synthesized polyisoprene seed latexes were studied.
- 1.2.2 To study the kinetic of surface grafting reactions of a hydrophilic vinyl monomer on the synthesized polyisoprene seed latexes using a redox initiator system. Effects of feed rate of the half redox initiator, tetraethylene pentamine, and particle size of the seed latex on the kinetics of grafting reaction were investigated.



1.2.3 To modify natural rubber by grafting with hydrophilic vinyl monomers.

Effects of the monomer and initiator concentration, reaction temperature and feed rate of the half redox initiator on the percentage of conversion and grafting parameters were determined. The effects of type of redox initiation systems, cumene hydroperoxide (CHP)/tetraethylene pentamine (TEPA), *tert*-butyl hydroperoxide (*t*-BHP)/TEPA, and potassium persulfate ( $K_2S_2O_8$ )/potassium metabisulfite ( $K_2S_2O_5$ ) on the percentage of conversion and grafting parameters were also studied.

### 1.3 Scopes of Research Work

In this research work, the purpose is to modify natural rubber latex by grafting with hydrophilic vinyl monomers. Practical application of this grafting process to NRL requires better mechanistic understanding, which is one of the aims of the present work. The broad size distribution or polydispersity (21) and presence of proteins, phospholipids and inorganic salts (22, 23), however, make it difficult to obtain this mechanistic understanding of the grafting process in isolation. For this reason, the first part of this work uses well-characterized synthetic polyisoprene latexes for obtaining the different seed particle sizes of the polyisoprene latexes. The targets are the effects of feed addition profile and particle seed latex size on kinetics of the grafting reaction of the second stage polymerization of poly(DMAEMA) onto the surface of synthetic polyisoprene latexes prepared via a conventional emulsion polymerization. All kinetic studies were carried out with an RC1 reaction microcalorimeter. This is ideal for following up the reaction rates accurately in a

redox system, which requires a continuous feed of one or both components of the redox couple.

#### 1.4 Outlines of the Thesis

This thesis consists of 5 chapters. The first chapter deals with the background, the interest and the scope of this research work. Chapter 2 provides the theory of emulsion polymerization and related theories that are important for understanding. Additionally, it includes the literature reviews of previous works that give beneficial information and trends for the work. The experimental work in Chapter 3 describes about chemicals, equipment, apparatus, procedure, and characterization of the product in this work. The result and discussion are explained in Chapter 4. The effects of the various reaction parameters on particle size of the synthesized polyisoprene seed latexes prepared via conventional free-radical emulsion polymerization, the influences of the feed addition profile and particle seed latex size on kinetics of grafting reaction of the second stage polymerization of poly(DMAEMA) onto the surface of synthetic polyisoprene latexes using redox initiation system by reaction calorimetric technique are investigated. The effects of reaction parameters on the properties of grafted product prepared by the modification of natural rubber latex by grafting with hydrophilic vinyl monomers, DMAMEA, DMAEA, and HEMA are also shown and discussed in details. Finally, the summary and suggestion are provided in Chapter 5.