PREPARATION AND CHARACTERIZATION OF CHITOSAN-ENR50 BIOCOMPOSITES AND THEIR POTENTIAL APPLICATION AS SLOW-RELEASE BIODEGRADABLE MATRICES FOR CU(II) AND 2-NAPHTHOL IN AQUEOUS MEDIA

by

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This thesis is especially dedicated to:

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My husband, my brothers, my sister in law, my kids, my nieces and my in laws who have filled my life with joy and happiness.

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LIST OF ABBREVIATION

CDCl$_3$	Deuterated chloroform
CTS	Chitosan
CTS-g-ENR-P1	CTS grafted onto the backbone of epoxidized natural rubber with high concentration of AlCl$_3$.6H$_2$O
CTS-g-ENR-P2	CTS grafted onto the backbone of epoxidized natural rubber with low concentration of AlCl$_3$.6H$_2$O
CTS/ENR50-control	Sample prepared by physically mixing appropriate amounts of CTS and ENR50
CTS/ENR	Biocomposites comprising CTS and ENR matrices prepared via melt blend
CTS-t-ENR	Biocomposites comprising CTS immobilized/trapped in ENR matrices
5 phr CTS-ENR	Biocomposites comprising CTS immobilized/trapped in ENR matrices in the absence of acetic acid
DSC	Differential Scanning Calorimetry
DTG	Derivative thermogravimetry
ENR50	50 mole percent Epoxidized natural rubber
FT-IR	Fourier Transforms Infrared
FT-NMR	Fourier Transforms Nuclear Magnetic Resonance
g	gram
hr	hour

Mw	Average molecular weight
NR	Natural rubber
phr	Part per hundred rubber
ppm	Part per milliom
SEM	Scanning Electron Microscope
Tg	Glass transition temperature
TGA	Thermolgravimetric analysis
TMS	tetramethylsilane

PENYEDIAAN DAN PENCIRIAN BIOKOMPOSIT KITOSAN-ENR50 DAN POTENSI APLIKASINYA SEBAGAI MATRIKS MUDAH BIODEGRADASI PELEPAS-PERLAHAN UNTUK CU(II) DAN NAFTOL DALAM MEDIUM AKUEUS

ABSTRAK

Sejak bertahun lamanya, penggabungan kitosan dalam matriks elastomer telah begitu menarik minat para penyelidik. Namun demikian, terdapat batasan kerana kitosan larut dalam medium akues berasid, sedangkan getah asli terepoksida tidak larut. Keadaan ini mendorong kami untuk mengkaji serta melaporkan dapatan tentang penyediaan, pencirian dan sifat daripada tiga jenis biokomposit yang mengandungi kitosan (CTS) dan getah asli terepoksida (ENR) yang disediakan melalui pelbagai kaedah. Jenis pertama, CTS-g-ENR diperoleh melalui tindak balas aruhan-asid daripada ENR50 dengan CTS dalam kehadiran $AlCl_3.6H_2O$. Analisis spektrum NMR menunjukkan bahawa kandungan epoksi daripada CTS-g-ENR-P1 adalah 22.36%, yang mencadangkan bahawa berlakunya cangkukan CTS pada tulang belakang atau rangka ENR. Hal ini terbukti berdasarkan pencirian jalur serapan CTS dan ENR, dan kehadiran jalur baru pada 1219, 902 and 733 cm^{-1} dalam spektrum inframerah CTS-g-ENR-P1. Tg bagi CTS-g-ENR-P2, ditemui pada 2.88 °C, yang secara signifikan lebih tinggi dibandingkan dengan ENR50 (-27.2 °C). Kestabilan haba CTS-g-ENR didapati lebih tinggi daripada CTS, tetapi lebih rendah daripada ENR50. Mikrograf SEM daripada CTS-g-ENR-P1 menunjukkan tektur topografi yang licin, yang mengesahkan bahawa CTS berjaya dicangkuk pada

rangka ENR. Jenis kedua, CTS/ENR disediakan melalui campuran-lebur daripada beban CTS yang berbeza (5, 10, 15, 20 dan 30 phr) dengan ENR50. Didapati bahawa pertambahan beban CTS menyebabkan peningkatan 100% dalam nilai tork matang, kekuatan tegangan dan modulus. Keputusan daripada kajian pengambilan air menunjukkan bahawa peningkatan beban CTS menyebabkan peningkatan dalam penyerapan toluena daripada biokomposit CTS/ENR. Jenis ketiga, CTS-t-ENR disediakan melalui penghomogenan jumlah CTS yang berbeza (2.5, 5, 10, 15 dan 20 phr) dalam lateks ENR50 dengan agen pematang dalam kehadiran asid asetik. Pembebanan CTS sehingga 5 phr mendorong kepada peningkatan kekuatan tegangan, pemanjangan pada takat putus, modulus dan kekerasan biokomposit. Peningkatan beban CTS mengurangkan daya serap toulena dan peningkatan pengambilan biokomposit CTS-t-ENR. Kemudahbiodegradasian CTS-t-ENR dalam tanah menunjukkan bahawa biodegradasi biokomposit meningkat dengan peningkatan beban CTS. Kapasiti penyerapan dan penyahjerapan CTS-t-ENR bagi Cu(II) dan 2-Naftol dalam air juga ditentukan. Biokomposit mempamerkan sifat pelepas-perlahan yang baik, yang terbukti melalui kajian kinetik melalui penggunaan tertib sifar, tertib pertama, persamaan Higuchi dan persamaan Kosmeyer Peppas.

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ABSTRACT

Over the years incorporation of chitosan in the matrices of elastomers has been of interest to researchers. However, solubility of chitosan in acidic aqueous media in contrast with epoxidized natural rubber which is not soluble has been a limitation. This has prompted us to investigate and hereby report our findings on the preparation, characterization, and the properties of three types of biocomposites containing chitosan (CTS) and epoxidized natural rubber (ENR) prepared via different methods. The first type, CTS-g-ENR, was obtained via acid-induced reaction of ENR50 with CTS in the presence of $AlCl_3.6H_2O$. Moreover, the NMR spectral analysis revealed that the epoxy content of CTS-g-ENR-P1 is 22.36%, suggesting that the grafting of CTS onto the backbone of the ENR had occurred. This revelation is affirmed by the presence of the characteristic absorption bands of CTS and ENR and the appearance of new bands at 1219, 902, and 733 cm^{-1} in the infrared spectrum of CTS-g-ENR-P1. The Tg of CTS-g-ENR-P2 is determined to be 2.88 °C which is significantly higher than that of ENR50 (-27.2 °C). The thermal stability of CTS-g-ENR is found to be higher compared to that of CTS, but lower than the one for ENR50. SEM micrographs of CTS-g-ENR-P1 show a smooth topographical texture with no phased-out entity, confirming that CTS has been successfully grafted onto the backbone of the ENR. The second type, CTS/ENR, was prepared via melt

blending of different loadings of CTS (5, 10, 15, 20 and 30phr) with ENR50. It is found that the increase in CTS loading caused an increase in cure, torque value, tensile strength, and modulus at 100%. Furthermore, the results of the water uptake study reveal that the increase in CTS loading led to an increase in water uptake and a decrease in the toluene absorbency of CTS/ENR biocomposites. The third type, CTS-t-ENR, was prepared by homogenizing different amounts of CTS (2.5, 5, 10, 15 and 20 phr) in ENR50 latex with curative agents in the presence of acetic acid. CTS loadings of up to 5 phr led to an increase in the tensile strength, elongation at break, moduli and hardness of the biocomposites. The increase in CTS loading led to a decrease in toluene absorbency and an increase in water uptake of CTS-t-ENR biocomposites. The biodegradability of CTS-t-ENR in soil revealed that the biodegradation of the biocomposites increases with the increase in CTS loading. Moreover, the absorption and desorption capacities of CTS-t-ENR for Cu(II) and 2-Naphthol in water were determined. The biocomposites reveal good slow release properties and this is proven by the kinetic study using zero order, first order, Higuchi equation, and Kosmeyer-Peppas equation.

CHAPTER 1

INTRODUCTION

1.1   General Introduction

Although there are over 2,000 species of Natural Rubber (NR), a renewable polymeric material that is obtained in latex form from *Heveabrasiliensis* tree is the only one that is widely used in industry. NR latex contains about 94% polyisoprene with almost 99% *cis*-1, 4- configuration (Figure 1.1). The remainder of the latex (as shown in table 1.1) consists of mainly protein and lipids (phospholipids, esters of higher fatty acids, and sterols) (Hourston and Tabe, 1996). The rubber particles range in size from about 50 Å to about 30,000 Å (3μm). The polydispersity is usually in the region of 2.5-10 (Bhowmick and Stephens, 2001).
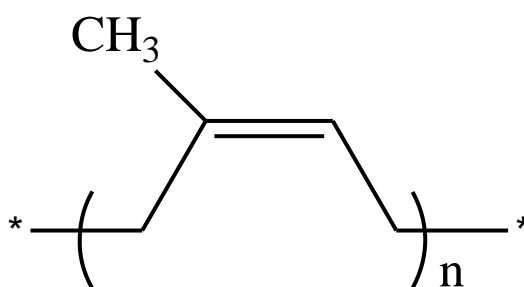
n = repeating unit

Figure 1.1: Chemical structure of *cis*1,4-polyisoprene.

Table 1.1: Typical composition of latex from *Heveabrassilinies* (Hourston and Tabe, 1996)

Content	%
Dry rubber	36
Protein	1.6
Inositols-carbohydrates	1.5
Neutral lipid	1
Phospholipids	0.6
Salts (mainly K,P and Mg)	0.5
Amino acids and N-bases	0.3
Water	58.5

Epoxidation of NR and other unsaturated elastomers is of great interest these days. Economy of modifying NR in latex stage with hydrogen peroxide formic acid has led to this process, being extensively studied by Gelling et al., 1991. Epoxidized natural rubber (ENR) is reported to have improved solvent resistance, adhesion, and resistance to gas permeation.

Furthermore, chemical modification of ENR (Figure 1.2) may lead to new products with technological interests. The presence of carbon–carbon double bonds and epoxide groups on the polymer backbone allows a number of chemical reactions of interest to be carried out. The reactivity of the epoxide groups toward carboxylic acids (Soutif and Brosse, 1984), amines (Jayawardena et al., 1984), alcohols (Derouet et al., 2001), and phosphoric acid derivatives (Derouet et al., 2001) is well known.
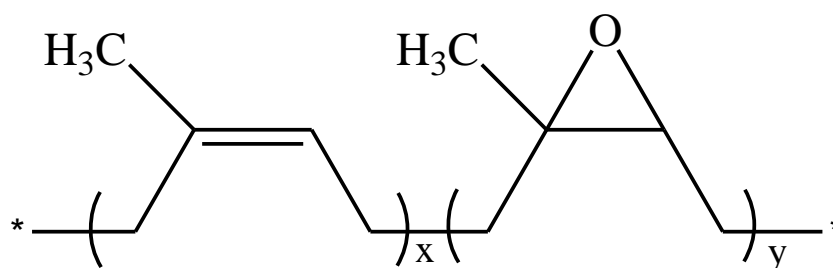
Figure 1.2: A simplified chemical structure of an epoxidized natural rubber.

Furthermore, ENR can be modified by physical and chemical means. Examples of physical modifications are blending with other polymers, master batching, etc. Although a limited level of chemical reaction may take place between the rubber and some of the additives, the properties of the resulting polymers are brought about mostly by the physical combination of materials. Chemical modification, on the other hand, may result in materials having entirely different or new properties.

Chitin is a linear biopolymer and the second most abundant natural polysaccharide after cellulose (Muzzarelli, 1977). The commercially available chitin is typically extracted from crab and shrimp shells, and chitosan is derived from chitin (Chandra and Rustgi, 1998). It is composed of predominantly $\alpha(1 \rightarrow 4)$-linked 2-amino-2-deoxy-β-D-glucopyranose with some amount of, depending on the degree of N-deacetylation, 2-acetamido-2-deoxy-D-glucopyranose sugars (Auze 'ly and Rinaudo, 2003), (Dutta et al.,2004) and (Munro et al., 2009). Due to the presence of the primary amino (C-2) and primary (C-6) and secondary (C-3) hydroxyl groups on each repeat unit, chitosan is a multi-nucleophilic material that may undergo specific reactions with other materials that contain electrophilic sites. Moreover, chitosan is

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being used in a wide range of applications ranging from biomedical engineering, pharmaceutical and cosmetic products, to water treatment and plant protection (Muzzarelli and Muzzarelli, 2005). Being a natural polysaccharide, chitosan exhibits high biodegradability but has poor mechanical properties. Thus, modification of polymers that possess excellent thermal and mechanical parameters with chitosan may result in the production of a new class of polymeric materials exhibiting not only desired biodegradability but also good physicochemical and mechanical properties (Svetlana et al., 2011).

The structure of chitosan is shown in figure 1.3. It is soluble in acidic media, but its solubility in neutral or basic media is poor (Loykulnant et al., 2012). Chitosan is widely used in waste water and effluent treatment as well as pharmaceutical, medical, agricultural and other fields (Sionkowska, 2011). A very important area of application is in waste water treatment and industrial toxic pollution control where it can be used as a chelating polymer for removal of metal cations such as mercury, copper, and many other elements (Monier, 2012).
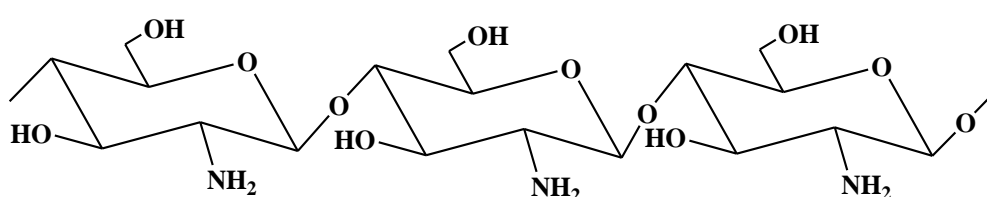
Figure 1.3: Structure of chitosan

Significant research efforts are currently being spent in developing a new class of fully biodegradable green composites by combining natural rubbers with biodegradable polymers. These composites are environmentally friendly, fully degradable, and sustainable. At the end of their life, they can be easily disposed of or

composted without harming the environment. Careful analysis of the literature indicates that no systematic studies have been reported about the use of chitosan in epoxidized natural rubber. The major attraction of this work is that both the matrix and the chitosan are naturally available. Hence, products based on this work will be both cheaper and sustainable.

1.2   Problem Statement

Chitosan is soluble in acidic aqueous media (Ravi Kumar, 2000), (Aranaz et al., 2009) whereas ENR, being hydrophobic in nature, is not (Gelling et al., 1991). This is the likely reason explaining why there is a very limited number of reports in the literature on homogenous (liquid-liquid phase) or semi-heterogeneous (liquid-solid phase) reaction condition involving chitosan and ENR. Furthermore, ENR is known to undergo ring-opening and double bond cleavage reactions (Gelling, 1991), (Derouet et al., 2001), (Derouet et al., 2001), (Gan and Hamid, 1997) (Derouet and Tillekeratne, 1990). Hence, there is a need to investigate the stability of the microstructure of ENR50 in different concentrations of acid [H+] prior to being able to establish a method for grafting chitosan (CTS) onto the backbone of ENR in an acidic media. Modification of natural rubber or its derivatives can be accomplished under three different reaction conditions: (i) in solution (clear liquid-liquid form), (ii) melt blending (solid-solid form), and (iii) in latex (emulsion form). To have a better or more comprehensive understanding of biocomposites comprising chitosan and ENR, it is deemed necessary to also prepare the biocomposites via melt blending and latex methods.

Lately, artificially synthesized fertilizers have been widely used in domestic agriculture. In spite of their low price in the commercial market, they are always evaded in practical use because they are easily swept away by rainfall, facilitating soil acidification and contributing to surface waters eutrophication (Jamnongkan et al., 2010). These problems can be resolved by using slow release formulation that relies on suitable media with a large surface area to mitigate the loss of fertilizer elements. This has prompted us to study the effectiveness of the CTS-t-ENR as a heavy metal absorbent and also as slow release material.

With regards to above problem statements, we have attempted to achieve the following research objectives.

1.3   Research objectives

1. Preparation and determination of the structural and physio-chemical properties of biocomposites comprising chitosan-grafted-epoxidized natural rubber (CTS-g-ENR) via an acid-induced reaction of ENR50 with chitosan.

2. Preparation and determination of the mechanical and thermal properties, water uptake, and toluene absorbency of CTS/ENR biocomposites prepared via melt blend.

3. Preparation and determination of the mechanical and thermal properties, water uptake and toluene absorbency of biocomposites comprising chitosan trapped in partially cross-linked epoxidized natural rubber (CTS-t-ENR), that is prepared via latex method.

4. Evaluation of the biodegradable properties of CTS-t-ENR.

5. Determination of the absorption and desorption properties of CTS-t-ENR for copper(II) ion and 2-naphthol in the aqueous media.

CHAPTER 2

LITERATURE REVIEW

2.1   Natural rubber

As an agricultural commodity, NR has numerous features that make it a significant component in tropical agronomy. It is a perpetual crop providing income for millions of people in developing countries. By means of coagulation, rubber from latex is recovered in almost pure form and processed into sheet, crepe or crumb which forms the raw material for various product manufacturing industries. Products from latex are also manufactured through dipping, extrusion etc. In addition to product manufacturing the high molecular weight polymer can be altered to yield other derivatives that find use in various applications like binders, anticorrosive coatings and process aids. The modifications are carried out by depolymerization, cyclization, carboxylation etc. These different forms provide better processability and special properties.

As a manufacturing raw material, despite heavy competition from various synthetic rubbers, NR is the elastomer of choice in many applications from the point that it retains certain specific merits. Natural rubber possesses excellent physical properties, such as high tensile and tear strength, remarkable elastic behaviour, which have not yet been competed by synthetic elastomers. Six decades of industrial research have not produced synthetic rubber materials (such as styrene butadiene rubber, butyl rubber, chloroprene rubber, or polyisoprene) with price-performance ratios that match those of NR. Consequently, NR is used in over 40,000 products,

including more than 400 medical devices, surgical gloves, aircraft tires and countless engineering and consumer products. The market share of NR has increased from close to 30% in the 1970s and 1980s to the present 40%. Over 90% of NR is produced in Asia, particularly in Malaysia, Indonesia and Thailand (Beilen and Poirier, 2007). Moreover, it is a renewable resource, whereas its synthetic counterparts are mostly manufactured from non-renewable oil based resources (Nakason et al., 2004).

2.2   Modification of natural rubber

The structure of NR is very close to that of an alkene. Therefore its chemical reactivity is influenced by the presence of carbon-carbon double bonds. However, being a long chain molecule, intramolecular reactions involving more than one double bond in the same chain is possible. Cis 1,4 polyisoprene has a carbon atom at the double bond which is more reactive to both free radicals and carbonium ions than 1,4 polybutadiene. The typical addition reactions associated with the double bond suggest that the ultimate hydrogenated, halogenated, hydrohalogenated and isomerised diene polymers would have the same structure. The reactions of diene rubbers which show anti Markonikoff addition, enhanced activity in the presence of peroxides and ultraviolet light, and inhibition by oxygen and chemicals such as hydroquinone, usually indicate that a free radical mechanism is operative. Chemically modified NR would increase the areas of application and well expanding opportunities for novel polymers such as ENR, chlorinated natural rubber, and hydrogenated natural rubber as well as liquid natural rubber (Brosse et al., 1981).

2.2.1   Grafting

NR is less resistance to ozone, oxidation, weathering and a wide range of solvents due to unsaturated nature of NR chains and its non-polarity. Therefore, to extend the uses various methods developed in and one of it if grafting the second polymer onto the NR backbone. (Kumar and Kothandaraman, 2008). It was reported that chemical grafting of styrene and methyl methacrylate onto TLNR of Mn 10000-20000 g mol-1 by radical polymerization (using peroxy or diazo compounds as initiator) gives 43% graft polystyrene and 49% graft poly(methy1 methacrylate), respectively (Brosse et al., 1981).

2.2.2   Hydrogenation

Hydrogenation is one of the useful methods for the reduction of unsaturated in diene polymers. It can be achieved with elemental hydrogen in the presence of a transition metal catalyst (Tangthongkul et al., 2005) or by a noncatalytic method (Samran et al., 2005). Hydrogenation reaction is as shown in Figure 2.1
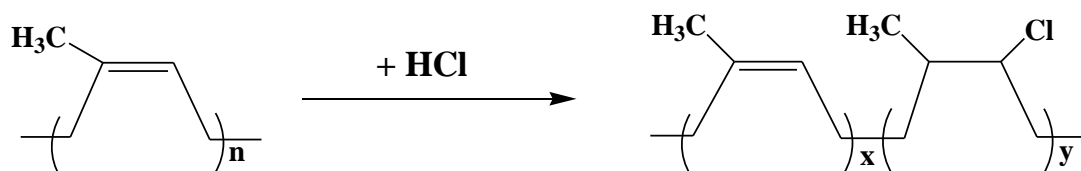
Figure 2.1: Hydrogenation of natural rubber

2.2.3 Hydrohalogenation

Hydrohalogenation NR (Figure 2.2.) can be modified with hydrogen chloride, bromide, iodide or fluoride to give rubber hydrochloride, hydrobromide, hydroiodide or hydrofluoride respectively. Hydrogen chloride addition is the cheapest and the most feasible while the hydrobromide product is unstable. Hydrogen iodide addition has received only limited attention and hydrogen fluoride is toxic. The main aim of the modification is to reduce chemical activity of rubber by addition to the double bonds as in the case of halogenation. The structure of rubber hydrochloride has been established by Bunn and Garner, 1942 who confirmed that the addition of hydrogen chloride to polyisoprene obeys Markonikoffs rule with the chlorine atom attaching itself to the carbon possessing least number of hydrogen atoms.
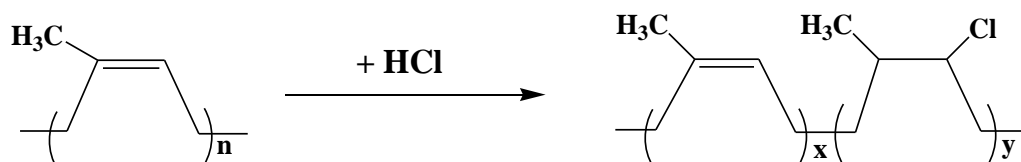
Figure 2.2: Hydrohalogenation of natural rubber

2.2.4 Chlorination

NR can be chlorinated to give chlorinated NR containing 65%-68% chlorine (Pande et al., 1956). The reaction proceeds as shown in Figure 2.3. The product obtained can be used as an anti-corrosion adhesive and its characteristics are comparable to those of the adhesives which are available commercially. Chlorinated rubber was one of the first modified forms that have found some real commercial application. During chlorination, substitution and cyclization reactions also occur

whether the modification takes place in solution, in latex or in solid rubber. In the first stage it was shown that one molecule of hydrochloric acid was liberated for each molecule of chlorine absorbed, and there was a considerable drop in the unsaturation of the rubber. Since a simple substitution reaction should not reduce unsaturation, this suggests that at least one rearrangement process is occurring such as cyc1ization.
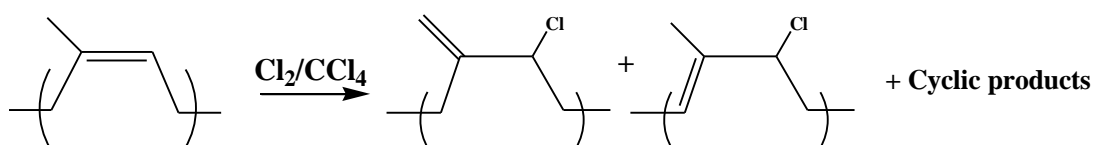
Figure 2.3: Chlorination of natural rubber

2.2.5 Epoxidation

In this process, backbone double bonds are converted into oxiranes (epoxides) using an organic peracid (Figure 2.4). NR can be epoxidized in situ in the latex form, using organic peracids derived from formic or acetic acids, in two-step reactions. In the first step, peracid is formed by reaction between the acid and hydrogen peroxide slow and endothermic reaction. In the second step the epoxidation is fast and exothermic where the peracid is reacted with NR to give ENR Gelling, 1991. Epoxidation has been shown by ^{13}C NMR to be random with one, two and three adjacent epoxide groups present at levels consistent with those predicted.

Gelling IR had also demonstrated that beside the main epoxide structure of the reaction in latex medium of NR with peracetic acid, secondary products were also occurred depending on the level of epoxidation. At low epoxide level, the majority of epoxide groups were isolated, probable side reactions expected can only

be hydrolysed derivatives such as vic-diol, hydroxyl carboxylate and ether linkage as shown earlier. When the modification level was increased, hence increasing of number of adjacent epoxide groups will bring about the formation of five-membered cyclic ether or hydrofuran formation.

$$HCOOH + H_2O_2 \rightleftharpoons HCOOOH + H_2O$$
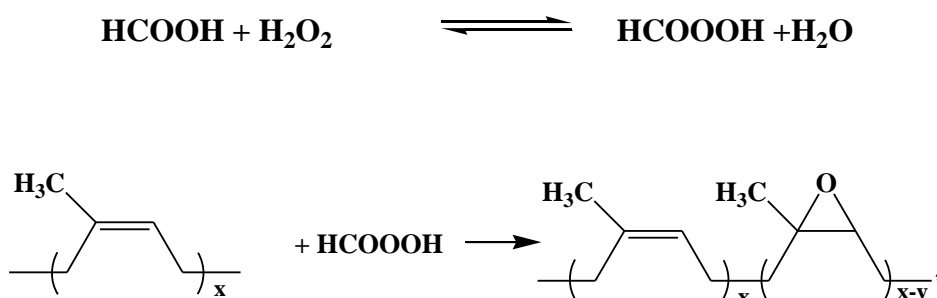
Figure 2.4: Epoxidation of natural rubber

2.2.6 Depolymerization of epoxidized natural rubber

Depolymerization of ENR is based on a reaction in which a chemical with reactive polar groups cleavage the active linkage in the polymer backbone. Depolymerization can reduce chain length of polymer and ENR that is subjected to depolymerization is called depolymerized epoxidized natural rubber (LENR) or "liquid epoxidized natural rubber". Due to strong adhesive properties and excellent crosslinking reactivity, LENR has been used widely as a raw material for adhesives, pressure-sensitive adhesives, sealing materials, caulking compounds and the like. It is now attracting attention in various industrial fields. As compared with solid rubber, liquid rubber is advantageous for the production of various products because it can be easily processed and requires less energy (Tangpakdee et al., 1998).

2.2.7   Reaction of Epoxidized Natural Rubber

Reactions of vinyl and epoxy groups in the polymer chain ENR50 by electrophilic and nucleophilic reagents have been identified long ago.   Although epoxides are readily reactive species, the ring opening reactions are greatly accelerated under acidic conditions. Under acidic condition the general substituted epoxides, when treated with acid yield to general ring opened species with the nucleophile attached to the more highly substituted carbon atom.

Ring opening reaction of epoxide groups in ENR chains catalysed by acids has been studied and reported previously. An observation on the reaction was observed that ring opening takes place during the formation of ENR with methanoic acid in situ. Based on this study it was found that the epoxy ring of ENR that is formed can be opened by excessive methanoic acid. Amu et al., 1986 reported that NR reacted with peroxide acid at elevated temperatures to form ENR50, ENR25, ENR75 and ENR100 by ring opening process.

Since epoxy group in ENR can still experience ring opening by methanoic acid, therefore further research on the phenomenon of catalysed epoxy ring opening by acid has also been done. That includes Loo, 1985 using two carboxylic acid functional groups and Gan and Burfield, 1989 using benzoic acid with one functional group. Carboxylic acid and benzoic acid have reacted as a nucleophilic reagent on ENR backbone. It is believed that the efficiency of chemical modification is dependent on the type of acid used, temperature and reaction time. Product obtained from this reaction was found to have higher Tg value than ENR50 itself. One of the proposed reactions is as shown in figure 2.5.
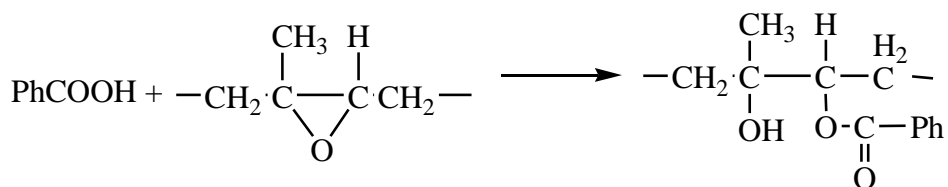
Figure 2.5: Reaction of ENR50 with Benzoic acid

In the early 1970s the discovery of new methods of epoxy ring opening was performed using functional groups such as amino, hydroxyl amine and aminothiol especially in aqueous media. Starting from there, further research on the reactivity of epoxy groups was done by reacting NR latex with aminothiol. An aminothiol reagent is known to be active and take very little time to make up the reaction with epoxide groups (Gelling, 1988).

In 1984, Jayawardena, et al., reported on successfulness of the reaction between ENR50 and amine. They managed to react ENR50 and 4-anilinoanilina in the presence of phenol. The mechanism is as shown in figure 2.7. Result of the reaction, Jayawardena and his colleagues believe that phenol has acted as a catalyst for protonating the epoxy ring. Electron density will then be directed to the oxygen which has become partially positive. Next amines group easily attack towards the least substituted carbon on the epoxy ring. In fact this is supported by Hashim and Kohjiya, 1994. They suggest that phenols play an important role in the formation of an intermediate structure as shown in figure 2.6. Based on the studies that have been done, phenol was found to have acted on ENR50 by protonating the epoxy rings. Nucleophilic reagents will be any easier to attack the epoxy rings which have been protonated and form a bonding through ring opening of the epoxide.
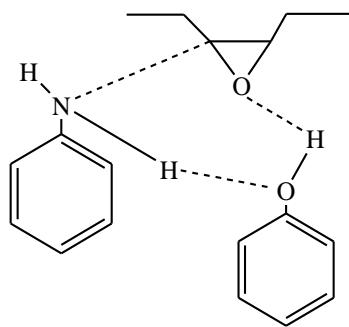
Figure 2.6: Formation of an intermediate structure
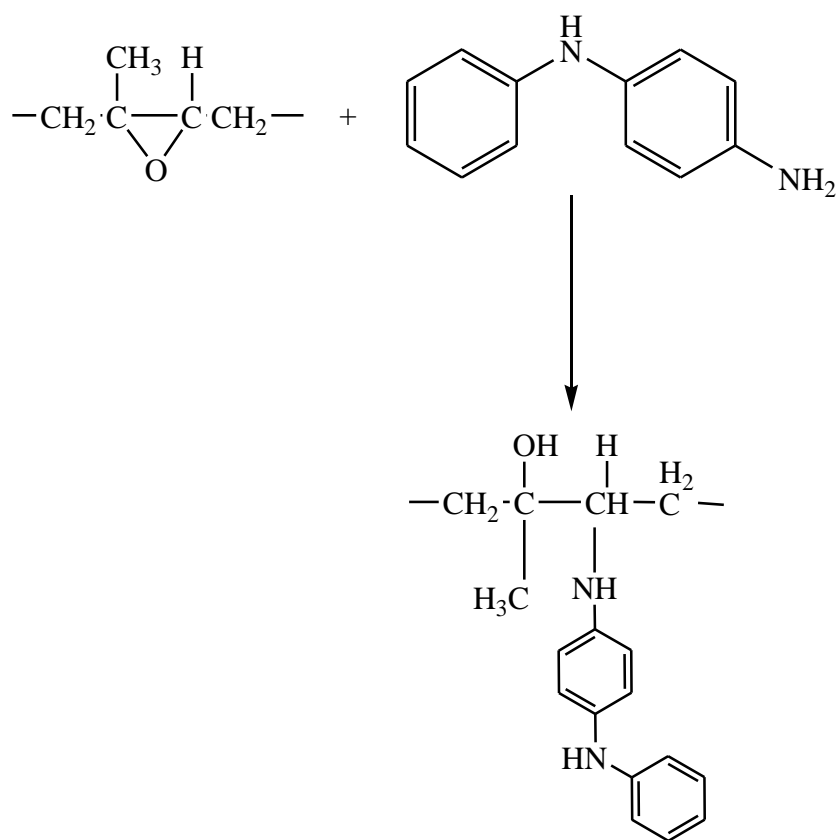
Figure 2.7: Reaction between ENR50 and amine.

2.3 Chitosan

Nature has chosen two different but related polysaccharides to provide structure and integrity to plants and animals like crustaceans and insects. Plants have cellulose in their cell walls while insects and crustaceans have chitin in their shells.

Cellulose molecules are large chains of glucose units while chitin molecules are large chains of N-acetyl glucosamine units. Cellulose and chitin are two of the most abundant biopolymers on earth. Chitin is a highly insoluble material resembling cellulose in its solubility and low chemical reactivity. It may be regarded as cellulose with hydroxyl at position *C-2* replaced by acetamido groups. The principle derivative of chitin is chitosan (Muzarelli, 1977). Chitosan is the *N*-deacetylated derivative of chitin, although this *N*-deacetylation is most never complete. A sharp nomenclature with respect to the degree of *N*-deacetylation has not been defined between chitin and chitosan. It is formed through N-deacetylation of the chitin molecule. The structure of chitin is shown in figure 2.8.
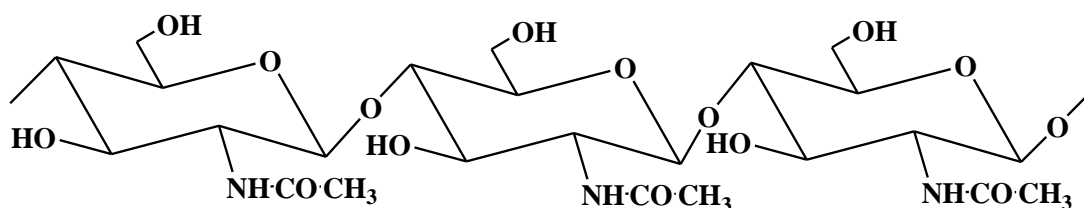
Figure 2.8: Structure of chitin

Chitin is a component of a complex network with proteins in which the calcium carbonates deposites to form the hard shell in crustacean. The processing of crustacean shells mainly involves removal of proteins and dissolution of calcium carbonate which is present in crab shells in high concentrations (Ravi Kumar, 2000). The resulting chitin is deacetylated in 40 % sodium hydroxide at 120°C for 1-3 hours (Figure 2.9).
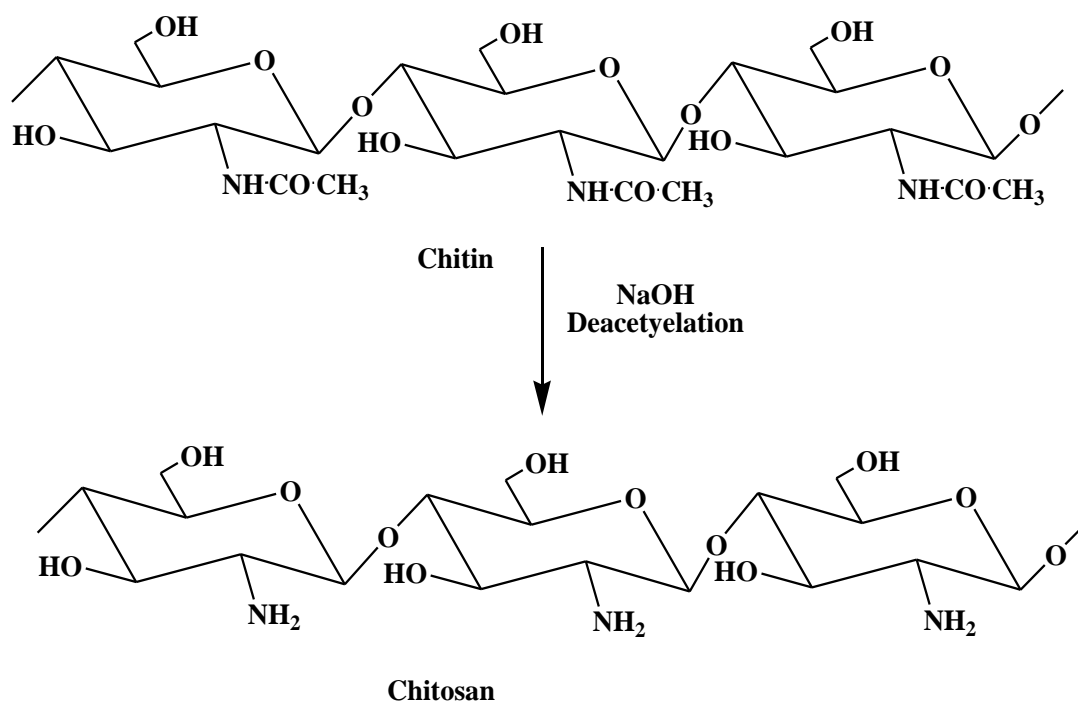
Figure 2.9: Deacetyelation of chitin to obtain chitosan

Chitosan is characterized either by the degree of acetylation (DA), which corresponds to N-acetylamino or the degree of deacetylation (DDA DDA = 100-DA), the D-glucosamine groups. The degree of acetylation affects the physico-chemical properties (molecular weight, viscosity, solubility, etc.). Chitosan is highly hydrophobic in nature and is insoluble in common organic solvents such as well. Chitosan the product of deacetylated chitin is soluble in dilute acids such as acetic acid, formic acid, etc. As most of the present-day polymers are synthetic materials, their biocompatibility and biodegradability are much more limited than those of natural polymers such as cellulose, chitin, chitosan and their derivatives. However, these naturally abundant materials also exhibit a limitation in their reactivity and process ability (Illum 1998; Mass, 1998). In this respect, chitin and chitosan are yield recommended as suitable functional materials, because these natural polymers have

excellent properties such as biocompatibility, biodegradability, non-toxicity, chelating properties, etc. Chitosan have the potential to reduce and to solve some environment pollution problems for creating greener environment and chitosan is renewable polymers. Chitosan carries a large number of amine groups on the chain and therefore can form multiple complexes. Chitosan can form complexes with dyes and heavy metals at higher pH (more than 4). The presence of the free electron pair of the amine groups of is assumed to be the origin of the dative bonds, an idea supported by the observation of a much lower binding chitin. The great potential for application of chitin and chitosan is reflected by the coexistence of approximately 3500 patents or patent applications, in addition to a much higher number of scientific articles which have appeared in the literature during the past decade. Many of the claims suggest uses for chitin and chitosan where these biopolymers actually replace existing synthetic or natural polymers, irrespective of economic aspects.

Due to the nature and properties of chitin and chitosan they have various potential applications in many fields (Jha et al., 1988) as listed in table 2.1.

Table 2.1: Potential applications for chitin, chitosan and their derivatives

Application	Specific use
Water Treatment	Coagulating agents for polluted water, removal of metal ions
Agriculture	Plant elicitor, antimicrobial agents, plant seed coating
Textile, paper industry	Fibers for textile and woven fabrics, paper and film
Biotechnology	Chromatography, packing, enzyme immobilizing material
Food/health supplements	Natural thickeners, food additives, Filtration and clarification, Hypocholesteromic agents (slimming agents)
Cosmetics	Ingredients for hair and skin care
Biomedical	Wound dressings, absorbable sutures, anticoagulant or antithrombogenic materials, homeostatic agents, drug delivery, gene delivery

2.4 Polymer Blend

Art of blending two or more polymers in order to produce an end product that has a combination of properties has achieved considerable industrial importance. The final characteristics of the multi-phase polymeric system are dependent on the individual components such as nature, composition, size and structure of the domains of. Components of the polymer mixture are generally chosen based on various

characteristics such as price, processability, mechanical properties, chemical resistance, weather resistance, thermal resistance, etc (Keskkula, 1970 and Bruins, 1970). Thus the blend can provide a series of properties that cannot be obtained by using the corresponding homopolyrners. Simply varying the composition of the components, various materials with unique properties can be obtained. The components of polymer blend adhere together by van der Waals forces. Dipole interactions or hydrogen bonding

2.4.1 Method of Blending

Basically there are two types of polymer blends: homogeneous and heterogeneous. Homogeneous blends can be obtained by blending polymers with different molecular weight or by blending certain miscible polymers. Where else, heterogeneous blends have two different types of dispersion states. The first type is the dispersed two-phase flow, in which one component exists as the distinct phase dispersing in the other component that forms the continuous phase. There are different techniques for the blending of polymers such as solution blending, melt blending, latex blending, formation of partial block or graft copolymerisation and synthesis of interpenetrating networks (IPN s).

2.4.2`Solution Blending

Solution blending involves the mixing of two polymers in a common solvent. The solid polymer is obtained by evaporating the solvent. Even though it allows easy

and rapid mixing of the components, the evaporation of the solvent leads to phase separation and poorly controlled morphology of the product.

2.4.3   Melt Blending

Melt blending of two polymers are carried out in the liquefied state and it does not involve any solvent or water removal but it requires high energy for mixing. One of the most widely used mixing devices are the Banbury and HAKEE mixer in which the mixing is done by two counter rotating rotors. The high viscosity of the polymer melts also enhances the possibility of degradation.

2.4.4   Latex Blending

Latex blending is blending of two polymers in the latex stage. The solid blend is obtained by the vaporization of water. Better dispersion is possible with latex blending and the contamination by solvents is prevented. There are some advantages of blending of the two polymers in the latex stage. A latex blend is easily obtained just by mixing two lattices together. There are some limitations whereby the components should be free from impurities and should be miscible.

2.4.5   Mechanochemical Blending

Under certain conditions, the mechanical working of polymers leads to interpolymerisation which results in the formation of block or graft copolymer. The

property-composition relationships of these blends differ from those of simple mill mixtures.

2.5   Natural Rubber Composites

Rubber is versatile and adaptable material that has been successfully used as matrix for the preparation of composite. The rubber is defined as a material that is capable of recovering from large deformations quickly and elastic force. It can be modified to a state in which it is essentially insoluble but swell able in solvents such as benzene, toluene, methyl ethyl ketone rubber, etc., but only to the following properties. Elastic deformation is much higher than that of metal. Therefore it can run at high strains. It stretched rapidly even under small load to about 1000% elongation.

The composites are constructed of two or more materials, commonly known as constituents, and having characteristics derived from the individual constituents. The constituent which is continuous and which is often, but not always, present in the largest amount in the composite matrix is called. The second component is referred to as the reinforcing phase or reinforcement or filler as reinforcing or improving the properties of the matrix

In order to prepare composites suitable filler need to be chosen. One of the main objective introducing fillers in polymeric composites was cost reduction. Most of this filler merely take up the space in the polymer matrices and further modifying the properties of the composites produced. The fillers that improvise the properties of the polymeric material is known as reinforcing filler. A significant characteristic of fiber-reinforced composites is that their properties often can be tailored greatly by

controlling the chosen filler, polymer matrices and the processing. The most important reinforcements used in constructing composites are particles, fibers, flakes, and laminas. Figure 2.10 shows the different potential forms of composite materials (Joen et al., 2005). The properties of the composites depend on the manner in which the components are put together. The resulting composites can have the combined characteristics of the constituents or properties substantially different from the individual constituents.

Good dispersion of short fibers in the rubber compounds is a prerequisite for high performance composites. The natural cellulosic fibers tend to agglomerate during mixing due to hydrogen bonding. Therefore it is sometimes necessary for pretreatment of fibers, to reduce the fiber-fiber interactions. A natural fiber treated with either carbon black or compositions containing latex was found to have a good dispersion in the rubber matrix (Dunnom et al., 1973). Fiber length also has a small effect to provide a better dispersion.

Particulate composites   **Flake composites**
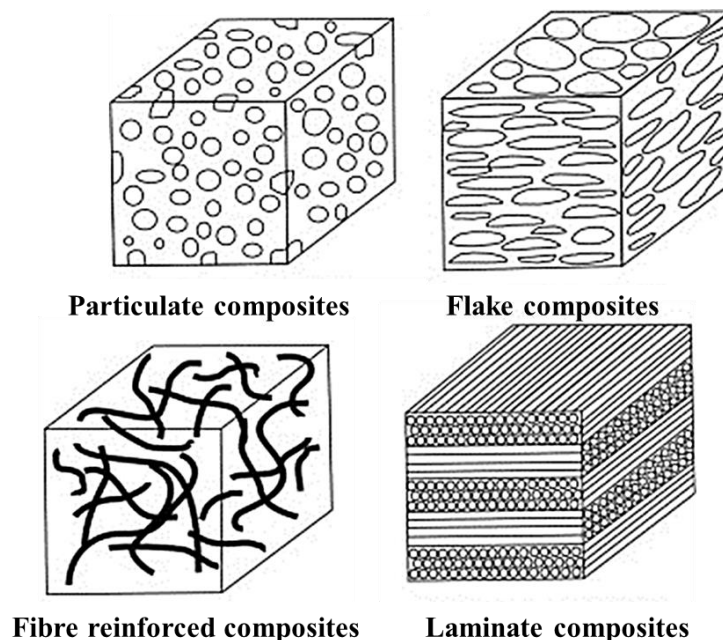
Fibre reinforced composites   **Laminate composites**

Figure 2.10: Illustration of different types of composites