PREPARATION, CHARACTERIZATION AND APPLICATIONS OF BIOCOMPOSITES CONSIST OF CHITOSAN DISPERSED IN EPOXIDIZED NATURAL RUBBER

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PREPARATION, CHARACTERIZATION AND APPLICATIONS OF BIOCOMPOSITES CONSIST OF CHITOSAN DISPERSED IN EPOXIDIZED NATURAL RUBBER

by

LUQMAN IDREES MAHMOOD

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SPECIAL DEDICATION

This thesis is especially dedicated to:

My parents May Allah forgive them

My wife, my brothers, my sister, my kids who have filled my life with joy and happiness

My Supervisor

To whom I am deeply grateful.

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In the Name of **Allah**, Most Gracious, Most Merciful Praise is due to Allah whose worth cannot be described by speakers. First I thank **Allah** for His mercy and blessing on me.

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LIST OF ABBREVIATIONS

CTS	Chitosan
CTS_{Ac}	Chitosan dissolved in acetic acid solution and dried
CTS_{Al}	Chitosan dissolved in $AlCl_{3.}6H_2O$ solution and dried
ENR	Epoxidized natural rubber
ENR25	25 mole percent epoxidized natural rubber
ENR50	50 mole percent high molecular weight of epoxidized natural rubber
LENR50	50 mole percent low molecular weight of epoxidized natural rubber
CTS-ENR	Biocomposites comprising CTS and ENR50
CTS-LENR	Biocomposites comprising CTS and LENR50
$\underline{z}phrCTS_{Ac}$-d-ENR	Biocomposites comprising $\underline{z}$ of CTS_{Ac} dispersed in 100 part of ENR + curatives
$\underline{z}phrCTS_{Al}$-d-ENR	Biocomposites comprising $\underline{z}$ of CTS_{Al} dispersed in 100 part of ENR + curatives
($\underline{z}phrCTS_{Ac}$+1N)-d-ENR	Biocomposites comprising $\underline{z}$ of CTS_{Ac}+1-Naphthol dispersed in 100 part of ENR + curatives
($\underline{z}phrCTS_{Ac}$+2N)-d-ENR	Biocomposites comprising $\underline{z}$ of CTS_{Ac}+2-Naphthol dispersed in 100 part of ENR + curatives
VOCs	Volatile organic compounds
POCs	polar organic compounds
GACs	Granular Activated Carbon
DSC	Differential Scanning Calorimetry
DTG	Derivative thermogravimetry
FT-IR	Fourier Transforms Infrared
FT-NMR	Fourier Transforms Nuclear Magnetic Resonance
NR	Natural rubber
UV-Vis spectrometer	Ultra Violet-Visible spectrometer

SEM	Scanning Electron Microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TMS	Tetramethylsilane
EOS	Emulsified organic solvents

PENYEDIAAN, PENCIRIAN DAN APLIKASI BIOKOMPOSIT TERDIRI DARIPADA KITOSAN TERSEBAR DALAM GETAH ASLI TEREPOKSIDA

ABSTRAK

Sifat biodegradasi kitosan (CTS) adalah secara relatifnya amat lebih tinggi berbanding dengan sifat biodegradasi getah asli terepoksida (ENR). Biokomposit yang mengandungi CTS dan ENR berkemungkinan mempunyai sifat biodegradasi yang diingini dan sesuai untuk pelepasan sebatian-sebatian tertentu secara terkawal. Memandangkan ini, kitosan berasid (CTS_{Ac}) disediakan dengan menggunakan larutan 2% asid asetik dan seterusnya muatan CTS_{Ac} yang berbeza disebar dalam matrik ENR50 dan ENR25 bagi menghasilkan biokomposit zphrCTS_{Ac}-d-ENR50 dan zCTS_{Ac}-d-ENR25, di mana z adalah muatan CTS_{Ac} seperti 1.5, 2.5, 3.5, 5, 10, 15, 20 dan 40 phr. Bahan polimer permulaan dan biokomposit dicirikan dengan beberapa teknik analitikal seperti spektroskopi FT-NMR, spektroskopi FT-IR, TGA, DSC, SEM dan BET. Keputusan analisis data FT-IR, TGA dan DSC menunjukkan CTS_{Ac} tidak bercantum pada tetapi tersebar luas dalam matrik ENR50 dan ENR25 yang tersambungsilang separa. Pembengkakan biokomposit dalam air, klorofom, toluena dan kerosen dikaji. Pengambilan air didapati meningkat dengan peningkatan muatan CTS_{Ac} manakala pengambilan pelarut organic tersebut meningkat secara mendadak dengan peningkatan muatan CTS_{Ac} sehingga 2.5 phr dan sterusnya menurun dengan penambahan muatan CTS_{Ac}. Pembengkakan biokomposit secara am dalam air dan pelarut organik tersebut yang diperhatikan itu adalah sejajar dengan peningkatan sifat hidrofilik matrik ENR50 dan ENR25 dengan peningkatan muatan CTS_{Ac}. Dapatan yang belum pernah diperhatikan tentang pengambilan pelarut organik tersebut khususnya oleh 2.5phrCTS_{Ac}-d-ENR50 dan 2.5CTS_{Ac}-d-ENR25 adalah disebabkan permukaan dalaman yang luas ekoran daripada ruang-ruang dalaman yang terbentuk akibat pengecutan entiti CTS_{Ac} bersaiz submikro dan keberangkalian nano semasa proses pengeringnan. Gambaran SEM bahagian pertegahan dan nilai BET bagi 1.5phrCTS_{Ac}-d-ENR50, 2.5phrCTS_{Ac}-d-ENR50, 3.5phrCTS_{Ac}-d-ENR50 dan 5.0phrCTS_{Ac}-d-ENR50, masing-masing 0.308, 1.539, 0.909 dan 0.561, menyokong dapatan ini. Biodegradasi 2.5phrCTS_{Ac}-d-ENR50 dalam tanah hitam humus didapati berlaku secara perlahan dan berterusan dalam lingkungan 6 bulan. Bagi kajian pelepasan terkawal, empat biokomposit (2.5phrCTS_{Ac}-d-ENR50, 5.0phrCTS_{Ac}-d-ENR50, 2.5phrCTS_{Ac}-d-ENR25 dan 5.0phrCTS_{Ac}-d-ENR25) dengan muatan 1- atau 2-naftol tertentu disediakan. Amaun 1- atau 2-naftol yang dilepaskan dalam media akues pada 25 ˚C dipantau setiap hari dengan kaedah spektroskopi UV-Vis sehingga 30 hari. Didapati kadar lepasan 1- atau 2-naftol adalah perlahan dan tidak bergantung pada keterlarutan sebatian-sebatian tersebut dalam air. Penggunaan 2.5phrCTS_{Ac}-d-ENR25 dan 2.5phrCTS_{Ac}-d-ENR50 untuk penyingkiran pelarut organik beremulsi dikaji dengan menggunakan turus lapisan-tetap. Sistem pelarut tunggal (*m*-xilena dan klorobenzena) dan sistem pelarut binari (klorobenzena/*m*-xilena dan kloroform/*m*-xilena) digunakan sebagai pencemar terangsang dalam air. Didapati bahawa biokomposit tersebut dapat menyerap (menyingkir) 93.5 – 99.5% EOS daripada sistem pelarut tunggal dan binari walaupun selepas 5 regenarasi (iaitu selepas biokomposit dikeringkan dan digunakan kembali). Model matematik digunakan untuk mengetahui mekanisme jerapan dan kinetik jerapan pelarut oleh biokomposit. Kinetik tertib pseudo-kedua dan mekanisme resapan pseudo-Fickian dipatuhi. Selanjutnya data jerapan permukaan tetap menepati model isoterma Langmuir, Freundlich dan Polyani yang mencadangkan liputan heterogen oleh molekul pelarut pada permukaan luar biokomposit.

PREPARATION, CHARACTERIZATION AND APPLICATION OF BIOCOMPOSITES CONSIST OF CHITOSAN DISPERSED IN EPOXIDIZED NATURAL RUBBER

ABSTRACT

Biodegradability of chitosan (CTS) is relatively very high as compared to that of epoxidized natural rubber (ENR). Biocomposites containing CTS and ENR would likely to biodegrade desirably and are suitable for controlled release of compounds of interest. In view of this, acidified chitosan (CTS_{Ac}) was prepared using 2% acetic acid solution and then different loadings of CTS_{Ac} were dispersed in matrices of ENR50 and ENR25 to produce biocomposites designated as $\underline{z}$phrCTS_{Ac}-d-ENR50 and $\underline{z}CTS_{Ac}$-d-ENR25, respectively, wherein $\underline{z}$ refers to CTS_{Ac} loadings of 1.5, 2.5, 3.5, 5, 10, 15, 20 and 40 phr. The starting polymeric materials and resulting biocomposites were characterized using several analytical techniques such as FT-NMR spectroscopy, FT-IR spectroscopy, TGA, DSC, SEM and BET. Results of the analysis of FT-IR, TGA and DSC data reveal that CTS_{Ac} was not grafted to but dispersed widely in partially crosslinked matrices of ENR50 and ENR25. Swelling behavior of the biocomposites in water, chloroform, toluene and kerosene was investigated. The uptake of water is found to increase with the increased of CTS_{Ac} loading whereas the uptake of the organic solvents increased rapidly with chitosan loading up to 2.5 phr and then decreased with further increased of CTS_{Ac} loading. The observed general swelling behavior of the biocomposites in water and organic solvents is in accordance to the increased in the hydrophilicity of the matrices of ENR25 and ENR50 with the increased in CTS_{Ac} loading. The unprecedented finding pertaining to the rapid increased in uptake of the organic solvents particularly by 2.5phrCTS_{Ac}-d-ENR50 and 2.5CTS_{Ac}-d-ENR25 is attributable to the large internal surface area due to the presence of numerous internal voids formed by the shrinkage of the widely dispersed submicron and possibly nano size entities of CTS_{Ac} during the drying process. Cross-sectional SEM images and BET value for 1.5phrCTS_{Ac}-d-ENR50, 2.5phrCTS_{Ac}-d-ENR50, 3.5phrCTS_{Ac}-d-ENR50 and 5.0phrCTS_{Ac}-d-ENR50 is 0.308, 1.539, 0.909 and 0.561, respectively, support this finding. The biodegradation of 2.5phrCTS_{Ac}-d-ENR50 in black humus soil occurred slowly and continuously within 6 months. For controlled-release study, four different biocomposites (2.5phrCTS_{Ac}-d-ENR50, 5.0phrCTS_{Ac}-d-ENR50, 2.5phrCTS_{Ac}-d-ENR25 and 5.0phrCTS_{Ac}-d-ENR25) loaded with known amount of 1- or 2-naphthol were prepared. The amount of 1- or 2-naphthol released into aqueous media at 25 ˚C was monitored daily by means of UV-Vis spectroscopic technique up to 30 days. It is found that the release rate of 1- and 2-naphthol was gradual and independence of their solubility in water. The use of 2.5CTS_{Ac}-d-ENR25 and 2.5CTS_{Ac}-d-ENR50 for the removal of emulsified organic solvents (EOS) was investigated by means of fixed-bed column. Single solvent system (*m*-xylene and chlorobenzene) and binary solvent systems (chlorobenzene/*m*-xylene and chloroform/*m*-xylene) were used as simulated pollutants in water. It is found that the biocomposites can absorb (remove) 93.5 – 99.5% of the EOS from both single and binary systems even after 5 regenerations (i.e., after drying and reusing of the biocomposites). Mathematical models were used in order to know the kinetics and diffusion mechanism of the solvents absorbed by the biocomposites. Pseudo-second order kinetics and pseudo-Fickian diffusion mechanism were obeyed. Furthermore, the fixed bed adsorption data fits well with Langmuir, Freundlich and Polyani isotherm models suggesting heterogeneous coverage by the solvent molecules at outer surface of the biocomposites.

Chapter 1: INTRODUCTION

1.1 General Introduction

Natural rubber (NR) is a biopolymer of high commercial value obtainable abundantly in latex form from *Hevea brasiliensis* tree and the solid rubber content consisted of almost 99% *cis*-1,4-polyisoprene (Figure 1.1). Due to its excellent elasticity and formability, NR is widely used not only in tire and glove industries and but also in many medical-related fields (Thomas, 2013). The chemical and physical properties of NR can be further improved by hydrogenation (Tangthongkul et al., 2005), chlorination (Pande et al., 1956) and modification by addition of filler or blending with other polymers such as polyethylene (PE) (Pechurai et al., 2008), propylene (PP) (Ahmad et al., 2012; Pechurai et al., 2008) and nitrile rubber (NBR) (Yehia et al., 2012).

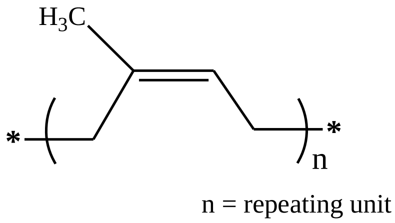
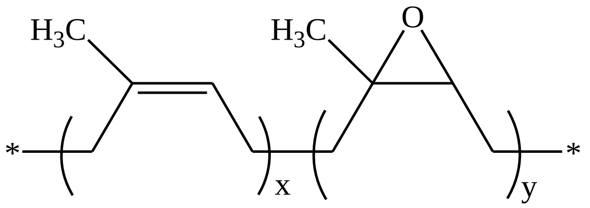


Figure 1.1: A simplified structure of NR (*cis*1,4-polyisoprene)

Epoxidation of NR, that is, the introduction of epoxy group onto the backbone of the polymer chain had been studied quite extensively (Gelling, 1985). Figure 1.2 depicted a simplified structure of epoxidized natural rubber (ENR) (Haris and Raju, 2014). The epoxy group is randomly distributed on the backbone of the polymer chain and the degree of epoxidation can be determined quantitatively by means of Fourier Transformed Nuclear Magnetic Resonance (FT-NMR) spectroscopy (Saito et al., 2007). Compared to NR, ENR has improved adhesion, organic solvent and gas resistance properties (Gelling, 1991). NR with epoxy content of approximately 50% and 25% are known as ENR50 and ENR25, respectively. These polymeric materials are available commercially.



Epoxy content = [y/(x+y)]

Figure 1.2: A simplified structure of an epoxidized natural rubber (ENR)

The chemical and physical properties of ENR change according to the epoxide content (Gelling, 1987; Heping et al., 1999; Ng and Gan, 1981). The reactivity of the epoxide group toward amines (Jayawardena et al., 1984), carboxylic acids (Soutif and Brosse, 1984), phosphoric acid derivatives (Derouet et al., 2001b), and alcohols (Derouet et al., 2001a) is well known. The physiochemical and mechanical properties of ENR-based materials can be improved by blending with cellulose (Ismail et al., 2006), gelatin (Vieira et al., 2007) and chitosan (Nawi et al., 2011; Raju et al., 2013). In this current work, the properties and potential applications of biocomposites consisting of chitosan (CTS) dispersed in the matrices of ENR are explored.

CTS is a linear polysaccharide composed of $\beta(1\rightarrow4)$-linked 2-amino-2-deoxy-p-*D*-glucopyranose and obtained via *N*-deacetylation of chitin (Figure 1.3) (Auzély and Rinaudo, 2003; Dutta et al., 2004; Munro et al., 2009; Muzzarelli, 2013).

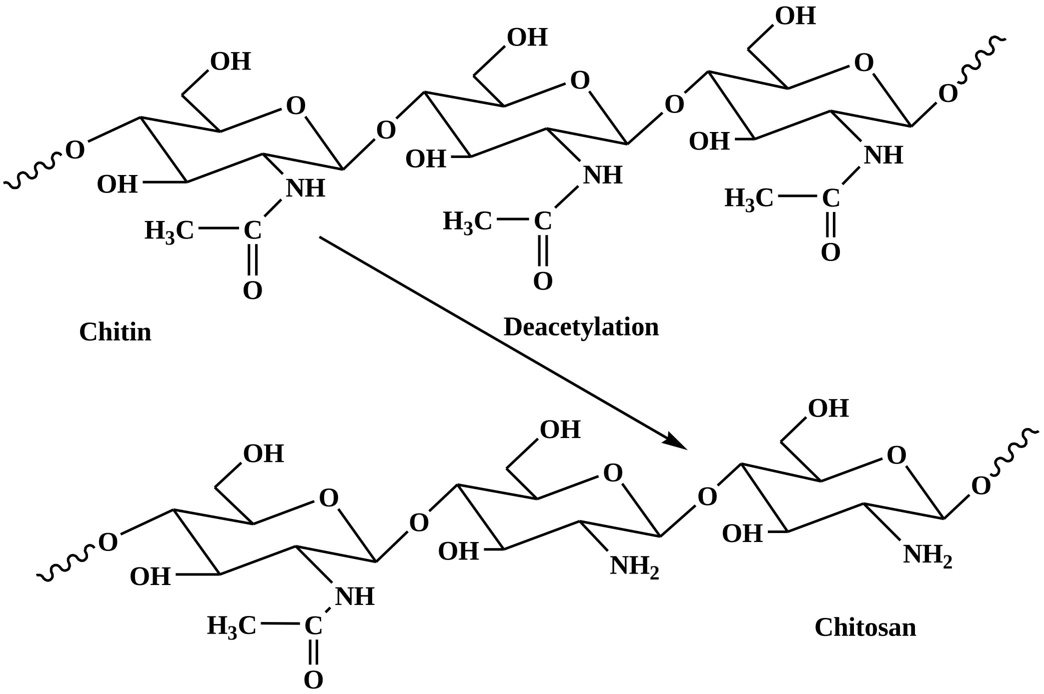


Figure 1.3: Structures of chitin and chitosan

CTS and chitin can be differentiated through the percentage of acetyl groups in their chemical structure. Chitin with less than 50 % of acetyl glucosamine is known as CTS (Khan et al., 2002). It is soluble in acidic media, but its solubility in neutral or basic media is poor (Loykulnant et al., 2012). CTS is known to increase the usage of marine waste due to its non-hazardous and biodegradable properties. CTS has many useful properties, such as non-toxicity, biocompatibility, biodegradability, good mechanical strength, excellent antimicrobial (Werathirachot et al., 2008) and antifungal activities (Muhd et al., 2011). CTS offers several advantages use over inorganic fillers with regard to their less abrasiveness to processing equipment, lower density, environmentally friendly, low cost and is being used widely in biomedical, engineering (Kurita et al., 1988; Wu et al., 2001), pharmaceutical, cosmetic products, water treatment (Park et al., 1983; Ravi, 2000), agricultural and other fields (Sionkowska, 2011). This polysaccharide was reported for its various morphologies such as fibers (Hirano et al., 1999), whiskers (Lertwattanaseri et al., 2009b) and nanoparticles (Pereira et al., 2014), and it has a high unit of crystallinity, that leads to good strength at normal temperature (Febrianto et al., 1999). Actuality the natural polysaccharide such as CTS exhibits poor mechanical properties but has a high biodegradability. So, polymer modification holds excellent mechanical and thermal parameters with CTS may result in the production of a new kind of polymeric components exhibiting not only wanted biodegradability but also wanted a good mechanical and physicochemical properties (Rogovina et al., 2011). A very important area of application is in industrial toxic pollution control and waste water treatment where it can be used as a chelating polymer for removal of metal cations such as mercury, copper, and many other elements (Monier, 2012).The incorporation of two polymers is an easy and effective way to reach a multiphase polymeric materials having a good balance of properties than available with a single polymer (Asaletha et al., 1999; Tanabe et al., 2002), an alternative way for preparation of biodegradable polymers with maintaining their transparency and biodegradability (Oksman et al., 2006). Solution blending is a convenient processing technique where a common solvent is used to dissolve the polymers. One of the advantages of natural fillers, apart from being biodegradable and biocompatible, is that they are naturally abundant, low cost and environment friendly, compared to traditional commercial fillers (Li and Xia, 2004; Zakaria et al., 2013). However, a literature survey exposes that there are a bounded number of reports relating to the incorporation of CTS into ENR via either grafting or entrapment techniques (Haris and Raju, 2014; Ismail et al., 2011; Lertwattanaseri et al., 2009a; Raju et al., 2013; Riyajan and Sukhlaaied, 2013; Shaari et al., 2011).

1.2 Problem Statement

ENR is a hydrophobic polymer and coagulates in acidic medium (Gelling, 1991) whereas CTS is a hydrophilic (biodegradable) polymer, soluble only in acidic aqueous media (Aranaz et al., 2009; Kumar, 2000). This is the most likely reason explaining why there is a very limited number of reports in the literature on homogenous or semi-heterogeneous interaction condition involving CTS and ENR (Ismail et al., 2011; Raju et al., 2013). Hence, there is a need to investigate the interaction of CTS with ENR, and to prepare biocomposites comprising of CTS dispersed in ENR matrices.

Attempts have been made to obtain biodegradable and environmental friendly biocomposites for the control release of pesticides (Tharanathan, 2003a). The increasing use of pesticides poses numerous environmental and health problems (Wilson and Tisdell, 2001), causing soil pollution and contributes severe surface and groundwater contamination (Jamnongkan and Kaewpirom, 2010). It is highly desirable to develop a method in order to prevent migration and leaching of pesticides (Abd El-Mohdy et al., 2011). Therefore, the controlled release formulation of biocomposites can be applied to provide active amount of pesticides over a long period of time (Sjogren, 1990). It also can be applied to minimize leaching and migration of pesticides into soil and water.

Removal of a wide range of trace organic contaminants and chlorinated organic compounds from water remains an important goal because they are causing serious public health and environmental problems. Several technologies such as advanced oxidation processes, air stripping, reverse osmosis, ultrafiltration and adsorption have been used to remove these contaminants (Chen et al., 2010; Chen et al., 1996; Jarvie et al., 2005; Shih et al., 2003). The literature study reveals that there is no cost effective method available to remove these contaminants completely. Hence, this problem motivates the researcher to develop a cost effective method for the removal of the organic contaminants from wastewater.

1.3 Research Objectives

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

1. To prepare and characterize biocomposites comprising of acidified CTS_{Ac} dispersed in partially crosslinked matrices of ENR25 and ENR50.
2. To determine the effect of CTS_{Ac} loading on the swelling properties of the biocomposites in water, chloroform, toluene and kerosene.
3. To evaluate the biodegradability of the biocomposites in soil.
4. To determine the absorption and desorption properties of the biocomposites for 1- and 2-naphthols: As a model study of slow-release system.
5. To determine the efficiency of the biocomposite for the removal of emulsified organic solvents in aqueous media (i) single solvent system (*m*-xylene and chlorobenzene) and (ii) binary solvent system (chloroform/*m*-xylene and chlorobenzene/*m*-xylene) by means of fixed-bed column.

Chapter 2: LITERATURE REVIEW

2.1 Natural rubber

Natural rubber is a hydrocarbon, a main biopolymer, known as poly (1, 4- *cis* - isoprene) and has the chemical structure exhibited in Figure 1.1. Polyisoprene is an elastomer originally resulted from a colloidal milky liquid from the sap of *Hevea brasiliensis* tree, is of commercial importance (Brown and Dunstan, 1914). Hevea is native to Brazil and produces a high molecular weight of ~ 97% poly (*cis*-1, 4-isoprene), roughly 20,000 units of isoprene. NR latex has a great molecular mass in an aqueous media and stabilized with ammonia, the water content can be reduced by concentration, then coagulated and dried (Mohapatra and Nando, 2013).

It was widely used in many fields such as medical fields and industrial goods, tire, hoses, rubberized fabrics; and conveyor belts, engineering products, for resilient load bearing and shock or vibration absorption components. Latex products such as adhesives and gloves have good physical properties. Meanwhile natural rubber can crystallize upon stretching. Nevertheless, the biodegradable and mechanical properties of NR are improved in several applications (Pechurai et al., 2008). The typical compositions of natural rubber latex and dry natural rubber are tabulated in Table 2.1. The Polyisoprene with weak intermolecular forces leading to quickly reversible stress-strain response, Irregularity is caused by cis double bonds in each repeat unit. While the double bonds produce a local rigidity they are geometrically asymmetric. The olefinic double bonds along the backbone of Polyisoprene allow the attachment of pendant groups and/or give chemically reactive locations for crosslinking or grafting (Hamzah et al., 2012).

Table 2.1: Components of fresh natural rubber latex in form of an emulsion (Henderson, 2001; Mosiewicki et al., 2007; Riyajan et al., 2007) and dry NR (Levin, 1996; Parulekar and Mohanty, 2006).

Rubber	**Component**	**Composition (%)**
NR latex	Total solid content	36
	Dry rubber content	33
	Resinous substances	1-2.5
	Proteinaceous substances	1-1.5
	Inorganic salts (mainly K, P and Mg)	0.5
	Ash	<1
	Sugars	1
	Water	60
Dry NR	Rubber content	93-95
	Resinous substances	2
	Proteinaceous substances	2-3
	Inorganic salts	<0.2
	Sugars	<0.2
	Cu and Mg	2-3 ppm
	Water	~0.5

Indeed, Polyisoprene is a sticky and soft solid with low elasticity and low tensile strength due to the weak van der Waals forces of its intermolecular attraction and occasional crosslinking. It hardens in cold weather but softens at room temperature in tropical countries (Burfield and Eng, 1989; Burfield and Tanaka, 1987). NR is soluble in some organic solvents, e.g. toluene, chloroform, acetone, methyl ethyl ketone, n-hexane, tetrahydrofuran, 2-butanone, benzene, etc. (Andrews, 1964; Healey et al., 1996; Jones, 1991; Lin et al., 2004; Suzuki et al., 1985; Toki et al., 2000; Toki et al., 2009). The properties of Polyisoprene deteriorate drastically by ozone, oxygen and sunlight because of its high level of unsaturation double bond, and such a material is of minimal interest in industry (Reis-Nunes et al., 2000). Vulcanization is the main important chemical modification of natural rubber. It is a chemical process where a long chains of polymer molecules are crosslinked, transforms the weak and soft plastic-like material into a strong elastic product with high and reversible deformability owing to strain-induced crystallization, good mechanical properties, low hysteresis, fatigue resistance, and excellent dynamic properties. After vulcanization, natural rubber loses its tackiness, becomes a polymeric material non-sticky and hardness with improved tensile strength, becomes more resistant to light, heat and ageing processes, and insoluble with higher resistance to organic solvents (Riyajan et al., 2012). The properties of pure and vulcanized natural rubber are tabulated in Table 2.2.

Table 2.2: Properties of pure and vulcanized natural rubber (Wood and Martin, 1964)

Properties	**Pure NR**	**Vulcanized NR**
Thermal expansion coefficient at 20˚C(K^{-1})	6.6 x10^{-4}	6.4 x10^{-4}
Isothermal compressibility at atmospheric pressure (bar^{-1})	5.0 x10^{-5}	5.0 x10^{-5}
Density at 20 ˚C (g cm^{-3})	0.9162	0.9093
Thermal conductivity (W m^{-1} K^{-1})	0.13	0.153
Specific heat capacity (J kg^{-1} K^{-1})	1.905 x10^{3}	1.828 x10^{3}
Dielectric constant at 1 KHz	2.37–2.45	2.68
Glass transition temperature (˚C)	-67	-63
Dissipation factor at 1 KHz	0.001–0.003	0.002–0.04
Conductivity (S m^{-1})	2.57 x10^{-15}	2–100 x10^{-15}
Isothermal bulk modulus (Pa)	1.94 x10^{6}	1.95 x10^{6}
Storage modulus (Pa)	4.07 x10^{5}	4.07 x10^{5}
Loss modulus (Pa)	2.88 x10^{4}	6.31 x10^{4}
Ultimate elongation (%)	625	750–850
Tensile strength (M Pa)	0.56	17–25

2.2 Epoxidized Natural Rubber

Epoxidized natural rubber is one of the most important products of chemical modification of natural rubber (Gelling, 1987). A formation reaction of ENR from poly (cis-1, 4-isoprene), employing peroxy formic acid is shown in Figure 2.1. (Gelling, 1985). The epoxidized isoprene and isoprene units act as monomer units, and distributed randomly along the polymer chain (Gelling, 1987). Many degree of 1-90% epoxidation of NR is available commercially. For examples, two kinds of ENR were considered as commercial, the isoprene units in the polymer chain are

25% and 50% epoxidized in ENR25 and ENR50, where the integers designate 25 and 50mole % of epoxide incorporated into the natural rubber chain respectively. Amu et al. (1986), reported that peroxide acid reacted with natural rubber at elevated temperatures to form ENR25 and ENR50 through ring opening method. The widespread interests in the technology and science of ENR in different field of polymer modifications (Noriman et al., 2010), polymer composites (Bakar et al., 2008), polymer blends (Gelling, 1985) and advanced green materials (Han et al., 2004; Lee et al., 2005; Mishra et al., 2007) create it inevitable to understand the detail structure of ENR. Thus ENR also exhibit properties the same as elastomer like increased in oil resistance, which is equivalent to acrylonitrile butadiene rubber (ABR) and reduction in air permeability, which is equivalent to a butyl rubber (BR) (Doshi and Charrier, 1989).

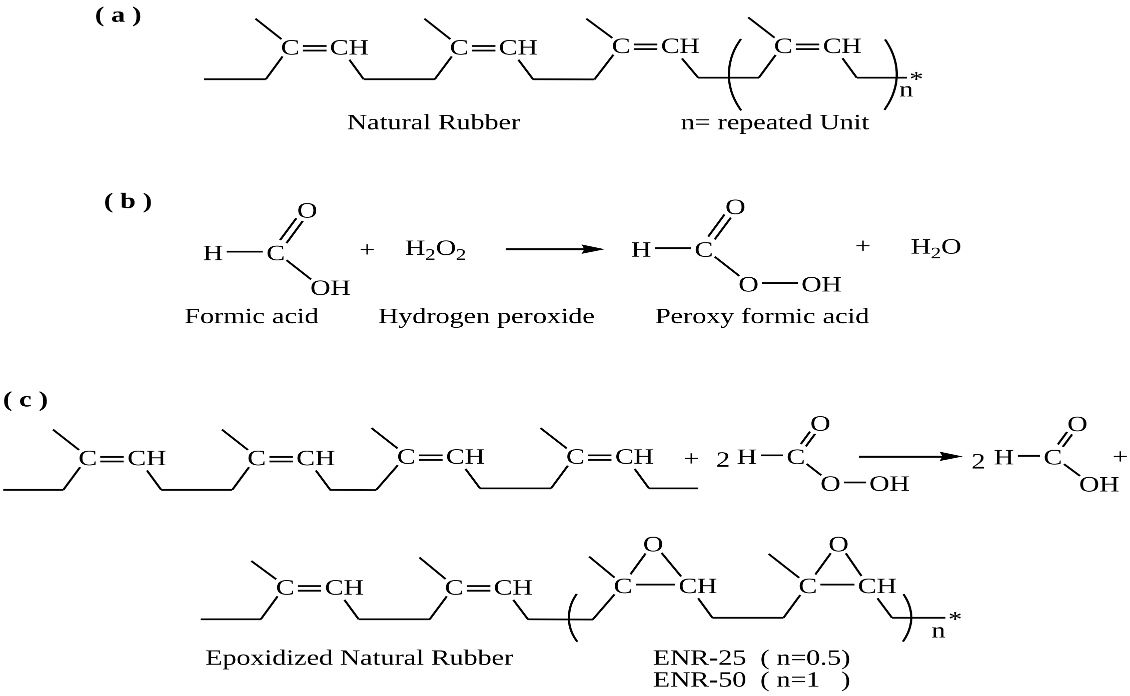


Figure 2.1: (a) Structure of natural rubber, poly (1, 4- *cis*–polyisoprene), (b) formation of peroxy formic acid and (c) the production of ENR (Gelling et al., 1991)

2.3 Utilization of ENR

ENR exhibits both rubber and special elastomer characteristics that can be tailored for various usages. Some of the potential commercial uses of ENR with respect to its special characteristics are shown in Table 2.3. Besides the proposed commercial uses shown, ENR has the potential to be further exploited for its usage as advanced materials such as in blends, additives and fuel cells applications.

Table 2.3: Potential commercial uses of ENR (Teoh, 2006)

Characteristics	**Applications**
Wet grip, low rolling resistance	Tires, non-slip flooring, sports shoe soles
Oil resistance, high strength	Hoses, seals, blow-out preventors, milking inflation, connector and tubing
Glass transition temperature, Tg, variable with degrees of epoxidation to that of room temperature	Coatings and paints
Silica and pigments reinforcements	Cosmetics, color coding
Damping	Anti-vibration mountings and other engineering applications
Adhesion	Adhesives, cover for PVC conveyor belt
Low gas permeability	Bladders, inner tubes, and tire liners

2.4 Chitosan

Nature has chosen two different components 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 can be obtained from various sources such as squid pen chitin (Liu et al., 2010), riftia tubes (Rattanasom et al., 2007), crab shells (Jarvie et al., 2005; Shih et al., 2003), and shrimp shells (Chen et al., 2010; Chen et al., 1996). It is an insoluble material resembling cellulose in its solubility and low chemical reactivity. It may be regarded as cellulose with hydroxyl group at position C-2 replaced by acetamido groups. The principle derivative of chitin is chitosan (Jarvie et al., 2005). Chitosan is deacetylated product of chitin, also classified as a natural polymer because of the presence of a degradable enzyme, chitosanase.

Chitin is a component of a complex network with proteins in which the calcium carbonate deposits to form the hard shell in crustacean. The processing of crustacean shells mainly involves the removal of proteins and dissolution of calcium carbonate which is present in crab shells in high concentrations (Crittenden et al., 1986). The resulting chitin is deacetylated in 40 % sodium hydroxide at 120ºC for 1-3 hr (Figure 1.3a). Chitosan is characterized either by the degree of acetylation (DA), which corresponds to N-acetylamino or the degree of deacetylation (DDA = 100-DA), the D-glucosamine groups (Figure 1.3b). The degree of acetylation affects the physicochemical properties (molecular weight, viscosity, solubility, etc.). Chitosan is product of deacetylated chitin, it is soluble in dilute acids such as acetic acid, formic acid, etc.

Biocompatibility and biodegradability are much more limited than those of natural polymers such as cellulose, chitin, chitosan and their derivatives because most of the present-day polymers are synthetic materials. However, these materials have limitation in their reactivity and process ability (Ko et al., 2001; Ma et al., 1996). Due to this, chitin and chitosan are recommended as suitable functional materials, because these natural polymers have excellent properties such as biocompatibility, biodegradability, non-toxicity, chelating properties and etc.

Chitosan, a renewable polymer has the potential to reduce the pollution in the environment pollution and creating greener environment. 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 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 the existing synthetic or natural polymers, irrespective of the economic aspects. Due to the nature and properties of chitin and chitosan, various potential applications in many fields as listed in Table 2.4.

Table 2.4: Potential applications for chitin, chitosan and their derivatives (Bautista et al., 2003)

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, and gene delivery.

2.5 Polymer composites

2.5.1 Natural Rubber Composites

Rubber is a versatile and adaptable material that has been successfully used as matrix for the preparation of composite. Rubber is defined as a material that is capable to recover from large deformations quickly and has elastic force. It can be modified to a state in which is essentially insoluble but swell able in solvents such as benzene, toluene, methyl ethyl ketone, etc., but only to the following properties. Its 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 100% elongation.

The composites are constructed of two or more materials, commonly known as constituents, having characteristics derived from the individual constituents. The constituent which is continuous, but not always, present in the largest amount in the composite is called matrix. 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 to introduce fillers in polymeric composites was cost reduction, low density and ease of processing. 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. 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 (Derringer et al., 1973). Fiber length also has a small effect to provide a better dispersion.

One of the common reinforcement in ENR is natural fillers. Ismail, and et al., (1997), reported that oil palm wood fiber can be reinforced in ENR(). With the reinforcement there was enhancement observed in few properties such as the cure time, increased tear strength, modulus and hardness but declined in tensile strength and elongation at break. They also proved that particles size does play a role in the reinforcement because the smaller particle size of oil palm wood fiber gives better mechanical properties.

Since most of the natural fillers do not impart good strength in rubber, researchers have improvised their method by adding coupling agents, surface modification of filler and pre-treatment. Chi Liu et al. (2008), reported that poly butyl acrylate modified starch has improved that the properties of NR as reinforcing filler. The modification was done on starch to prevent hydrogen bonding and crystallization of the starch. The properties of the composite were proved to be much superior to unmodified starch paste. Basically the unmodified starch acts as inert filler which decreases the mechanical properties.

Sae-Ou et al. (2002), made a comparison on the reinforcing effect between rice husk ashes and other commercial fillers such as talcum, China clay, calcium carbonate, silica, and carbon black, found that rice husk ash provide inferior mechanical properties. Yet, the mechanical properties of the vulcanizates filled with rice husk ash are comparable to those filled with inert fillers.

Nuraya et al. (2012), investigates the effect of incorporating banana stem powder, surface modified with 2% of sodium hypochlorite solution, as reinforcing filler on the properties of NR latex (NRL) compound and its films. They found that certain mechanical properties of the NR latex deteriorate with banana stem powder loading. However, the tear strength of the composites were higher than the unfilled NR latex. When compared with other commercial filler, such as calcium carbonate and colloidal silica, banana stem powder produced prevulcanised NRL films with comparable mechanical properties.

2.5.2 Chitosan/Natural Rubber Composites

Polymers are the most widely used matrix materials for chitosan-reinforced composites lately. Their main advantages are low cost, easy processabilty, good chemical resistance and low specific gravity. Lots of attention has been paid to chitosan-poly (L-lactide) blends (Droste, 1997; Tharanathan, 2003b), chitosan-g-poly(acrylic acid) (Wilson and Tisdell, 2001), and chitosan and Poly (e-caprolactone), before researcher involved in chitosan rubber composites. Initially work on chitin whiskers as the reinforcing matter in latex was carried by Kalaprasad and Alain, (2003). Unvulcanized and prervulcanized NR latex and colloidal suspension of chitin whiskers were used to prepare chitin whisker reinforced NR nanocomposites. They prepared the solid composites by casting and evaporating methods after they had mixed and stirred the aqueous suspensions of chitin whiskers and rubber. Where else, freeze drying method was used for the unvulcanized systems followed by hot pressing. They indicated that the technical processing plays a major role in the properties of the final composites developed. Nano scale Chitin whiskers form a three-dimensional rigid network in the samples which were evaporated and this was probably overseen as percolation mechanism. Analysis of the cryo-fractured surface of the composite materials showed a better dispersion of the filler using evaporation that hot press method. This was probably as they claimed due to the rigid chitin-chitin network within the host matrix was formed since the whiskers had enough time and flexibility as the evaporation was a slow step process. They also stated that addition of chitin whiskers reduces the degree of swelling in all methods.

Kalaprasad and Alain, (2003) reported again on the chitin whiskers reinforced NR, focusing on the mechanical properties of the composites. Mechanical behavior of chitin whiskers obtained from crab shell reinforced vulcanized and unvulcanized natural rubber nanocomposites showed a linear and nonlinear. Besides, structure there is an improvement in mechanical properties of the filler content, higher than 5% by weight, improvement in thermal stability of the composite material is also observed to 220-230 ℃. All results show that the main aspect that governs the mechanical behavior of chitin whisker nanocomposites reinforced NR is the processing technique. Kalaprasad et al., (2003), reported again on the effect of chemical modification of chitosan whiskers before reinforcing in NR. They concluded that various chemical treatments had improvised the adhesion between the matrix and filler though the mechanical properties decreased after modification. They suggested that this could be due to the partial or total destruction of the three-dimensional network of chitin whiskers. With all this knowledge on chitin researcher had move to study on the chitosan-rubber composite. Solution casting method was used to prepare chitosan NR latex blend. It was observed that the composites showed an improvement in the mechanical properties. Even after aging, the composites exhibited an increase in the tensile strength probably due to the crosslinking in the NR phase. They also revealed that the blend with dicumyl peroxides further improves the mechanical properties. Based on this they concluded that there is a good adhesion between the matrix and filler (Gelling, 1991). They reported again in 2008 that the blending of chitosan with NR had enhanced the thermal properties of chitosan. They discovered that the mass loss for the blends were lower than chitosan by itself. However the proved by DSC that this blend is incompatible as they bund two glass transition value. Johns and Rao (2009), reported on further characterization of NR chitosan blend, the bonding has shown a stronger interfacial interaction between the matrix and filler based on the amount of bound rubber and this is further supported by FTIR spectrum. This blends also indicated that the crystallinity of NR decreases with increase in the amount of chitosan and the water absorption increases with chitosan loading.

Lertwattanaseri and et al, (2009a), prepared bionanocomposite by mixing epoxidized natural rubber latex with nanofibrous chitosan after drying the sheets, followed by blending with crosslinking agents using a Labtech two roll mill at 40ºC and vulcanized by a Vantage compression molding at 150ºC and they expected it be a novel ENR functional material. They claimed that this was a reactive blend as the bionanocomposite was formed through the epoxy group of ENR and amino and hydroxyl group of chitosan. They had proved this with F'I'IR analysis. They also proved that the bionanocomposite had superior properties such as enhancement in the surface roughness and stiffness, tensile strength and copper adsorption.

Ismail and colleagues (2011), reported a slight contradiction to what earlier researchers had proven. They had reported that the increment was found in the maximum torque and tensile modulus with chitosan loading. Where else other properties such as scorch time, cure time, tensile strength and elongation at break declined with chitosan loading for NR, ENR and styrene-butadiene rubber (SBR), chitosan compounds (Correlo et al., 2007). However, they have proved their SEM data that chitosan did not interact well with these rubbers and the rubber-filler interactions are also reduced.

Biodegradable blends of NR latex/chitosan have been developed by solution casting followed by compression (Weber and DiGiano, 1996). X-ray diffraction study showed a decrease in crystallinity in NR with addition of chitosan. 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 2.2.

Raju et al. (2013), reported the preparation, mechanical properties, water uptake and toluene absorbency of biocomposites comprising different loadings of chitosan (CTS) (5, 10, 15, 20 and 30 p.h.r.) into matrixes of ENR50 and LENR50 (high and low molecular weight epoxidised natural rubbers with epoxy content of about 50%, respectively). It was found that the increase in CTS loading increased cure torque, tensile strength and modulus at 100% but there was a decline in cure time and elongation at break for CTS-ENR50 biocomposites. SEM micrographs of the tensile-fractured materials showed that at 15 phr loading, for example, CTS underwent a breakout, indicating good interactions in the CTS-ENR50 biocomposites. Results of the water uptake study revealed that increase in CTS loading led to an increase in water uptake of CTS-LENR50 biocomposites. This is considerably higher at every loading compared to that of CTS-ENR50 biocomposites. Results of the toluene absorbency study revealed that LENR50 is a superior sorbent for toluene compared to ENR50. However, increase in CTS loading led to a decrease in toluene absorbency of both CTS-LENR50 and CTS-ENR50 biocomposites (Raju et al., 2013).

Riyajan, and Sukhlaaied (2013), studied the effect of chitosan on gel content of epoxized natural rubber grafted with chitosan in latex form using potassium persulphate as an initiator. The grafting yield between ENR and chitosan can be controlled by appropriate selection of grafting condition. The optimum condition of modification with chitosan was 3 h of reaction time at 65 °C, ratio of ENR /chitosan at 9:1. The toluene resistances of the modified ENR decreased with increasing chitosan due to degradation of ENR molecule during chemical modification. The ether linkage between ENR and chitosan was observed at 1154 and 1089 cm^{-1} by ATR-FTIR and 3.60 ppm by ^{1}H-NMR. The morphology of ENR-g-chitosan particle exhibited the core-shell structure confirmed by TEM.

Haris, and Raju (2014), prepared a biopolymers comprising of chitosan-grafted-ENR via $AlCl_3 \cdot 6H_2O$ as acid-induced reaction of ENR50 with chitosan in dual-solvent consisting of 1, 4-dioxane and water. NMR spectral analysis of biocomposites revealed that its epoxy content is 22.36%, which is considerably lower than 44.93%, as determined for ENR50-control. This means that the grafting of CTS onto the backbone of ENR had occurred. The 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 FTIR spectrum of CTS-g-ENR-P1. Further evidence that CTS had been successfully grafted onto the backbone of ENR.

2.6 Diffusion and Transport of solvents through Natural Rubber composites

The transport of liquids, vapors and gases through rubber is an important property that must be considered for utilizing the rubber material in various applications, such as in biomedical products, packaging, tire industry etc. The diffusion of such penetrants through the rubber materials are critical factor in the existing shelf life of products made of these rubber materials. In packaging, materials that protect liquids, vapors and gases passing through them are required. This is one of the criteria for polymer composite and nano composite system, which have been developed as an increasing barrier in order to minimize the penetration of liquids, vapors and gases. Therefore, the basic knowledge of theories of diffusion and transport behaviors could be stated to determine the suitable property and understand their mechanism. Liquid can pass through materials by different processes, depending on the nature or physical property of the materials. In the case of porous materials, such as rock or wood, the liquid flow through the holes within the materials. On the other hand, liquids pass through non-porous materials such as rubber via permeation processes of absorption and diffusion. The quantity of liquids that can pass through the materials will be determined as the constant value at steady or equilibrium state. The diffusion of molecules of liquids into materials depends on the physicochemical properties of both permeants and the permeable materials (Ahmad et al., 2012; Móczó and Pukánszky, 2008; Pechurai et al., 2008; Yehia et al., 2012). Free volume or holes that exist in the rubbery matrix are one of the critical factors influencing diffusion process of liquid molecules to migrate from hole to hole. The transport of liquid through non-porous polymer under applied driving force was described on variety models of solution–diffusion that contain a large number of diffusion parameters and equilibrium constant (Hull and Clyne, 1996). The suitable model depends on experimental data that fit the most of model's parameters, which is highly system specific to the permeating species. However, the general parameters which are important to describe the permeation process through permeable material, the so-called solubility **S** and diffusivity **D** are displayed in equation Eq. 2-1: (Wood and Bekkedahl, 1967; Peukert et al., 2003)

$$P = D \times S \text{ ……………. (Eq. 2-1)}$$

where **P** is the permeation coefficient, a direct measure of the permeation process; **D** is the diffusion coefficient of a gas or liquid molecule inside the polymer network; **S** is the soluble value of the total amount of gas or liquid trapped in the rubbery matrix. Therefore, the diffusion process is a kinetic parameter depending on the free volume within the permeable material, segmental mobility of polymer chains, polymer structure, the size and shape of penetrant molecule and crystallinity

(Niu and Conway, 2003). The *diff*usion coefficient (**D)** is described by the equation Eq. 2-2: (Jarvie et al., 2005)

$$\boldsymbol{D} = \boldsymbol{\pi}\left(\frac{\boldsymbol{h\theta}}{4\ \boldsymbol{Q}_{\infty}}\right)^{2} \text{ .... (Eq. 2-2)}$$

where h is rubber sample thickness, **θ** is the slope of the initial linear portion of the sorption curve $\mathbf{Q_t}$ vs. $\mathbf{t^{1/2}}$, $\mathbf{Q_t}$ and $\mathbf{Q}_{\infty}$ are the number of mole of liquid or gas sorbed by gram of rubber sample at time t and at equilibrium, respectively. The thermodynamic solubility parameter (**S)** is estimated by the number of grams of liquid or gas sorbed per gram of rubber compound, which is given as Eq. 2-3: (Jarvie et al., 2005)

$$\mathrm{S} = \frac{\text{weight of solvent uptake of equilibrium}}{\text{initial weight of rubber sample}} \text{ .... (Eq. 2-3)}$$

Several diffusion models have been used to propose transport mechanism of liquid molecules through the polymer. A model described by Fick’s laws is frequently used and known as Fickian diffusion. The diffusion behaviour in the rubbery polymers, represented by permeation, migration and sorption processes, can be described by the equation of Fick’s first law Eq. 2-4:(Shih et al., 2003)

$$\mathrm{J} = -D\frac{\partial \varnothing}{\partial X} \text{ .... (Eq. 2-4)}$$

where **J** is the flux density of the solute molecules through the rubbery matrix, **D** is the liquid diffusion coefficient, $\boldsymbol{\partial \varnothing / \partial X}$ is the concentration gradient applied across the rubbery matrix and Ø is the concentration of the dissolved liquid given as the amount of dissolved molecules per cubic centimeter of rubbery matrix.

In non-steady state diffusion, the concentration of dissolved molecules changes with respect to time in one direction within diffusion volume. This phenomenon is described by Fick’s second law of diffusion Eq. 2-5 : (Shih et al., 2003)

$$\frac{\partial Ø}{\partial t} = D\frac{\partial^2 Ø}{\partial x^2} \text{ .... (Eq. 2-5)}$$

Although Fickian diffusion has been used to describe the diffusion mechanism of liquid through the rubbery material because of its simplicity and mathematical tractability, most of the rubber–solvent systems do not fit such a simplified explanation. Then, non-Fickian diffusion was developed. The case of non-Fickian diffusion was investigated using the Eq. 2-6 : (Chen et al., 1996; Chen et al., 2010)

$$log\,\frac{Q_t}{Q_\infty} = \log k + n\log t \text{ .... (Eq. 2-6)}$$

where **Q** represents mass uptake, which at equilibrium swelling or sorption $\mathbf{Q_t}$ becomes $\mathbf{Q_\infty}$, k is the value due to the structural features of the polymer and **n** is the value for determining the diffusion mechanism.

Whereas the value of **n** equals 0.5, the mechanism of diffusion described by **Case I** of Fickian model, when **n** values range between 0.5 and 1 that exhibits anomalous transport model and when **n** value equals one, **Case II** of non-Fickian model is used to determine. Fickian model describing the rate of diffusion of