

**CURING CHARACTERISTICS, TENSILE PROPERTIES AND  
MORPHOLOGY OF KENAF FIBRE FILLED NATURAL RUBBER  
COMPOSITES**

**by**

**NORJULIA BINTI AHMAD MAHIR**

**Thesis submitted in fulfilment of the requirements  
for the degree of  
Master of Science**

**November 2011**

## ACKNOWLEDGEMENT

بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

Alhamdulillah.

I owe my deepest gratitude to my supervisor Professor Dr. Hanafi Ismail, who was abundantly helpful and offered invaluable assistance and guidance. One simply could not wish for a better or more inspirational supervisor.

To my co-supervisor Associate Professor Dr. Zulkifli Ahmad, who has supported me throughout completing my thesis with his patience and knowledge, thank you very much.

Special thanks to the technicians in School of Materials and Mineral Resources especially Mr Gnanasegaran a/l NB Dorai for the moral support and for keenly assisted me whenever I needed help in the lab.

The one and only Puan Rokiah Mohamad, thank you for the love, encouragement, understanding and above all, thank you for believing in me.

My family and friends, who have been supported me in any aspect during the completion of the project, who directly or indirectly gave me the courage to finish what I've started, I am indebted to all of you.

This thesis would not have been possible without all of you.

## 61-12TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENT	iii
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF SYMBOLS	xiii
LIST OF ABBREVIATION	xiv
LIST OF PUBLICATIONS	xv
ABSTRACT	xvi
ABSTRAK	xviii
CHAPTER 1: INTRODUCTION	
1.1 Introduction	1
1.2 Problem Statement	3
1.2 Research Objectives	4
CHAPTER 2: LITERATURE REVIEW	
2.1 Rubber	5
2.1.1 Natural rubber	5
2.1.1.1 Strain-induced crystallization behaviour	7
2.1.2 SMR L	8
2.1.3 Epoxidized natural rubber	10
2.1.3.1 Nature of ENR	10
2.2 Rubber compounding	11
2.2.1 Vulcanizing system	12

2.3 Reinforcing Phase	14
2.3.1 Natural fibre	16
2.3.1.1 Kenaf	17
2.3.2 Filler	19
2.3.2.1 Nanoparticle	20
2.3.2.2 Halloysite Nanotubes	21
2.4 Fibre treatment	24
2.4.1 Treatment with sodium hydroxide	25
2.5 Hybrid fillers	27
2.5.1 Use of natural fibres in hybrid fillers	28
2.6 Compatibilizer	29
2.6.1 Polymer as compatibilizer	29
2.7 Coupling agent	31
2.7.1 Bis-(3-triethoxysilylpropyl) tetrasulphide	32

## CHAPTER 3: METHODOLOGY

3.1 Raw Materials	35
3.1.1 Preparation of kenaf fibre and halloysite nanotubes	35
3.2 Preparation of composites	36
3.3 Alkali treatment	39
3.4 Measurement of the Curing Characteristics	39
3.5 Preparation of Moulded Sheets	41
3.6 Physical Testing	41
3.6.1 Measurement of Tensile Properties	41
3.6.2 Measurement of Rubber-Filler Interaction	42
3.7 Scanning Electron Microscopy (SEM)	43

## CHAPTER 4: RESULTS AND DISCUSSION

4.1 The Effect of Kenaf Loading on Properties of Kenaf Filled Natural Rubber Composites	44
4.1.1 Curing Characteristics	44
4.1.2 Tensile Properties	46
4.1.3 Rubber-Filler Interaction	49
4.1.4 Morphological Studies of Tensile Fractured Surface	50
4.2 The Effect of Kenaf Treatment, ENR 50 as Compatibilizer and Si-69 as Coupling Agent on Properties of Kenaf Filled Natural Rubber Composites	53
4.2.1 Curing Characteristics	53
4.2.2 Determination of Tensile Properties	60
4.2.3 Rubber-Filler Interaction	73
4.2.4 Morphological Studies of Tensile Fractured Surface	75
4.3 The Effect of Kenaf Fibre/Halloysite Nanotube Loading on Properties of Kenaf/Halloysite Nanotube Hybrid Filled Natural Rubber Composites	80
4.3.1 Curing Characteristics	80
4.3.2 Tensile Properties	82
4.3.3 Rubber-Filler Interaction	86
4.3.4 Morphological Studies of Tensile Fractured Surface	87

## CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions	88
5.2 Recommendations for Future Research	89

REFERENCES	91
PUBLICATIONS	98

## LIST OF TABLES

	Page
Table 2.1 Typical analysis for Natural Rubber	7
Table 2.2 Properties of SMR L	9
Table 2.3 Chemical composition of kenaf fibre (after 138 days planting)	17
Table 2.4 Typical characteristic of halloysite	23
Table 2.5 Chemical analysis XRF	23
Table 3.1 Formulations for the kenaf filled NR compounds	36
Table 3.2 Formulations for the treated kenaf filled NR compounds	37
Table 3.3 Formulations for Kenaf /Halloysite Nanotubes hybrid filled NR compounds	37
Table 3.4 Formulations for kenaf filled NR compounds with ENR 50 as a compatibilizer	38
Table 3.5 Formulations for kenaf filled NR compounds with Si-69 as a coupling agent	38
Table 3.6 Vulcanization parameters obtained from a rheometer curve	39

## LIST OF FIGURES

	Page
Figure 2.1 The structure of cis-1,4-polyisoprene	6
Figure 2.2 Epoxide natural rubber (ENR) chemical structure	10
Figure 2.3 Rubber Basic Process	12
Figure 2.4 Network formation	13
Figure 2.5 Classification of fillers according to average particle size	15
Figure 2.6 Kenaf fibre	18
Figure 2.7 Lignin chemical structure	19
Figure 2.8 TEM micrograph of 2% nylon-clay nanocomposite; inset shows schematic of montmorillonite aluminosilicate layer structure	20
Figure 2.9 Types of composite structure of polymer-layered silicate clay materials	21
Figure 2.10 Halloysite Nanotubes	22
Figure 2.11 Silane coupling agent chemical structure	32
Figure 2.12 Silane coupling agent general mechanism	33
Figure 3.1 Preparation and testing for kenaf fibre filled NR composites	36
Figure 3.2 The shape and dimensions of tensile test specimen	41
Figure 3.3 Shape and dimension of swelling test specimen	42
Figure 4.1 Variation of scorch time ( $t_{s2}$ ) of NR compounds with kenaf fibre loading	44
Figure 4.2 Variation of cure time ( $t_{90}$ ) of NR compounds with kenaf fibre loading	45



Figure 4.3 Variation of max torque ( $M_H$ ) of NR compounds with kenaf fibre loading	46
Figure 4.4 Variation of tensile strength of NR compounds with kenaf fibre loading	47
Figure 4.5 Variation of elongation at break of NR compounds with kenaf fibre loading	48
Figure 4.6 Variation of stress at 100% elongation of NR compounds with kenaf fibre loading	48
Figure 4.7 Variation of stress at 300% elongation of NR compounds with kenaf fibre loading	49
Figure 4.8 Variation of $Q_f/Q_g$ value of NR compounds with kenaf fibre loading	50
Figure 4.9 SEM micrographs of NR compounds with untreated kenaf fibre (a) 10phr (50x magnification) (b) 40phr (30x magnification) (a) 10phr (30x magnification) (b) 40phr (30x magnification)	52
Figure 4.10 Variation of scorch time ( $t_{s2}$ ) of NR compounds with untreated and treated kenaf fibre loading	53
Figure 4.11 Variation of cure time ( $t_{90}$ ) of NR compounds with untreated and treated kenaf fibre loading	54
Figure 4.12 Variation of scorch time ( $t_{s2}$ ) with fibre loading of kenaf filled NR composites with and without ENR 50 as a compatibilizer	55
Figure 4.13 Variation of cure time ( $t_{90}$ ) with fibre loading of kenaf filled NR composites with and without ENR 50 as a compatibilizer	55
Figure 4.14 Variation of scorch time ( $t_{s2}$ ) with fibre loading of kenaf filled NR composites with or without Si-69	56

Figure 4.15 Variation of cure time ( $t_{90}$ ) with fibre loading of kenaf filled NR composites with or without Si-69	57
Figure 4.16 Variation of max torque of NR composites with untreated and treated kenaf fibre loading	58
Figure 4.17 Variation of max torque ( $M_H$ ) of kenaf filled NR composites with and without ENR 50 as a compatibilizer	59
Figure 4.18. Variation of max torque ( $M_H$ ) with fibre loading of kenaf filled NR composites with or without Si-69.	60
Figure 4.19 Variation of tensile strength of NR composites with untreated and treated kenaf fibre loading	61
Figure 4.20 Variation of tensile strength with fibre loading of kenaf filled NR composites with and without ENR 50 as a compatibilizer	62
Figure 4.21 Variation of tensile strength with fibre loading of kenaf filled NR composites with or without Si-69	64
Figure 4.22 Variation of elongation at break of NR composites with untreated and treated kenaf fibre loading	65
Figure 4.23 Variation of elongation at break with fibre loading of kenaf filled NR composites with and without ENR 50 as a compatibilizer	66
Figure 4.24 Variation of elongation at break with fibre loading of kenaf filled NR composites	67
Figure 4.25 Variation of stress at 100% elongation ( $M_{100}$ ) of NR composites with untreated and treated kenaf fibre loading	68
Figure 4.26 Variation of stress at 300% elongation ( $M_{300}$ ) of NR composites with untreated and treated kenaf fibre loading	68

Figure 4.27 Variation of stress at 100% (M100) elongation with fibre loading of kenaf filled SMR L/composites	69
Figure 4.28 Variation of stress at 300% (M300) elongation with fibre loading of kenaf filled SMR L composites	70
Figure 4.29 Variation of stress at 100% elongation (M100) with fibre loading of kenaf filled NR composites with or without Si-69	71
Figure 4.30 Variation of stress at 300% elongation (M300) with fibre loading of kenaf filled NR composites with or without Si-69	71
Figure 4.31 Variation of $Q_f/Q_g$ value of NR composites with untreated and treated kenaf fibre loading	72
Figure 4.32 Variation of $Q_f/Q_g$ value with fibre loading of kenaf filled NR composites with and without ENR 50 as a compatibilizer	73
Figure 4.33 Variation of $Q_f/Q_g$ value with fibre loading of kenaf filled NR composites with or without Si-69	74
Figure 4.34 SEM micrographs of NR composites with treated kenaf fibre (a) 10phr, (b) 30phr (50x magnification)	75
Figure 4.35 SEM micrographs of NR/kenaf fibre composites with ENR 50 at (a) 10phr (b) 30phr kenaf loading	77
Figure 4.36 SEM Micrographs of NR/kenaf fibre composites with Si-69 at (a) 10phr (b) 30phr kenaf loading	78
Figure 4.37 Variation of scorch time ( $t_{s2}$ ) of hybrid kenaf/halloysite nanotubes filled NR composites	79
Figure 4.38 Variation of cure time ( $t_{90}$ ) of kenaf/halloysite nanotubes hybrid filled NR composites	80

Figure 4.39 Variation of max torque ( $M_L$ and $M_H$ ) of kenaf/halloysite hybrid nanotubes filled NR composites	81
Figure 4.40 Variation of tensile strength of kenaf/halloysite nanotubes hybrid filled NR composites	82
Figure 4.41 Variation of elongation at break of kenaf/halloysite nanotubes hybrid filled NR composites	83
Figure 4.42 Variation of stress at 100% elongation ( $M_{100}$ ) of kenaf/halloysite nanotubes hybrid filled NR composite	84
Figure 4.43 Variation of stress at 300% elongation ( $M_{300}$ ) of kenaf/halloysite nanotubes hybrid filled NR composites	84
Figure 4.44 Variation of $Q_f/Q_e$ value of kenaf/halloysite nanotubes hybrid filled NR composites	85
Figure 4.45 SEM micrographs of kenaf/halloysite nanotubes hybrid filled NR composites (a) 30/0 (b) 20/10 (c) 0/30 (100x magnification)	87

## LIST OF SYMBOLS

$M_H$	Maximum torque
$t_{s2}$	Scorch time
$t_{90}$	Cure time
$Q$	Quality factor
$M_{100}$	Stress at 100% elongation
$M_{300}$	Stress at 300% elongation

## LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CBS	N-Cyclohexyl-2-Benzothiazole Sulfenamide
ENR	Epoxidised natural rubber
EV	Efficient vulcanization
HNT	Halloysite nanotubes
ISO	International Organization for Standardization
NR	Natural rubber
SBR	Styrene butadiene rubber
SEM	Scanning Electron Microscope
SMR	Standard Malaysia Rubber

## LIST OF PUBLICATIONS

	Page
Publication A Tensile properties, rubber-filler interaction and morphological of kenaf fibre/halloysite hybrid nanotubes filled natural rubber compounds	98
Publication B The effects of untreated and treated kenaf loading on properties of kenaf fibre filled natural rubber compounds	99
Publication C The effects of untreated and treated kenaf loading on properties of kenaf fibre filled natural rubber compounds	100
Publication D Curing characteristics, mechanical and morphological properties of kenaf fibre/halloysite nanotubes hybrid filled natural rubber compounds	101
Publication E The Effect of Bis-(3-triethoxysilylpropyl) Tetrasulphide (Si-69) as a Coupling Agent on Properties of Natural Rubber/Kenaf Fibre Composites	102

**CURING CHARACTERISTICS, TENSILE PROPERTIES AND  
MORPHOLOGY OF KENAF FIBRE FILLED NATURAL RUBBER  
COMPOSITES**

**ABSTRACT**

Natural fibres such as kenaf had been widely studied over the years as reinforcement in rubber composites. Natural fibres were found to be comparable to common synthetic fibres for application that do not require very high load bearing capabilities. Natural rubber (NR) composites with different kenaf loading i.e 0, 10, 20, 30, 40 phr was used to study the effect of kenaf loading in NR composites. Kenaf treated with NaOH was prepared to study the effect of fibre treatment on properties of kenaf filled NR composites. Natural rubber composites were prepared with different kenaf/HNT ratio loading; 30/0, 20/10, 15/15, 10/20, 0/30 (phr/phr). Kenaf fibre filled natural rubber (NR) composites with and without ENR 50 as a compatibilizer and bis-(3-triethoxysilylpropyl) tetrasulphide as a coupling agent were also prepared. Curing characteristics showed that scorch time and cure time decreased with increasing of fibre loading and for treated fibre. Tensile strength of kenaf filled natural rubber composites decreased with increasing of fibre loading but increased with for treated fibre. Swelling measurement and morphological study showed that better rubber-filler interaction was obtained with treated kenaf. Curing characteristics showed that scorch time and cure time increased with increasing of HNT in kenaf/HNT ratio loading while minimum and maximum torques decreased. When HNT ratio in kenaf/HNT loading was increased, the tensile strength and elongation at break increased but tensile modulus decreased. Swelling measurement and morphological study showed that better rubber-filler interaction was obtained with higher HNT ratio in kenaf/HNT



loading. Scorch time and cure time decreased but tensile strength, elongation at break and tensile modulus increased with the presence of ENR 50 as a compatibilizer. Kenaf filled NR composites with the presence of ENR 50 and Si-69 gave better rubber-filler interaction. With the presence of Si-69 in the NR composites, the scorch time and cure time decreased but tensile strength, elongation at break and tensile modulus increased.

**SIFAT-SIFAT PEMATANGAN, TENSIL DAN MORFOLOGI KOMPOSIT  
GETAH ASLI TERISI GENTIAN KENAF**

**ABSTRAK**

Gentian semulajadi seperti kenaf telah banyak dikaji penggunaannya dalam bidang penguatan komposit getah sejak beberapa tahun kebelakangan ini. Gentian semulajadi didapati mempunyai ciri-ciri yang setanding dengan gentian yang biasa digunakan bagi aplikasi-aplikasi yang tidak memerlukan kemampuan penahanan beban yang terlalu tinggi. Komposit getah asli dengan pembebanan gentian kenaf yang berbeza iaitu pada 0, 10, 20, 30 dan 40 bsg telah disediakan. Gentian kenaf yang telah dirawat dengan NaOH digunakan untuk mengkaji kesan perawatan alkali terhadap komposit getah asli berpengisi gentian kenaf. Komposit getah asli dengan kandungan pembebanan pengisi hybrid gentian kenaf/HNT yang berbeza telah disediakan dengan kandungan 30/0, 20/10, 15/15, 10/20, 0/30 bsg. Sebatian getah berpengisi gentian kenaf juga telah disediakan dengan penambahan ENR 50 sebagai pengserasi dan bis-(3-trietoksililpropil) tetrasulfida sebagai agen pengkupel. Sifat pematangan getah menunjukkan masa skoj dan masa pematangan komposit meningkat dengan peningkatan kandungan gentian kenaf dan dengan rawatan alkali. Sifat mekanikal getah asli berpengisi gentian kenaf menurun dengan peningkatan kandungan gentian di dalam komposit tetapi meningkat dengan penggunaan gentian dengan rawatan alkali. Sifat pembengkakan dan morfologi menunjukkan interaksi getah yang lebih baik dengan gentian yang telah dirawat dengan NaOH. Sifat pematangan menunjukkan masa skoj dan masa pematangan komposit meningkat bagi komposit dengan kandungan HNT yang lebih tinggi manakala tork maksima berkurangan. Apabila kandungan HNT ditingkatkan, kekuatan tensil dan

pemanjangan takat putus meningkat manakala modulus tensil menurun. Ujian pembengkakan dan morfologi menunjukkan bahawa interaksi getah-gentian yang lebih baik didapati pada komposit getah asli dengan nisbah kandungan HNT yang lebih tinggi. Masa skoj dan masa pematangan berkurang dengan kehadiran ENR 50 sebagai agen pengserasi dalam komposit getah asli, manakala kekuatan tensil, pemanjangan takat putus dan tensil modulus semakin meningkat. Kehadiran ENR 50 memberikan interaksi getah-gentian yang lebih baik bagi komposit getah asli berpengisi kenaf. Dengan penambahan Si-69 di dalam komposit, masa skoj dan masa pematangan berkurang manakala kekuatan tensil, pemanjangan takat putus dan modulus meningkat.

# CHAPTER 1

## INTRODUCTION

### 1.1 Introduction

The common fibres used in polymer reinforcement such as carbon, glass and aramid are said to have some disadvantages which they are costly and unable to be renew and recycled. As a trend of replacing these frequently used fibres, natural fibres reinforcement in polymer had been studied these days.

Natural fibres (NR) reinforcement in polymer was found to be as good as the common fibres for applications that do not require very high load bearing capabilities (Wambua et al., 2003). Even though natural fibres have list down many advantages such as abundantly available, low weight, biodegradable, cheaper besides offer good mechanical properties, there are also a few disadvantages listed like moisture absorption, quality variations, low thermal stability and hydrophilic.

There were many natural fibres filled rubber composites studies had been done throughout the years. Jacob et al. (1990) studied the influence of various flax fibre parameters on the properties of flax fibre-epoxy composites while Geethamma et al. (1998) studied the coir fibre usage as the reinforcement in natural rubber composites. Ismail et al. (1997) and Rozman et al. (2001) have done research on another known natural fibre used in polymer research that is oil palm fibre. Ismail et al. (2001) studied the effect of filler loading and bonding agent on the properties of bamboo fibre filled natural rubber composites. Besides that, mechanical properties of sisal/oil palm hybrid fibre reinforced natural rubber composites also had been done by Jacob et al. (2004). Jute and flax fibres reinforced PP composites offer an increasing in

tensile strength and impact properties and further increment achieved with incorporation of maleated PP (MaPP) as coupling agents (Kenner et al., 2004)

Kenaf (*Hibiscus Cannabinus* L.), an annual plant, is a string fibre and have the properties of high toughness, specific strength properties and enhanced energy recovery. Until today, kenaf has been used in many applications including carpet padding and poultry house bedding. Besides that, kenaf, as well as other natural fibres have the advantages of renewability, recyclability and biodegradability. Kenaf also is used widely in automobile industry, which is used in exterior components or semi-structural applications (Xue et al., 2007).

The ultimate cell dimensions of kenaf and many other fibre-bearing dicotyledons are similar to those of jute. A distinction must be made between jute like fibres and flax, however, for although all are described as bast fibres, the ultimate cells in flax are much longer, averaging 20-25 mm. They are also greater in cross-sectional area, and, because of the longer length, a coherent fibre structure can be built up from only two or three overlapping ultimates. The single fibres of flax are thus much finer than those of jute.

Kenaf fibre has been widely used in polymer research like other natural fibres. Nishino et al. (2003) studied the comparison of kenaf fibre and poly-lactic acid (PLLA) composites to the traditional composites. From the research, it was proved that kenaf fibre can be a good candidate for the reinforcement fibre of high performance biodegradable polymer composites. When kenaf fibre was blended with thermoplastic natural rubber (TPNR) and maleic-anhydride-grafted polypropylene (MAPP) as a compatibilizer, the composites showed an enhancement in tensile strength but decreasing of maximum strain and impact strength (Sameni et al., 2003).

## 1.2 Problem Statement

Although natural fibres are proved to be enhancing most properties of polymer composites when used as reinforcement, the problem faced with natural fibres is from the point that they have poor adhesion and compatibility to most polymer matrices. Natural fibres, including kenaf are lignocellulosic fibre with the presence of hydroxyl group. This makes the natural fibres hydrophilic, whereas most polymer matrices are hydrophobic.

Fibre treatment with chemical solution is one of the prominent methods to increase the natural fibre-polymer compatibility. Fibre treatment is done basically to remove unnecessary components of natural fibres; which limit the fibre-polymer interaction and increase the fibre surface roughness. Hybrid fillers in polymer composite offer better properties than single filler used. In such, natural fibre hybrid with other fibre or filler is another approach of enhancing the properties achieved by the natural fibre itself when compositeed with polymer.

ENR 50 has been proved to increase mechanical properties of polymer composites when used as a compatibilizer. Another major method in increasing the compatibility of natural fibre-polymer is by incorporation of coupling agent. Silane coupling agent is proved to be increasing the adhesion between reinforcement and polymer matrix (Li, 2010).

### **1.3 Research Objective**

The main objective of this research is to look into the potential of using kenaf fibre as filler in natural rubber composite with the aim to study:

1. The effect of kenaf loading on the curing characteristics, mechanical properties and morphology of the NR composites.
2. The effect of kenaf treatment, ENR 50 as compatibilizer and Si-69 as coupling agent on the curing characteristics, mechanical properties and morphology of the NR composites.
3. The effect of kenaf fibre/halloysite nanotubes hybrid loading ratio on the curing characteristics, mechanical properties and morphology of the NR composites.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Rubber

Rubber is basically defined as a material which has the ability to have the elastic changes, that is to stretch when a force is applied and back to its original state when the force is removed in a short period. The more precise definition of a rubber vulcanizate is specified in ASTM D1566-98: Standard Terminology Relating to Rubber (Ciesielski, 1999). Rubber can be categorized into two types; natural rubber and synthetic rubber.

##### 2.1.1 Natural Rubber

Natural rubber is a hydrocarbon with a polymer of isoprene units ( $C_5H_8$ ) built up in a form of a continuous chain which is highly stereo regular, with density of 0.93 at 20°C. The repeating unit in natural rubber has the *cis* configuration (with chain extensions on the same side of the ethylene double bond), which is essential for elasticity. The presence of the double bond is very significant, since it is this that largely determines the chemical reactivity of the molecules and its ability to react with sulphur or other reagents in the vulcanization process. Besides, the double bond also is responsible for the susceptibility leading to a deterioration of physical properties due to aging.



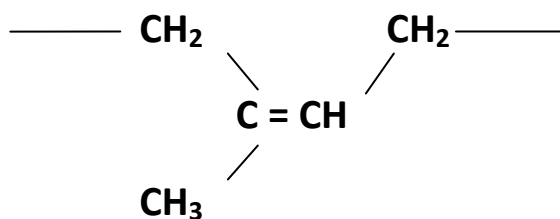


Fig. 2.1 The structure of cis-1,4-polyisoprene

(<http://www.accessscience.com/content/Polyolefin-resins/535900>, 6 July 2011)

Figure 2.1 shows the chemical structure of cis1,4-polyisoprene. Natural rubber hardens below 0°C and softens and weakens above 80°C, losing its strength and becoming tacky. In between these temperatures it can flow under stress and permanent deformation occurs under prolonged strain. The undesirable properties are reduced by vulcanization, in which the reactivity the double bonds impart to the molecule is utilised to make it react with added material to form crosslink between the chains. The crosslinking increases the useful temperature range of the rubber and hardens the rubber so that it becomes much stronger and does not creep but return to its original shape on release of stress. Its surface properties are improved and its solubility decreased. Sulphur is still the most important vulcanizing compound for natural rubber, but not the only one.

Natural rubber is widely used in rubber industry because of the self-reinforcing nature. The self-reinforcing nature of natural rubber is given by the effects strain induced crystallization. The difference in strain induced crystallization of natural rubber occurs when filler is added to the natural rubber due to the changes in strain (Chenal et al, 2007). [Gutta](#) percha is another polymer with isoprene units repeat but are composed of *trans* configuration. Although gutta percha has a structural isomer that is similar to natural rubber, they do not have identical properties.

There are three major properties of natural rubber that are most important key in product manufacturing – viscosity, fatty acid bloom and compliance with the technical application. Among these three, viscosity is known to be the most important factor. Viscosity impacts the initial mixing of the rubber with other compounding ingredients and subsequent processing of the compounded materials to form the final manufactures product. The typical analysis of a natural rubber can be seen in Table 2.1.

Table 2.1 Typical analysis for natural rubber (Coran, 2005)

<b>Component</b>	<b>%</b>
Moisture	0.6
Aseton extract	2.9
Protein	2.8
Ash	0.4
Rubber hydrocarbon	93.3
	<b>100.0</b>

#### **2.1.1.1 Strain Induced Crystallization Behaviour**

Rubber behaves with the absence of crystal and is usually in the form of elastomer that is not changed. However, there are few crystals present at normal temperatures in some elastomer including EPDM with a high content ethylene.

If there is sufficient irregularity on rubber backbone structure, the amorphous rubber will crystallized at lower temperatures. Non-orientated natural rubber crystallizes through the existence of lamellar on radial spherules and has two

morphologically different forms that is lamella- $\alpha$  which is more stable and lamella- $\beta$  which formed slower. Both types of lamella units have the same set of crystal but different in terms of growth rate, lamellar thickness and morphology (Gent, 2005).

Although natural rubber is amorphous, crystallization can occur when strain is induced. Strain induced crystallization is a general phenomenon to most rubber vulcanizate like natural rubber, polyisobuthylene and cis-1,4-polybutadiene, except styrene butadiene rubber (SBR) (Chenal et al, 2007; Gent, 2005). The crystallization occurred below the stress increased the modulus and failure properties of most rubber and happen to be a priority in many applications for natural rubber, crystallization strain tendency directly related to the characteristics of failure.

Crystallization of natural rubber under strain occurs through convergence lamella that appears to grow perpendicular to the direction of attraction (Gent, 2005). This high rate of crystallization which can then decrease during the secondary crystallization occurs where the rates are not influence by strain (Chenal et al, 2007). Effect of filler on the strain induced crystallization depends on the density of natural rubber and filler chemical cross-linking.

### **2.1.2 SMR L**

Malaysia natural rubbers are classified into several grade depending on the properties under the Standard Malaysia Rubber Scheme (SMR), which was introduced in 1965 (Waddell, 2005). Several properties of rubbers that is taken into consideration for the grading are dirt, ash and nitrogen content, volatile material and Wallace plasticity.

Malaysia rubber graded as SMR L has light colour, produced by high quality latex. The latex was added with ammonia or ammonia and boric acid mixture. 0.05% sodium metabisulphate was also added to prevent enzyme darkening (Ismail and Hashim, 1998). SMR L has low ash and dirt content (Waddell, 2005). Specific properties of SMR L are shown in Table 2.2.

Table 2.2 Properties of SMR L (Coran, 2005)

<b>Parameter</b>	<b>SMR L</b>
Dirt on a 44 µm net (% of maximum weight)	0.03
Ash content (% maximum weight)	0.50
Nitrogen content (% maximum weight)	0.60
Vaporize material (% maximum weight)	0.80
Wallace plasticity (P <sub>o</sub> (initial minimum value))	30
PRI (min., %)	60
Colour (Lovibond maximum)	5.0

SMR L shows good thermal aging property and gives good vulcanizate properties, such as tensile strength, modulus and elongation at break. SMR L usually is used for light colour or opaque products.

### 2.1.3 Epoxidized Natural Rubber

Epoxidized natural rubber (ENR) is modification of natural rubber by converting the chemical part of the unsaturated natural rubber to an epoxide group, distributed randomly along the polymer chain. Epoxidation method of cis-1,4-polyisoprene has been patented by Gelling in 1985 with any degree of oxidation can be obtained when the modification is done using a controlled situation.

Oxidation process increases the glass transition temperature,  $T_g$ , approximately  $1^\circ\text{C}$  for each mole percent of epoxidization and cause large changes in some properties of the ENR produced. However, the nature and strength of ENR is high because like natural rubber, ENR is able to perform strain induced crystallization.

#### 2.1.3.1 Nature of ENR

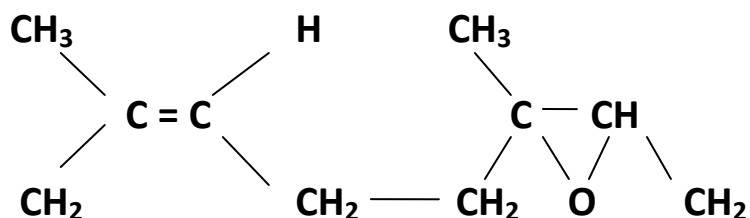


Fig. 2.2 Epoxide natural rubber (ENR) chemical structure (Ismail, 2004)

Natural rubber chemical structure is cis-1,4-polyisoprene stereoregular structure. Therefore ENR retain to have the cis-1,4-polyisoprene stereoregular configuration. ENR vulcanizate vulcanized with sulphur is able to experience the strain induced crystallization especially when using the ENR with 50 mol% oxidation or less. ENR 50 chemical structure can be seen in Figure 2.2.

In a normal mixing temperature, ENR 50 tends to stick onto the two-roll mills due the higher glass transition temperature compare to natural rubber. To reduce this problem, mixing time must be shortened and the low temperature mixing with water cooling is necessary.

ENR 50 can be vulcanized with sulphur and peroxide. When using sulphur vulcanization, the ENR 50 vulcanization process is improved. This is because the isolated double bonds in ENR prevent the formation of sulphide bonds between molecules and cause an increase in cross-linking (Gelling & Morrison, 1985). Sulphur conventional vulcanization system (CV) which containing 2 phr sulphur or more is not suitable in practise. This is because the vulcanizate produced will have poor aging characteristic. Semi efficient (semi-EV) and efficient (EV) vulcanization systems are most suitable for ENR.

## **2.2 Rubber compounding**

Compounding is the process for obtaining a uniform compound for all rubber compounding ingredients in a homogenous distribution. It is also done to obtain a constant mixture of rubber in the term of viscosity and degree of distribution especially for the fillers. The production sequence is mixing, forming and vulcanizing. The solid rubber and the other materials have to be well mixed. This is done with two basic machines, a two-roll mill in which the materials is passed between two heavy metal rollers mounted horizontally, and a Banbury mixer, an internal mixer in which the materials are sheared between the internal rollers and the inside of the casting (Ciesielski, 1999). The raw rubbers, composed essentially of long polymer chains, are

joined together with a crosslink in a process called vulcanization to give the final compound its characteristic properties. Figure 2.3 shows the basic process of a rubber compounding.

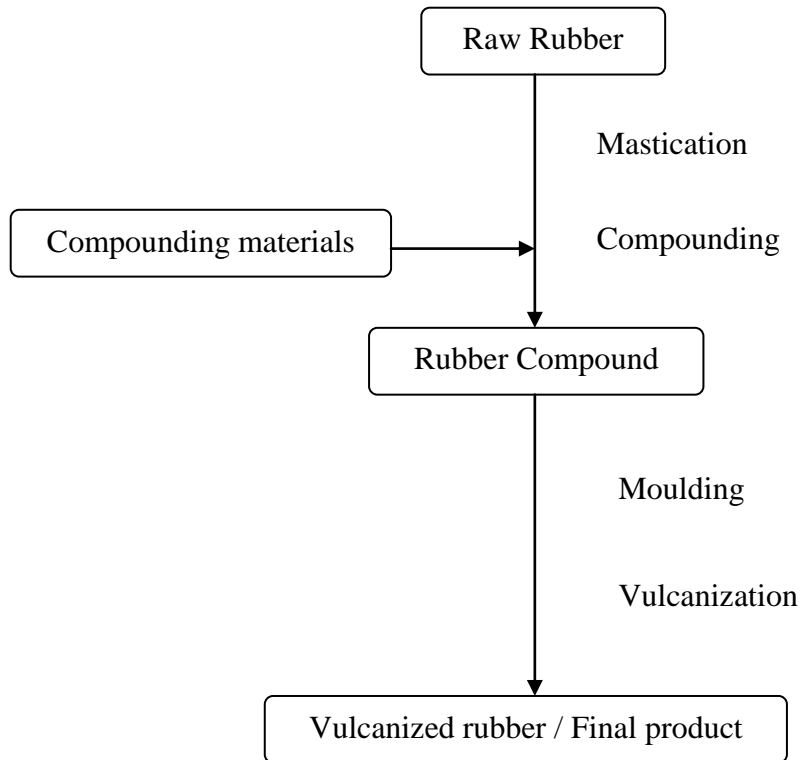


Fig. 2.3 Rubber Basic Process ( Ismail & Hashim, 1998)

### 2.2.1 Vulcanization system

Vulcanization process can be defined as the process of increasing the recovery force and decreasing the total permanent deformation of a material after the deformation force is removed. Thus, the process of vulcanization increased the elasticity and reduces plasticity of rubber compounds. This characteristic is generally achieved by forming a network of cross-linked molecules such as in figure 2.4.

Vulcanization with sulphur is the main method used in rubber compounds where it involves the formation of crosslink between chains polysulphide.

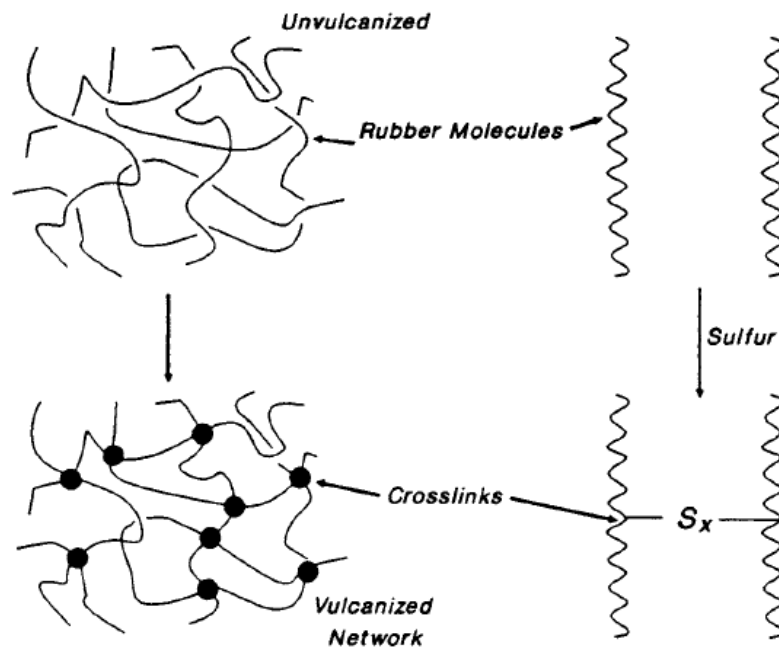


Fig. 2.4 Network formation (Coran, 2005)

According to the theory of rubber elasticity, the recovery forces to the resistance of deformation of the rubber is directly proportional to the number of networks that support the polymer chains per unit volume of the elastomer. Polymer chain that supports is a linear polymer molecule segments between junctions in the network. The increases in the crosslink number will increases the number of chain support (Coran, 2005).

If only sulphur is used, the time required to cure a rubber compound can reach up to 8 hours. The modern methods use accelerator and activator to reduce the curing time required as well as to reducing the sulphur bonds to only one or two sulphur atoms (Whelan, 1994). Shorter sulphur bonds give better thermal stability and improve the aging characteristics. With the addition of accelerator and activator used



in the processing, some part of accelerator can be used in place of the element sulphur.

### **2.3 Reinforcing phase**

In general, the filler in rubber compounds can be divided into two; reinforcing and non-reinforcing. Reinforcing fillers are fillers that are capable in enhancing rubber vulcanizates properties such as tensile strength, tear strength, abrasion and tensile modulus. The corporation of reinforcing filler also may possibly increase the energy needed for rubber vulcanizate failure. Meanwhile, non-reinforcing filler is used to increase the hardness, modulus and to reduce the cost of the compound in general.

The main factors that influence the effect of filler on the hardening of rubber are (Frohlich et al., 2004):

- a. particle size or prime specific surface area and its contents to the effective area of contact between the face of the filler and rubber matrix;
- b. structure or the degree of irregularities of the filler units to be among the main factors limit the movement of elastomeric chain under strain;
- c. surface activity, where it is a pre-dominant factor with consideration of the interaction of the filler-filler and filler-rubber.

The most important parameter in determining the reinforcing effect is the average particle size filler, as shown in Figure 2.5. Filler particle with size greater than 10 nm does not give a significant reinforcing effect and usually increase the viscosity with the hydrodynamic effects. Better reinforcing effect is provided by the

filler with particle size smaller than 10 nm. However, it will also be influenced by particles structure factor (LeBlanc, 2002).

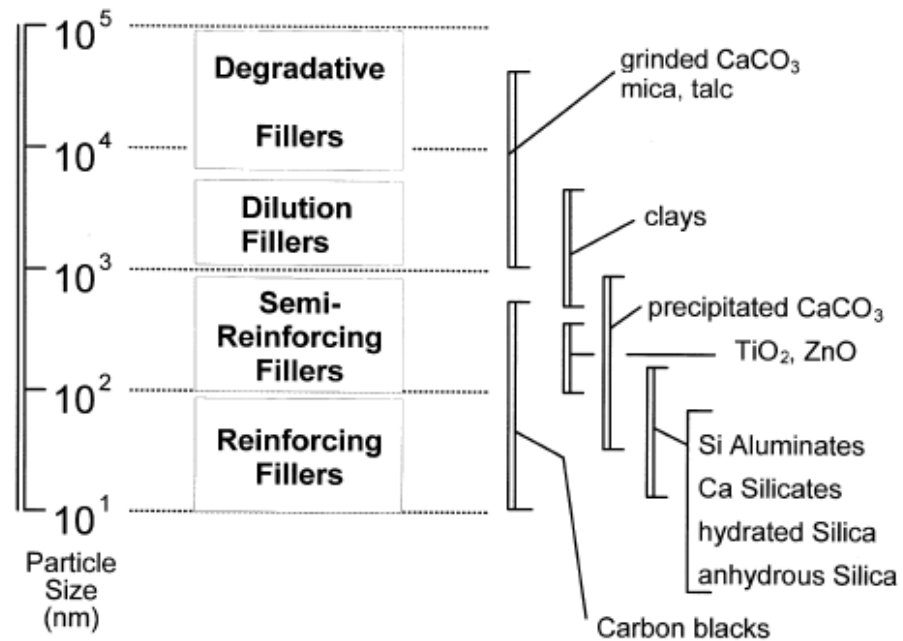


Fig. 2.5 Classification of fillers according to average particle size (LeBlanc, 2002)

There are various types of filler shape in general, such as spherical, oval, straight and non-uniform. Fillers can be categorized relating to their reinforcing effects, as can be seen in Figure 2.5. Fillers with smaller structure and shape is better for reinforcement in rubber because they are able to disperse better in the compounds. For fibres and filler used in rubber compounds, the effectiveness of the fibre structure is evaluated with by the fibre aspect ratio.

Apart from the specific surface area, interaction between the rubber and filler are also affected by the surface activity of the filler particle. The surface activities mentioned are including the Van der Waals forces and any specific chemical interactions. The presence of different functional groups for each of the filler and fibre give different effects on the filler or fibre surface activity with the rubber.

### 2.3.1 Natural Fibre

The main difference between natural and synthetic fibre is in structure. Synthetic fibre is produced by extruding the polymer through a nozzle and subsequent drawing thus result in simple, almost regular structure while natural fibres have non-even and non-homogeneous structure surface. Natural fibres can be subdivided into three main categories depending on the nature of their source: vegetable, animal and mineral. Vegetable or plant-based fibres and animal fibres are fully biodegradable while mineral fibres are not.

Besides natural fibres had a lot of advantages which differ to common fibres such as renewability, biodegradability, recyclability and show high toughness, high specific stiffness and strength (Jacob et al. 2004). The natural fibres exhibit brittle fracture and have only a small extension at break with very little recoverable elasticity.

Natural fibres have three principle chemical constituents, namely  $\alpha$ -cellulose, hemicelluloses and lignin (Rowell & Stout, 1998). Natural fibres like kenaf, jute, hemp and flax are able to impart the rubber compounds with benefits such as low density, less machine wear during processing than rubber compounds produced by mineral reinforcement.

Hemicelluloses comprise a group of polysaccharides and it differs from cellulose in terms of high degree of chain branching. The cellulose, hemicelluloses and lignin contents in plant fibres vary depending on the plant species, origin, quality and conditioning. The mechanical properties of the fibres vary depending on their constitution and the amount of cellulose and the crystallinity.

### 2.3.1.1 Kenaf

Kenaf (*Hibiscus Cannabinus L.*) (Fig. 2.6) is an annual plant, originating from Africa and has traditionally been a source of bast fibre in India, Iran, China, Bangladesh, Nigeria and Thailand. Kenaf is a strong fibre, owned desirably properties for instance, high toughness, acceptable specific strength properties, recyclable and enhanced energy recovery (Xue et al., 2007). The chemical composition of the fibres is shown in Table 2.3. Kenaf is used in many applications worldwide from carpet padding, pulp, poultry house bedding, to higher application such as a fibre glass substitute in moulded plastic.

Table 2.3 Chemical composition of kenaf fibre (after 138 days planting) (Rowell & Stout, 1998)

Component	Bottom part	0.66m top part
Hot water extractives	21.6	35.2
Lignin	9.9	6.4
$\alpha$ -cellulose	28.0	18.5
Pentosan	14.9	16.1
Protein	9.3	16.1

On the other hand, kenaf has problem with adhesion and compatibility to polymer matrices. This is due to the hydrophilic nature of natural fibres with the presence of hydroxyl group in the lignocellulosic chain, while most of polymers, namely natural rubber are hydrophobic. Because of the low specific gravity of these

fibres, the specific mechanical strength and modulus of some fibres are excellent and comparable to glass fibres. As a result, they have been used to replace glass fibres in some applications.



Fig. 2.6 Kenaf fibre (<http://www.habutextiles.com/webfile/xs-20.html>, 21 June 2011)

Lignin is the second most abundant of all organic molecules, and it is localized in plant cell walls. The chemical structure of lignin is shown in Figure 2.7. Lignin forms a polymer comprised of three large alcohol subunits (coumaryl (primarily in flowering plants), coniferyl (primarily in gymnosperms), and sinapyl (primarily in grasses), and the structure of lignins varies widely with species. Lignin provides compressional strength to the cell wall, unlike the flexible strength conferred by cellulose. Without lignin, terrestrial plants probably could not have reached the sizes they do today, as cellulose does not provide enough resistance to gravity itself.

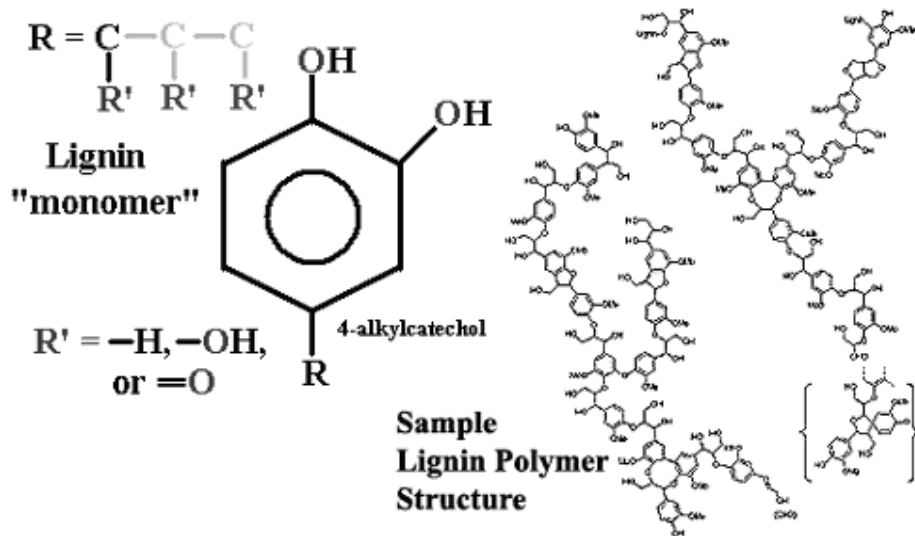


Fig. 2.7 Lignin chemical structure (Kozłowski & Władysław-Przybylak, 2003)

### 2.3.2 Filler

Filler can generally be divided into two types; reinforcing and non-reinforcing. Most gums are weak when vulcanized and they need reinforcing filler. As the terms implies, there is a reinforcement effect, the empirical results of which are to increase stiffness. Addition of filler increases hardness of the cure product. The strengthening effect by filler typically offer an increase in tensile strength, tear resistance and modulus values that can exceed expectations based on the theory of Einstein-Guth and Gold, taking into account the effects of spherical particles colloids (hydrodynamic effect) and occlusion of rubber (Fröhlich et al., 2002).

### 2.3.2.1 Nanoparticles

Nanoclays are mineral silicates produced in nanoparticle sizes. Nanoclay can be divided into several major groups such as montmorillonite, bentonite, kaolite, hectorite and halloysite. The categorization is made based on the chemical composition and the nanoparticle morphology. Nanoclay is one of the most affordable materials that have shown promising results in polymers.

Nanoclay is made from montmorillonite mineral deposits known to have “platelet” structure with average dimension of 1 nm thick and 70 to 150 nm wide. Clay minerals are mostly the end products of weathering. All clay minerals are sheet silicates, each clay type owing its distinctive character to the cations such as sodium (Na), potassium (K), magnesium (Mg) or calcium (Ca), which occupy positions in and between the sheets.

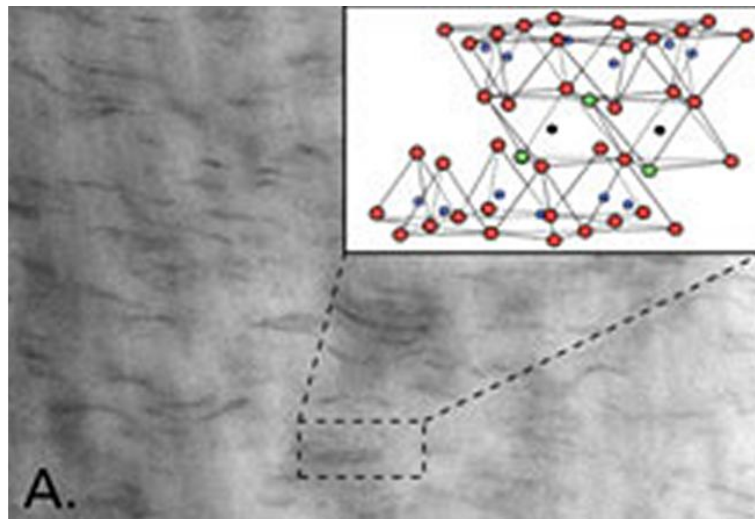


Fig. 2.8 TEM micrograph of 2% nylon-clay nanocomposite; inset shows schematic of montmorillonite aluminosilicate layer structure.

(<http://www.sigmaaldrich.com/materials-science/nanomaterials/nanoclay-building.html>, 12 August 2010)

When nanoclay is incorporated in polymer compounds, it can form either tactoid, intercalated or exfoliated structure (Fig. 2.9) (McGlashan & Halley, 2003). The exfoliated structure gives the best properties of compounds when the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix.

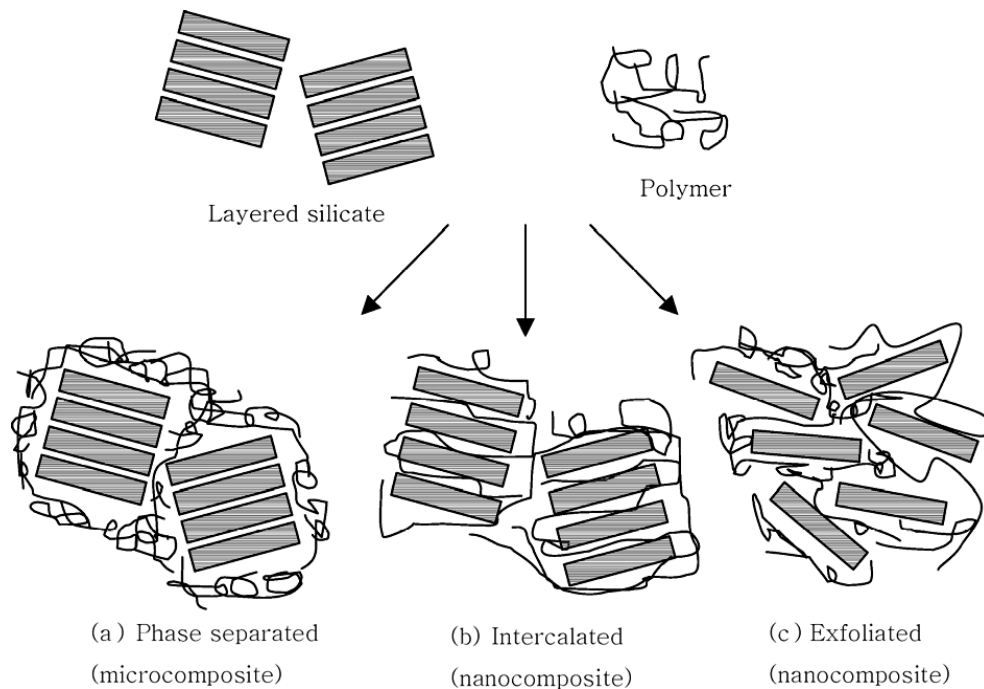


Fig. 2.9 Types of composite structure of polymer-layered silicate clay materials (Camargo, 2009)

### 2.3.2.2 Halloysite Nanotubes

Halloysite nanotubes (HNT) with the chemical composition  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \cdot n\text{H}_2\text{O}$  is a member of kaolin group of clay minerals. HNT is categorized as a two-layer clays. (1:1 clay; Si-Al lattice) with fixed distance hydrogen-bonded (-O-OH-) between the silica and alumina sheets. It is formed through rapid leaching of silica in volcanic soils (allitic weathering) and consist of a



tetrahedral silica and an octahedral alumina layer. These are rich in alumina, have poor cation-exchange capacity, stable structure and swell very little when moistened.

HNT has hollow nanotubular structure and its typical dimension is nanoscale. As it is composed of siloxane and very few hydroxyl groups, it has better dispersion property than other natural silicates. HNT is usually 150nm-2 $\mu$ m long with 20-100nm outer diameter and 5-30nm inner diameter.

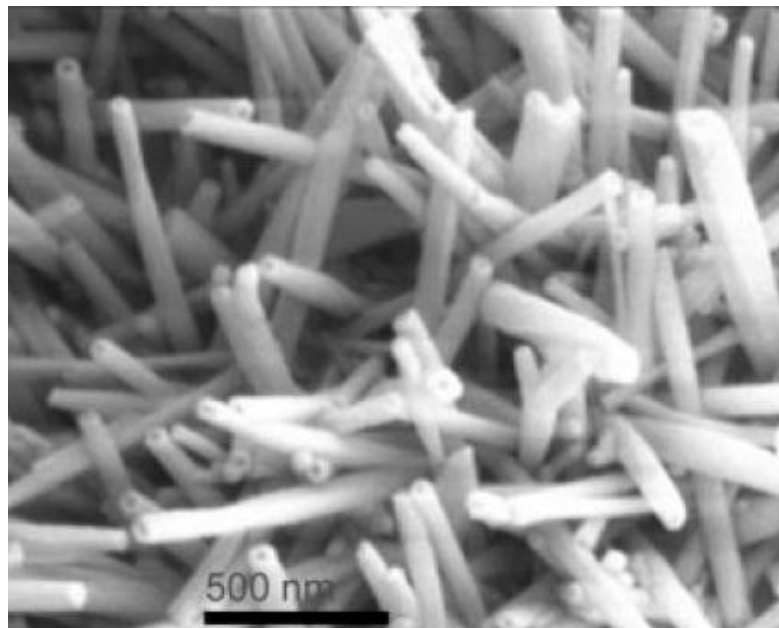


Fig. 2.10 Halloysite Nanotubes (<http://www.northstar-halloysite.com/halloysite.html>, 21 June 2011)

HNT contains interlayered water between its tetrahedral and octahedral sheets to disrupt the hydrogen bonds across the interlayers. Figure 2.10 shows halloysite nanotubes. Due to their unique crystal structure, low density of hydroxyl functional groups and tubular shape, HNT has better dispersion property in polymer matrix even at high loading compare to other natural silicates such as kaolinite. Typical characteristic and chemical analysis of halloysite nanotube can be seen in tables 2.4 and 2.5.

Similar to kenaf, HNT has drawn many attentions for it to be the substitute of several fillers in polymer. Hedicke-Hochstotter et al. (2009), Ning et al. (2007) and Deng et al. (2008) investigated the effect of HNT on PA-6, polypropylene and epoxies respectively. There are also studies on HNT effect on EPDM by Ismail et al. (2008), carboxylated butadiene-styrene rubber (Du et al., 2008) and SBR with sorbic acid modification (Guo et al., 2009).

Table 2.4 Typical Characteristic of Halloysite (<http://www.northstar-halloysite.com/halloysite.html>, 21 June 2011)

True specific gravity	2.53
Index of refraction	1.54
Bulk density	15.6 lbs./ft <sup>3</sup>
% linear dry shrinkage	1.01
% linear fired shrinkage (cone 10)	20.39
% total shrinkage	21.40
Initial pH	6.5-6.9
BHT surface area	64.66 m <sup>2</sup> /gm
Carbon exchange capacity	8.0
Particle size (jet milled)	Average 4.7 microns
Range of length	0.5 – 4 microns

Table 2.5 Chemical Analysis XRF (<http://www.northstar-halloysite.com/halloysite.html>, 21 June 2011)

Al <sub>2</sub> O <sub>3</sub>	36.9 %
SiO <sub>2</sub>	48.0 %
Fe <sub>2</sub> O <sub>3</sub>	0.14 – 2.5 %
Na <sub>2</sub> O	< 0.05 %
K <sub>2</sub> O	< 0.01 %
C <sub>2</sub> O	0.20 %
MgO	< 0.05 %
TiO <sub>2</sub>	0.04 %
LOI	13.8

## 2.4 Fibre Treatment

Reinforcing fibres can be modified by physical and chemical methods to correct for deficiencies in these materials, especially to impart bonding and adhesion, dimensional stability and thermoplasticity. Surface modification of natural fibres can be used to optimize properties of the fibre-matrix interface. Fibre treatment has been proven to remove impurities, wax, pectin, lignin and non-cellulosic compounds from natural fibre as well as to assist in separating fibres from their bundles (Li & Pickering, 2008).

Over the years, there have been few researches regarding the treatment of natural fibres in a way to improve its compatibility with polymer as well as its strength. There are various types of fiber treatment that has been studied, among