

DEVELOPMENT AND CHARACTERIZATION OF
NATURAL RUBBER-CELLULOSE SPONGE

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โฟมยางธรรมชาติ (NR) เป็นวัสดุโพลีเมอร์ชีวภาพทดแทนที่ได้จากน้ำยางธรรมชาติจากต้นยางพารา งานวิจัยนี้ ได้ทำการขึ้นรูปโฟมยางคอมโพสิตของยางพาราธรรมชาติและเซลลูโลสที่มีองค์ประกอบแตกต่างกัน โดยใช้กระบวนการดันลอปในการเตรียมโฟมยางที่มีเส้นใยเซลลูโลสปริมาณแตกต่างกันเป็นสารเสริมแรง โดยเส้นใยเซลลูโลสที่ใช้ได้มาจากเยื่อกระดาษของต้นยูคาลิปตัส และใช้โซเดียมอัลจิเนตเป็นสารที่ช่วยในการกระจายตัวของเซลลูโลส วัตถุประสงค์ของงานนี้ คือ การพัฒนาคอมโพสิตจากยางพาราที่มีความเป็นมิตรต่อธรรมชาติให้มี ความพรุนที่สูง มีความยืดหยุ่น และคุณสมบัติชอบน้ำ (ไฮโดรฟิลิก) ทำการตรวจสอบผลของการเติมเซลลูโลสต่อคุณสมบัติเชิงกลของโฟมยาง วิเคราะห์ลักษณะโครงสร้างรูพรุนและพื้นที่ผิวของโฟมยางด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด นอกจากนี้ยังอัตราการดูดซับน้ำและปริมาณความจุน้ำที่โฟมสามารถกักเก็บจะถูกทดสอบ จากการทดสอบสมบัติเชิงกลของโฟมยางพบว่า โฟมยางที่เติมเซลลูโลสสามารถทนต่อแรงกดทับและให้ค่าโมดูลัสยืดหยุ่นที่สูงขึ้นกว่าโฟมยางปกติ นอกจากนั้นคุณสมบัติทางด้านความชอบน้ำ (ไฮโดรฟิลิก) ของโฟมยางสามารถเพิ่มขึ้นโดยการเติมสารที่มีสมบัติชอบน้ำ (เซลลูโลสและโซเดียมอัลจิเนต) ซึ่งจะช่วยให้เพิ่มความเป็นขั้วของวัสดุให้สูงขึ้น พบว่าโฟมยางที่ใช้โซเดียมอัลจิเนตในสัดส่วน 1 ส่วนในร้อยส่วนของยางโดยน้ำหนัก (phr) เป็นสารกระจายตัว แสดงโครงสร้างที่มีความพรุนสูงขึ้น มีขนาดรูพรุนที่ใหญ่กว่าโฟมยางที่ไม่มีการเติมอัลจิเนต โดยรวมค่าการดูดซับน้ำหรือปริมาณน้ำที่โฟมยางสามารถกักเก็บไว้ได้เพิ่มสูงขึ้นตามการเพิ่มของปริมาณเซลลูโลสที่เติมลงไปจนถึง 45 phr และพบว่าค่าการดูดซับน้ำสูงสุดคือ 406.73% จากการเติมเซลลูโลสที่ 30 phr และ 1 phr ของโซเดียมอัลจิเนต ซึ่งสูงกว่าค่าจากโฟมยางปกติถึง 1.81 เท่า จากการศึกษาลักษณะการย่อยสลายทางชีวภาพแสดงให้เห็นว่า โฟมยางที่มีส่วนผสมของเซลลูโลสสามารถถูกย่อยสลายในดินภายใต้สภาวะแวดล้อมธรรมชาติได้สูงกว่าโฟมยางปกติ เมื่อพิจารณาจากคุณสมบัติของโฟมยาง โฟมยางคอมโพสิตยางพาราเซลลูโลสสามารถถูกใช้เป็นวัสดุดูดซับหรือตัวพองในการประยุกต์ใช้ได้หลากหลาย



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Natural rubber (NR) sponges are a renewable biopolymer material derived from milky sap (latex) from rubber trees. In this study, composite sponges of natural rubber and cellulose (NR-C) with various compositions were synthesized. The Dunlop process was employed to prepare the NR-C sponges in various contents of cellulose fibers as reinforcing agent. The cellulose fibers were extracted from the pulp of eucalyptus trees and sodium alginate (SA) was used as dispersing agent. The aim of this work was to develop a green composite sponge with highly porous, flexible, and hydrophilic properties. The effects of cellulose loading on mechanical performance of sponge were investigated. The porous structure and surface morphology of NR-C sponges were characterized by SEM. In addition, absorption rate and water holding capacity of the sponges were determined. Under the mechanical tests, the NR-C sponges revealed higher compressive stress and higher modulus of elasticity than the NR sponge. It was also shown that the hydrophilic property of the NR-C sponges was improved by adding hydrophilic substances (cellulose and SA) that increased the polarity of the material. The NR-C sponges using 1 phr SA as dispersing agent exhibited highly porous structure with larger pore size than those without SA. Overall, the water adsorption capacity of the NR-C sponges increased with increasing cellulose fibers up to 45 parts per hundred rubbers (phr) and the maximum value was 406.73% at 30 phr cellulose and 1phr SA, which was about 1.81 times that of normal NR sponge. The study of biodegradation behavior showed that NR-C sponges could be higher degraded in soil under the natural environment as compared to NR sponges. According to their properties, NR-C composite sponges can be used an adsorbent or supporting material in many applications.

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CHAPTER I

INTRODUCTION

1.1 General introduction

The regions of Asia is considered as the world's crucial sources of natural rubber (NR), especially Southeast Asian countries accounting for one-third of global supply [1]. Thailand has grown to become the world's largest producer and exporter of natural rubber according to the data in 2019. Thai rubber farmers received high yields of rubber product because of a hot weather and monsoon climate in Thailand, it is highly conducive to rubber tree cultivation in several regions of Thailand. NR latex is an important raw material from the agricultural sector to many industries. It is one of materials that has many potential products and has a significant economic impact. Natural rubber is mainly used as a raw material for gloves, shoes, mattresses, condoms, vehicle tires, balloons, and other high-value products. However, the price of rubber in world market is considerably sensitive or unreliable. It depends on the world economic situation, petroleum price and product demands [2]. Hence, research and development of NR products are required in order to increase the demand and enhance the value of NR products for processing in many applications.

Fresh NR latex is white colloidal suspension with about 30% wt. of rubber particle contents, 55% wt. of water and other slightly components such as protein, inorganic substances, carbohydrate constituents and resin constituents from latex rubber tree [3, 4]. It is considered as a renewable and indispensable natural resource. For the utilization, fresh NR latex was centrifuged and added with ammonia as the preservative for increasing concentration of rubber fraction in latex components. NR is an elastomeric material of containing 93-95% of isoprene molecules. NR has excellent elastic properties. NR has also many outstanding properties such as high elasticity, excellent compression set, high stretch recovery and good resistance to organic acids. NR is successfully produced by plants and it has no health hazards that is required in the manufacture of many industrials. However, NR has some undesirable properties such as low heat and abrasion resistance because the high unsaturated molecules and the non-polar character in the chemical structure of isoprene are extremely quick to react at high temperature or when exposed to oxygen, ozone and sunlight. Oxidation reaction leads to the deterioration in physical and mechanical properties, leading to a negative effect on its special application [5]. Furthermore, its poor resistance to fats oils greases and strong acid. To overcome these drawbacks, the improvement of NR properties is required for usable application in the future.

1.2 Motivation of this research work

In recent years, research work on the chemical modification of NR which has been investigated for enhancing the properties of NR that involves reaction at the carbon-carbon double bond in polymer chains. Thereby, drawbacks can be successfully defeat by a number of methods, including crosslinking and grafting on polymeric side chains. The physical and mechanical property of NR improved by a chemical process called vulcanization has received much attention. Vulcanization is a chemical process that involves the formation of cross-links between long rubber molecules with sulfur bridge. The network structure formed by crosslinking conditions is the key leading to modified properties. This chemical reaction of rubber latex occurs through the application of heat and accelerators. The presence of these crosslinks increases the elasticity, tensile strength, resilience, and hardness of rubber. Due to sulfur bridges, individual chains can no longer slip over one another but are locked molecule together in an enormous size. Some additives such as zinc oxide is added to accelerate the rate of vulcanization. The vulcanized rubber is still very elastic and has good resistance to organic solvents as well. It is resistant to attack of oxidizing agents. In addition, the vulcanization rubber has good mechanical properties over the temperature ranges in which non-vulcanized rubber could not perform [6-8]. Dunlop process is a technology technique that was developed after vulcanization discovered for creating latex foam. This process was invented to obtain air cells in a matrix of latex materials by foaming with wire whip rotates in epicyclic motion. The mechanical agitation of wire whip created a void behind the latex liquid and filled latex matrix with air cells by hitting before essential gelling process that lead to the production of natural rubber foam. Finally, NR foam product was heated up for vulcanization process. However, NR polymeric materials were considered as non-polar molecules therefore the hydrophobic properties of all NR materials were clearly defined that its hydrophobic properties is incompatible with the hydrophilic substances so the converted products in these properties is exactly interesting to novel development, which was curiously carried out by adding hydrophilic materials inside the matrix of NR for composite material or by changing some molecules in NR polymer chains to polar molecules by holding hydrophilic molecules with chemical reaction.

Rubber foam are known as cellular materials because they are made by providing tiny air cells that are trapped in a soft matrix. Rubber based reinforcement materials can be made by the Dunlop process which involved mechanical agitation or whipping of latex compound into a foam with additives like soap and other ingredients for assisting the foaming process. The number of air cells, their average size and properties of latex foam rubber were carefully considered after designing to produce the finished product. As of today, green composites in term of sustainable development come into drastic attention in the population of the world. The green

composite is a composite material with environmental and ecological advantages. It can contain either natural fiber reinforcements or a natural polymer matrix, or it can be a combination of natural fiber reinforcement and natural polymer matrix together. NR is a natural matrix in raw material. The reinforcing filler from renewable resources, such as cellulose fibers can be used to improve mechanical, hydrophilic and biodegradable properties. NR composites using cellulosic fiber reinforcements are currently regarded as a priority area of research worldwide because cellulose can be extracted from agricultural waste that is the most abundant renewable biomass on the earth. The effects of cellulosic fiber on NR composite are related to the nature of cellulose, which increased many mechanical properties such as strength and modulus.

Therefore, the present study focuses on preparation of green composite sponge of natural rubber and cellulose (NR-C) with various compositions synthesized via Dunlop and vulcanization process. Cellulose fibers extracted from the pulp of eucalyptus trees were used as reinforcing agent and sodium alginate was used as dispersing agent in the fabrication of NR-C green composite sponge. The aim of the work was to develop a green composite sponge with highly porous, flexible and hydrophilic properties in order to convert general composite sponge that is hydrophobic material to composite sponge with highly hydrophilic properties by adding of hydrophilic substances that would be increased the polarity of material therefore the hydrophobic groups of NR were reduced to improving the hydrophilic properties. Moreover, the absorption capacity could be enhanced by the formation of highly connected macropore distributed throughout the composite sponge. The particle size of cellulose was characterized by SEM and PSD analysis. The porous structure and morphology of NR-C sponges were characterized by SEM and a dynamic mechanical analyzer was used to evaluate the mechanical performance of the sponges. In addition, hydrophilic property and water absorption capacity were determined.

1.3 The objectives of the research

1. To fabricate eucalyptus cellulose reinforced green composite sponge of natural rubber (NR-C) with various compositions by using Dunlop and vulcanization process for water absorbing material.
2. To improve hydrophilic properties of green composite sponge of natural rubber by cellulose loading as hydrophilic substances that could be increased the polarity of rubber material
3. To develop a green composite sponge with highly porous properties for absorption capacity by using sodium alginate toward the formation of connected macropore distributed throughout the sponge.

1.4 Scope of the research

1. Preparation of cellulose powder from eucalyptus papers, which were cut and grounded into small particles and then they were sieved with a fine mesh to obtain the cellulose powders with the average particle size of $\approx 106 \mu\text{m}$.
2. The cellulose reinforced natural rubber composite (NR-C) sponge was prepared under different loading of cellulose fibers (0–45 parts per hundred rubber) w/wo a dispersing agent by Dunlop process
3. The effects of sodium alginate loading as dispersing agent at 1 phr on the properties of NR-C sponge were investigated.
4. NR-C sponges were characterized for physical, chemical, and mechanical properties by using
 - a. Scanning electron microscopy (SEM)
 - b. Particle size analysis with PSD
 - c. Density testing
 - d. Percent shrinkage
 - e. FTIR spectroscopy
 - f. Thermal Gravimetric Analysis (TGA)
 - g. Water absorption and swelling test
 - h. Biodegradation by soil test
 - i. Compressive stress and modulus of elasticity
 - j. Compression set

1.5 Implementation plan

There are 7 steps conducted in this research work as described in **Table 1.1**

- 1.1.1 Literature review with a focus on composite materials
- 1.1.2 Preparation of cellulose particles from eucalyptus papers by using powder grinding.
- 1.1.3 Preparation and fabrication of green composite sponges of NR-C via Dunlop process.
- 1.1.4 Fabrication of bio-composite sponges of NR-C by using sodium alginate as dispersing agent.
- 1.1.5 Characterization of NR-C sponges
- 1.1.6 Discussing all experiment results and making conclusions on the research study.
- 1.1.7 Thesis writing and thesis defending examination
- 1.1.8 Preparation of manuscript for publication.

Table 1.1 Implementation plan

Activity	Monthly (2019)				Monthly (2020)				
	9	10	11	12	1	2	3	4	5
1.Literature reviews									
2.Preparation of cellulose particles									
3.Preparation and fabrication of composite sponges of NR-C									
4. Fabrication of composite sponges NR-C with sodium alginate loading.									
5.Characterization of the sponges									
6. Discussing all experiment result and making a research conclusion.									
7.Thesis writing and thesis defending examination									
8.Preparation of manuscript for publication									

1.6 Expected benefit

The developed process for the fabrication of green composite sponges of NR and cellulose (NR-C) with a highly porous structure and good chemical stability and hydrophilic properties obtained in this study can be further applied to produce the novel products used in water treatment for removal of heavy metal ions in aqueous solution and agricultural area or used in supporting material in many other applications. The development of novel products from NR can increase the demand and promote the more stable NR-Latex price in Thailand.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Natural rubber (NR) latex

NR is considered a renewable resource and an environmentally friendly material. It is a globally traded raw material used in numerous products. It is used extensively in many applications and products, either alone or in combination with other materials. The most important usage is the automotive industry. Approximately 70 percent of the world's natural rubber ends up in car tires because it has a large stretch ratio and high resilience, and is extremely water proof [9].

2.1.1 Rubber tapping and latex storage

Most of the NR latex obtained mainly from the rubber trees. *Hevea Brasiliensis* are the rubber plant species which originates from Brazil, South America that commonly grown for the milky latex of raw material. This species is preferred because it grows well under cultivation. In general, rubber trees grow in the equatorial regions around the world [10, 11]. Approximately 90 percent of the world's rubber comes from Southeast Asia. The rubber tree takes between seven and ten years to deliver the first harvest. The milky latex occurs in latex vessels in the bark outside the phloem of the rubber tree. Rubber tapping is the harvest process of latex products from the rubber tree. The harvesters make incisions across the latex vessels, deep enough to tap the vessels without harming the tree's tissue. After that, the latex is collected in small cup below the trunk of rubber. The latex is refined into rubber that is ready for commercial processing.

Fresh NR latex as a colloidal suspension is renewable natural resource which often contains 30 % wt. of rubber particles. Moreover, there is 55 %wt. of water and minor impurities of other slightly components such as protein, inorganic substances, carbohydrate constituents and resin constituents from rubber tree [12, 13] as shown in Table 2.1. Those minor impurities components as protein are important foods for the growth of micro-organisms that float in the air. Therefore, when micro-organisms attach to the surface of aqueous latex, they multiply rapidly microbial population and create acid substance which is a waste product from bacteria in latex. The aqueous latex will gradually change to acid. The pH of latex decreases occurs as a result of acidic by-products produced (volatile fatty acids). In the final step, the rubber becomes solid by coagulation process. The time period between tree tapping and coagula processing is called maturation. For latex storage, the aqueous latex will be added with ammonia solution which can be used to prevent the coagulation of natural latex as preservation of their physical properties. The aqueous latex is then centrifuged for increasing concentration to 60% as high concentrated rubber latex [14]. After centrifugation, the latex can be divided into three principal phases, namely

rubber particles phase, aqueous phase and luteoid phase. The aqueous non-rubber phase is made up of carbohydrates, proteins and amino acids that encourage the propagation of bacteria that causes latex unsteadiness due to their metabolic activities. According to, preservation of latex can be divided into two types. First, short term preservation retains field NR latex in a liquid condition for a few hours or days before processing and is particularly applied in dry rubber production. Second, long-term latex preservation is a preservation system that permits the shipment and storage of liquid latex until it is ready to be processed by the product manufacturer.

Table 2.1 Composition of fresh natural latex [13].

Constituent	Concentration (% wt.)
Dry rubber contents	25-35
Protein constituents	1.0-1.8
Lipids	0.4-1.1
Carbohydrate constituents	1.0-2.0
Amino acids	0.5-0.8
Water fraction	50-70

2.1.2 Chemical structure of rubber particles

Rubber particles is produced by centrifuged process, and its main constituent is stable dispersion of cis-1,4-polyisoprene in an aqueous phase. Some natural rubber sources, such as gutta-percha, are composed of trans-1,4-polyisoprene. Besides, the hydrocarbon composition, natural rubber contains approximately 6% non-rubber constituent of 2.2% proteins, 3.4% lipids (fatty acids), glycolipids and phospholipids and 0.4% carbohydrates. Typically, a small percentage of other materials, such as proteins, fatty acids, resins, and inorganic materials are found in natural rubber. When discussing polymer structures, natural latex can be divided into types of chemical structure.

Macrostructure considerations, The NR latex is the result of biochemical reactions which start with isopentenyl pyrophosphate within the rubber plant [15] that shown in Figure 2.1. Natural rubber is a long polymer chain like molecule that contains repeating units of glucose. The chemical name is polyisoprene. It is worth mentioning that, although natural rubber is built of repeating isoprene units, isoprene is not the starting monomer for the chemical structure. The long chain length allows for entanglement. The entanglement can help high mass of particle by holding single polymer together. When a forced is applied to the polymer strand, it is uncoiled and rotated. The single polymer strands will also slide by each other and when the force is released the polymer chains may not fully return and recover to its original structure. This movement of polymer strands is limited the usage of natural rubber. With the discovery of vulcanization, a structure could be formed with sulfur bonds linking between the individual polymer chains into a 3-dimensional network [15].

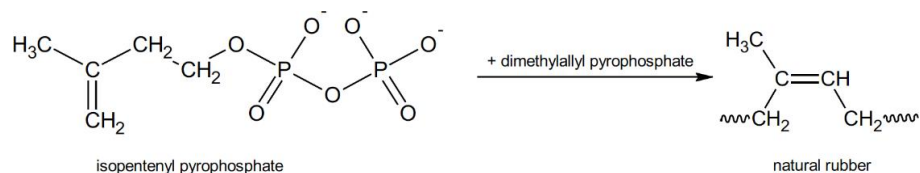


Figure 2.1 Chemical reaction of natural rubber product originated from plant [16].

Microstructure considerations, polyisoprenes can separately feature four different isomers in its polymer chain. They composed of cis-1,4; trans-1,4; 1,2; and 3,4. Isomers contain the same number of atoms of each chemical structure but have a different arrangement of those atoms. The numbers in the different isomer name refers to the individual carbon atom in each unit which is attached to adjacent units. Hence, in a 1,4 structure, carbon atoms 1 and 4 are joined in forming the chain [16]. that shown in Figure 2.2. However, natural rubber consists almost entirely of the cis-1,4 structure. When the chain unit in a polymer consists of the same isomer it is said to be stereoregular that two molecules with the same structural formula or connectivity but different 3-dimensional arrangements of atoms.

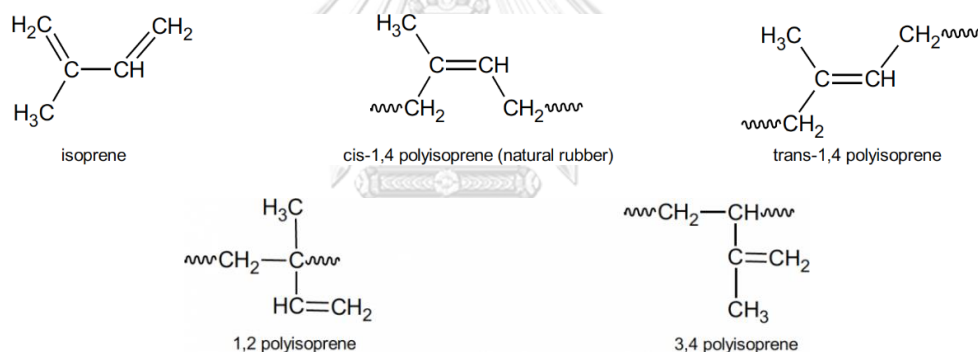


Figure 2.2 Different isomers with same structural formula of polyisoprene [16].

The dispersion of polyisoprene of natural rubber, that confers of the desirable properties to the many mechanical materials. The crystallinity of NR is a unique characteristic provided by the microstructure. If the molecular units of a polymer chain are in a regular enough spatial arrangement then interactions between these units from polar attraction, hydrogen bonding or functional groups, will form crystalline structures which stiffen the polymer. Because the chain unit in polymer molecules consists of the same structural formula called stereoregularity, NR will form crystallites upon storage and upon stretching. Specifically, these are its excellent green strength and building tack, both of which are of superior importance in tire making. For resilience, the result of natural rubber's polymer network upon curing which allows for elasticity and flexibility.

The overall chemical structure of NR latex, it consists almost entirely of the cis-1,4 polyisoprene structure and other slightly components such as protein,

inorganic substances, carbohydrate constituents and resin constituents. For nuclear magnetic resonance (NMR) studies, the structure of chain ends of rubber particle were found to contain two trans-isoprene units and an oligopeptide (protein) at one end (ω -terminal), connected to a long chain of cis-1,4-polyisoprene, and a phospholipid terminal group (α -terminal) at the other [16] that shown in Figure 2.3 and Figure 2.4 [17, 18]. These polymer terminations might also permit natural rubber to act as a functionalized polymer resulting in branching at the chain ends. The ω -terminal is often associated with proteins from the biosynthesis, while the α -terminal has been assumed to be covalently linked to a phospholipid. In addition, the non-rubber constituents in natural rubber contribute significantly to the effective properties of natural rubber in finished products.

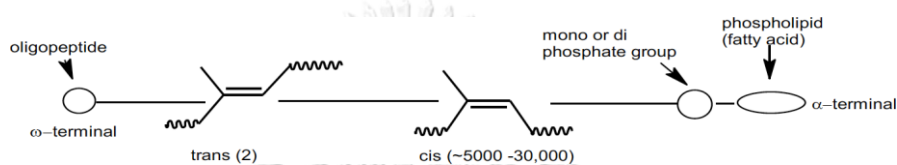


Figure 2.3 Schematic representation of natural rubber polymer chain [16].

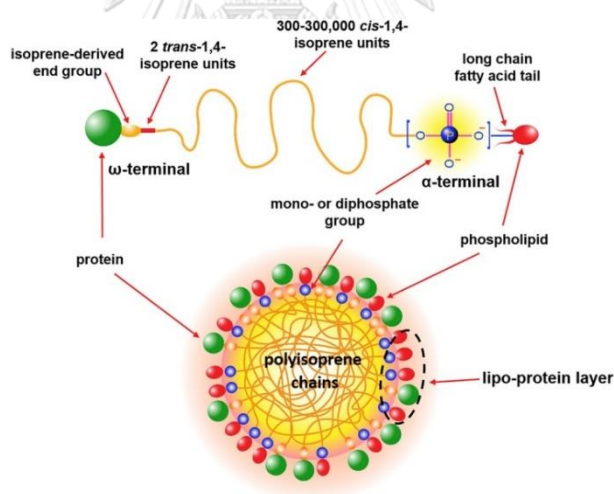


Figure 2.4 Microstructure of the natural rubber particle [17].

2.1.3 The chemical process of NR for improvement

Natural rubber is an important material in the rubber industry as it possesses excellent physical properties including high elasticity and high tensile strength. Natural rubber also has some undesirable properties such as low heat and abrasion resistance and poor ageing properties. These drawbacks might be due to the high unsaturation of the molecular chain which gives NR low heat, ageing and ozone resistance. Moreover, the non-polar character of hydrocarbon is also giving poor oil

and abrasion resistance. To overcome these drawbacks, rubber researcher either the compounding formulation, blend the natural rubber with other synthetic materials.

The main types of chemical modification of NR, it is a highly cis-1,4-polyisoprenic structure. It has a very high molecular weight of about one million. The almost pure cis-configuration results from the head-to-tail addition of an isoprene unit. The chemical reactivity of the carbon-carbon double bond of the isoprene repeating unit may be considered as C=C of alkenes. Therefore, all reactions with alkene may be applied to NR. When considered as an alkene molecule, NR is a very reactive polymer. In every repeating unit, methyl substituent is an electron donor which promotes the reactivity of C=C towards an electrophilic reagent and improves the stability of positive ions and free radicals arising from certain chemical reactions. The stability of these ions and radicals is due to the number of resonance or conjugated structures. The chemical modification of NR may be successfully carried out under various conditions including in organic solution, aqueous medium, solid, and surface modifications. The reaction could be occurred by one-step or two-step modification to obtain the required properties [19].

Chemical modification has become an required method for enhancing the properties of NR. Having a highly cis-1,4-polyisoprenic structure, the chemical reactivity of the carbon-carbon double bond can be considered similarity to that of simple olefins. Therefore, the organic chemistry reactions of olefins could be applied to NR such as halogenation and hydrogenation. Also, the non-rubber constituents may affect the undesirable reaction. Chemical reactions under environmentally friendly conditions of NR are of increasing interest. Based on the fundamentals of organic chemistry, the hydrogenation of NR latex has been successfully investigated, despite the lack of clear understanding of the reaction of the rubber particles in latex form. The epoxidation is also another chemical modification of NR which has been explored by researchers. The reaction can be carried out with NR latex by using formic acid and hydrogen peroxide, which is commercially accessible and viable. The epoxidized rubber shows better performance than original NR in terms of oil resistance, decreasing gas permeability and good compatibility with silica filler. The chemical reaction may facilitate degradation of NR, giving a low molecular weight material which can be used industrially as a viscosity modifier in rubber compounding. Numerous studies have discovered graft polymer with various vinyl monomers of new NR derivatives for the production such as thermoplastic elastomers and as a host for polymer electrolyte membranes. Moreover, NR latex can be chemically modified to photo-sensitive material used for coating applications. Another benefit obtained from the chemical modification of NR is the alteration of its properties for non-traditional applications.

2.1.4 Vulcanization process of sulfur cross-linked isoprene

Most natural rubber in utilizable everyday usage is vulcanized to improve its properties. The final properties of a rubber material depend not just on the NR polymer, but also on modifiers and fillers, such as carbon black, whiting and others. Natural rubber is susceptible to vulcanization as well as being sensitive to ozone cracking. The reaction of ozone cracking occurring between double bond of cis 1,4 polyisoprene and oxygen molecule is known as oxidative cleavage when some molecules of the oxygen gas reacts with the double bond. Vulcanization is a chemical process in which the rubber is heated with sulfur, accelerator, and activator. The process involves the formation of cross-links between rubber molecules in polymer chains so as to achieve enhanced elasticity, resilience, tensile strength, and weather resistance. Use of accelerator alone yields only a small increase in cross-link efficiency. Moreover, maximum efficiency is achieved by using accelerators together with a metal oxide. The selection of a suitable vulcanization system depends on the nature of the rubber and the service requirements of the product. Vulcanization changes the material from a formable viscoelastic to a highly elastic substance that material can return shape to its original shape after large strength.

Vulcanization is a cross-linking reaction by sulfur that generates three-dimensional network structures in rubber. It is the best process of giving rubber products greater stability. Vulcanization was discovered by Goodyear in 1839 before the development of the concept of macromolecules by H. Staudinger in the 1920s. Since then, sulfur cross-linking reactions have been improved by successive innovations in accelerators, activators, retarders, and so on, to improve processing and mechanical properties. Almost all rubber products, such as pneumatic tires for automobiles and airplanes, are still produced by using the vulcanization process [20].

Many research articles and review papers on vulcanization have been reported both from an academic and a technological viewpoint. Two conclusive reaction mechanisms of sulfur cross-linking of cis-1,4-polyisoprene are explained as models of vulcanization for natural rubber. The first is a benzothiazolesulfenamide-accelerated sulfur vulcanization reaction mechanism that is reported by Coran [20], illustrated in Fig. 2.5 while Nieuwehuizen et al. presented bis(dimethyldithiocarbamate)zinc(II)-mediated sulfur vulcanization [22] as shown in Fig. 2.6. However, details of the relationship between the reaction mechanism and the network structure of the resulting vulcanizates have not yet been conclusively clarified due to complicated chemical reactions between rubber, elemental sulfur and other cross-linking reagents during processing step of reaction. Up to now, most vulcanization processes have been developed by trial and error. Each rubber company has developed its own methods to produce materials according to customer requirements. Thereby, new aspects of vulcanization have been revealed which may help to clarify the mechanism

of vulcanization. More fundamental studies on vulcanization are needed to develop rubber science further.

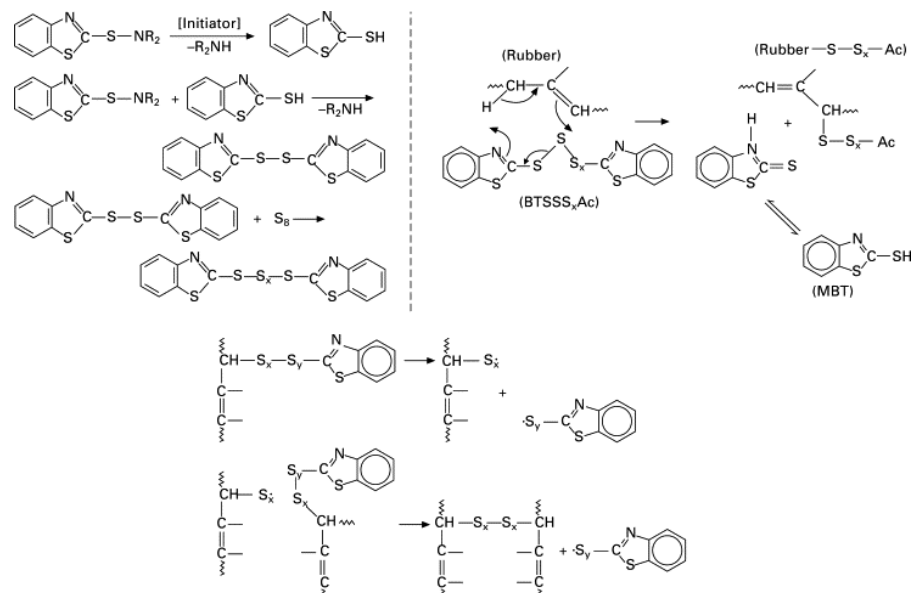


Figure 2.5 Reaction for a benzothiazolesulfenamide-accelerated; sulfur vulcanization [21].

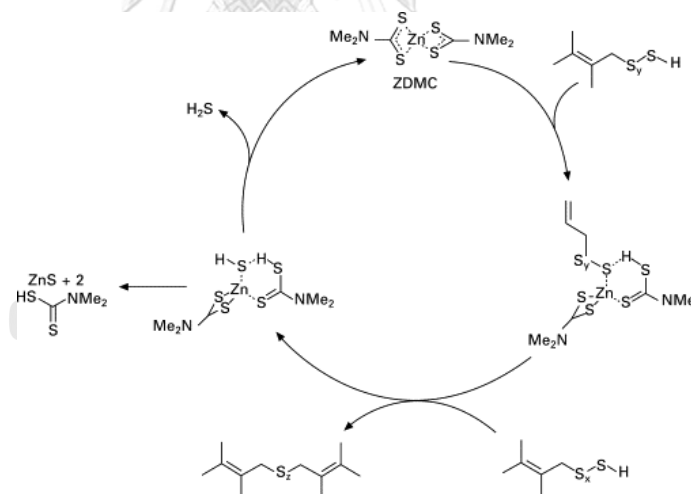


Figure 2.6 Bis(dimethyldithiocarbamato)zinc(II)-mediated sulfur cross-linked formation [21].

On the network structure of sulfur cross-linked isoprene rubber, zinc oxide has been recognized as an important component in the sulfur cross-linking reaction, but the exact role of ZnO on the network structure has not been well clarified. The stearic acid is responded with ZnO to form solubilized zinc stearate in the rubbery matrix. Generated zinc stearate reacts with sulfur and an accelerator in the rubbery matrix to form sulfur cross-links. Thus, the concentration of zinc stearate is one of the factors

that control the mesh size in the matrix. The amounts of sulfur and accelerator relative to that of ZnO become important in the presence of stearic acid in controlling the size of network domains. In other words, vulcanization reactions were activated by ZnO in the presence of stearic acid. Stearic acid was also found to effectively disperse ZnO particles in the rubber matrix [21].

2.2 Latex Foam

2.2.1 Cellular material of NR latex

Latex foam known as latex based cellular material because they are made by providing tiny air cells in a matrix. Their properties of latex foam such density, average size of air cells, water absorption was determined for involved process of latex into a foam in the presence of additives with mechanical agitation. The Dunlop and Talalay process are the most important commercial methods used for manufacture of NR foam making. The delayed action gelling agent by using sodium silicofluoride for setting is the essential key leading to the production of NR latex foam for the Dunlop process. Talalay process involved adding hydrogen peroxide or a low boiling organic solvent to the compounded NR latex and then subjecting the mixed compound to reduced pressure for foaming.

2.2.2 Dunlop process

The Dunlop process can be operated by a batch process or a continuous process. The suitable formulation has selected in order to obtain a product as in the case of general rubber product that shown in [Table 2.2](#) which is typical formulation based on natural rubber latex for compounding. Usually the formulation consists of four fragments, latex base, foaming agent, gelling agent, and curing agent. NR latex containing about 60% dry rubber content and ammonia as the preservative is the basic latex base used that is the major, either concentrated ingredients high ammonia or low ammonia, but before compounding the ammonia content has to be reduced to 0.15%. Potassium oleate solution is used as foaming agent. This also acts as a latex stabilizer when the ammonia content of the latex is decreased for foaming. Sodium silicofluoride is the primary gelling agent, while a zinc oxide/ammonium acetate combination acts as the secondary gelling agent for converting the aqueous phase of NR latex into solid phase. Diphenyl guanidine (DPG) acts as the foam stabilizer. A filler like kaolinite clay also may be used. Sulfur is the crosslinking agent while zinc diethyldithiocarbamate (ZDEC), zinc salt of mercaptobenzothiazole (ZMBT) are vulcanization accelerators. Usually compounding is done in two stages to obtain the optimal properties for the foam. This is because it is advisable to mature the first stage compound for 24 hours to get uniform distribution of ingredients

2.2.3 The steps in the batch of Dunlop process

Steps in the batch process is divided into ten topics as follows:

- Deammoniation of latex

NR latex containing about 60% dry rubber content and high ammonia as the preservative (HA) is the ordinary latex base used. For high ammonia latex concentrate, the natural rubber latex with 0.7% of ammonia contents should be declined to 0.12-0.22%. This is successfully finished by blowing in the current of wind over the surface of latex while it is being stirred by a drum shaped stirrer at 50 rpm. Moreover, Potassium oleate solution could be added carefully at a level of 0.25 to 0.5% ammonia content to reduce any risk of destabilization of the latex during deammoniation.

- Preparation of the compound

The latex is mixed with the various compounding ingredients as dispersion, emulsion, and solution in the first stage compound formulation (Part A). The ingredients added in the first stage are soap, curing agent (sulfur and accelerator required for vulcanization), antioxidant and optionally mineral fillers. The fillers of low particle size can be directly added to the latex as dry powders or can be added as slurry that is a mixture of water and small pieces of a solid. The compounding ingredients are combined with latex by stirring. Controlled addition of optional filler with appropriate stirring is essential to forestall destabilization of the latex and locally concentrated layers.

- Maturation of the compound

After the stage compound formulation in part A, the latex compound should be matured for 24 hours. This process is known to improve the uniformity and quality of the product. For commercial method, the maturation of the compound is not done in the process.

- Foaming (whipping)

The foaming process known as a Hobart mixer compose of a bowl in which a wire whip rotates in epicyclic motion. During whipping, the wire whip should take or move so fast that hitting of wire whip can create a void behind the latex. The void gets filled with air and thus a large bubble from the air gets trapped in the latex compound. Subsequent rotation of the whip breaks the large bubble into little ones so the whipping rotation can have various speeds. This process is continued carefully until the desired expansion is achieved. The last epicyclic motion of the whip receives a few large air bubbles, which usually operate at the surface of the compound. After whipping proceeds, the volume of the foamed latex compound spreads and passes through a maximum. Therefore, the compound contains bubble of varying rang of size in this step. Next, after the compound has achieved the volume of foamed latex at maximum expansion, the whipping speed of mixer is reduced known as refining process. During refining process, all of the large air bubble is comminuted to little uniform size and the foam stabilizer is added.

- Addition of gelling agent

A commonly used gelling agent is sodium silicofluoride in conjugation with zinc oxide. The amount of sodium silicofluoride to be used depends upon the pH of the latex and it is added as dilute aqueous solution. The sodium silicofluoride performs as the primary gelling agent. It is added carefully for setting the foam before vulcanization, while integrating reagent of zinc oxide and ammonium acetate acting as the secondary gelling agent is added separately in the small air bubbles of latex compound. Normally, the gelling agent is added as aqueous dispersion at 20% w/w and its pH ranging is adjusted to 6-7 before addition to latex compound.

- Pouring the sensitized compound into mould

The latex compound is immediately transferred into a mould by pouring that is designed to create the shape and size of the finished product. For standard form of designing product, mould shrinkage should be considered when ending the process. While pouring the compound into the mould, some excess compound will run over through the sides of the mould. This surplus is useful for checking the gelling product.

- Gelling

After the latex compound is attached by addition of gelling agent, the rubber particles assemble to become a single existence together that is the destabilization of the colloidal phase. The gelling can be observed by checking the consistency of surplus on the sides of mould. Usually, the time required for gelling is about 3-5 minutes. The gelling time depends on the quantity of gelling agent and temperature of the mould after pouring the compound foam.

- Curing

After finished gelling step, the compound foam in mould is kept in a steam chamber for vulcanization. The vulcanization is the process of establishment of sulfur bridges between different chains of latex molecules. The network structure formed by crosslinking condition is the key leading to modified properties. The suitable time of vulcanization depends on the thickness of the final product that varies from 20-50 minutes.

- Removal of the product from the mould

After curing, the mould is taken out from the steam chamber. The cured product is stripped carefully from the mould.

- Washing and drying

The finished product is washed in running water by passing it through water sprays and squeeze rolls. Finally, the rubber foam is dry squeezed to remove water inside the porous structure. Washing of product removes residual soluble substances, which can lead to poor ageing, poor resilience and unfavorable odour. Next, the rubber foam is taken in circulating oven at 60-70 °C for 12-14 hours for actual drying.

During drying the product is usually laid on strong flat without distortion to avoid permanent deformation of rubber form such as mesh grid. If the product dried in touching with each other, product has tendency to stick together because slight post curing takes place during drying. After drying step, the finished product is trimmed carefully to displace some defect points [22, 23].

Table 2.2 A typical formulation of natural rubber latex foam via Dunlop process [22].

Part A (First stage compound)		
Compounding ingredients	Dry weight (g)	Actual weight (g)
Centrifuged natural rubber latex	100	167
Potassium oleate solution (20%)	0.5	2.5
Sulfur dispersion (50%)	2.0	4.0
ZDEC dispersion (50%)	1.0	2.0
ZMBT dispersion (50%)	1.0	2.0
SP emulsion (50%)	1.0	2.0
Part B (During processing compound)		
Potassium oleate solution (20%)	0.5	2.5
Potassium castor oil soap solution (30%)	0.25	0.83
Kaolinite clay (dry powder)	20	20
DPG dispersion (50%)	0.75	1.5
Zinc oxide dispersion (50%)	5.0	10.0
Ammonium acetate solution (20%)	1.0	5.0
Sodium silicofluoride dispersion (20%)	1.0	5.0
Colour concentrate dispersion (20%)	1.0	5.0

2.3 Cellulose fiber

2.3.1 General introduction of cellulose

Cellulose was discovered in 1838 by Anselme Payen, French chemist. He isolated cellulose from plant components and obtained its chemical formula. Cellulose is the most abundant of all naturally occurring organic compounds on the earth. It is the main substance in the walls of plant cell as primary cell wall, helping plants to remain strong and upright. First, cellulose was used to produce successful thermoplastic polymer by Hyatt Manufacturing Company in 1870. Next, production of rayon as artificial silk from cellulose began in the 1890s and production of cellophane was successful invented in 1912. Cellulose is a natural linear polymer as polysaccharide with the formula ($C_6H_{10}O_5$). The molecular repeating unit comprised of a pair of glucose ring units joined by β (1 \rightarrow 4) glycosidic oxygen linkages around which molecular structure can bend and twist. The polysaccharide molecule consists of several hundreds to many thousands of glucose units which is composed of carbon, hydrogen, and oxygen atoms. Generally, the cellulose content of cotton fiber is 90 percent and 50 percent of wood [24, 25]. As of today, the cellulose for industrial products as raw material is mainly obtained from wood pulp and cotton by separation process from lignin and other components of plant constituents.

The four different pathways that were determined the major processing routes that shown in Fig. 2.7. The most famous and highly used pathway is the manufacture

of cellulose from plants. It is established that cellulose is found in its purest form from the seed hairs of cotton. The wood cellulose, on the other hand forms a composite with lignin and other polysaccharides, which is separated by large scale chemical pulping and purification processes in many commercial scale [26]. Cellulose can be derived from algae, some specific bacteria, and fungi. The molecular structures of cellulose from bacteria are used for research on nanocellulose structures, reactivity, and crystallinity with further note on development of biomaterials and new substances. Cyanobacteria are known to biosynthesize cellulose. The first synthesis of cellulose *in vitro* is reported as the cellulucellulase. Cellulose formation was processed in a ring opening polymerization of the d-glucose moieties by catalyzed cellobiosyl fluoride and the chemosynthesis.

In human nutrition, cellulose is a non-digestible constituent of insoluble dietary fiber however it is important in the diet as fiber. Cellulose can act as hydrophilic bulking agent for feces and potentially aiding in defecation which can support digestive system due to keeping food moving through the alimentary tract and pushing waste out of the body. The cellulose is a mainly food for herbivorous animals particularly termites and ruminants such as horses, cows, and sheep. These can digest cellulose with the help of symbiotic micro-organisms that retain cellulose long enough for digestion by their guts in the alimentary tract. Micro-organism living in the guts is very importance for this digestible process. In addition, protozoans in the alimentary tract of insects such as termites also digest the cellulose. Therefore, they can receive energy and essential nutrients for their life from grass.

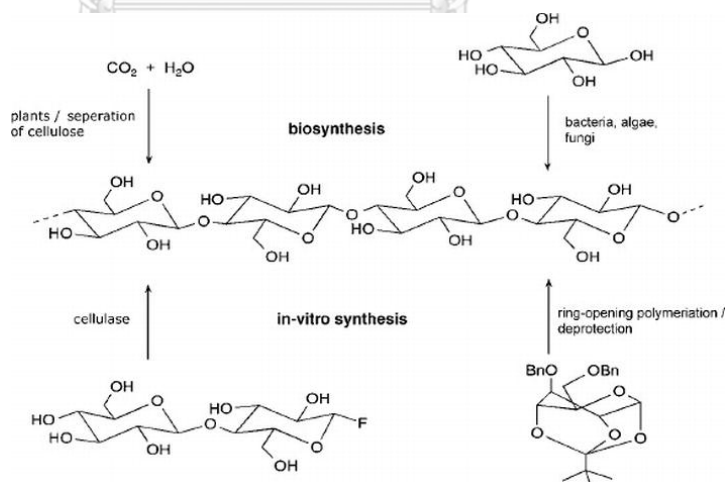


Figure 2.7 The different pathways of cellulose processing [26].

2.3.2 Chemistry and structure of cellulose

Plant-derived cellulose is usually found in a mixture with hemicellulose, lignin, pectin, and other substances while bacterial cellulose is quite pure. The Cellulose is made up of a d-glucose unit which condense through $\beta(1\rightarrow4)$ -glycosidic

bonds at one end and a C4-OH group, the non-reducing end, while the terminating group is C1-OH, the reducing end with aldehyde structure. The molecular structure is responsible for its significant properties: Chirality, hydrophilicity, degradability, and chemical variability due to high reactivity from the donor group—OH. The superior hydrogen bonds add crystalline fiber structures to cellulose. This linkage motif contrasts with that for α (1 \rightarrow 4)-glycosidic bonds present in starch and glycogen. Compared to starch, cellulose is also much more crystalline. Whereas starch undergoes a crystalline to amorphous transition when heated beyond 60–70 °C in water, cellulose requires a temperature of 320 °C and pressure of 25 MPa to become amorphous in water. Cellulose is a straight chain polymer. Cellulose contains 44.44% carbon, 6.17% hydrogen, and 49.39% oxygen. The chemical formula of cellulose is $(C_6H_{10}O_5)_n$ where n is the degree of polymerization and represents the number of glucose groups [27].

The structure of cellulose as depicted in Fig. 2.8 consists of hydroxyl groups of β -1,4-glucan cellulose at C₂, C₃ and C₆. The CH₂OH group is positioned relative to the C₄ and C₅ bonds along with shear relativity with O₅-C₅ bonds. The crystal structure in particular is determined by the X-ray. The investigations was clearly indicated that the cellulose crystalline structures have a triclinic and monoclinic unit cell. As described above, the cellulose consists of crystalline and amorphous regions. Several different crystalline structures of cellulose are known, corresponding to the location of hydrogen bonds between and within strands. Natural cellulose is cellulose I, with structures I α and I β . Cellulose produced by bacteria and algae is enriched in I α while cellulose of higher plants consists mainly of I β . Cellulose in regenerated cellulose fibers is cellulose II. The conversion of cellulose I to cellulose II is irreversible process.

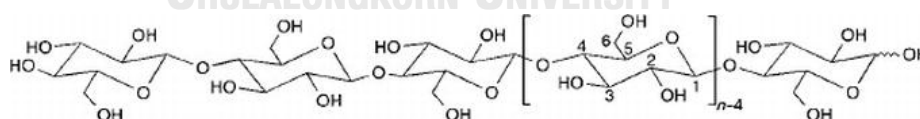


Figure 2.8 Molecular structure of cellulose [26].

2.3.3 Breaking down of cellulose

In general, cellulose can be chemically broken down into glucose units by cellulolysis process, The cellulolysis is the process of breaking down cellulose into smaller polysaccharides called cellooligosaccharides. Cellulolysis is a hydrolysis reaction because cellulose molecules bind strongly to each other. This process can be essentially intensified in a proper solvent such as in an ionic liquid and acid solvent [28, 29]. Moreover, cellulose can be broken down by enzymatic process. Some ruminants like cows and sheep contain symbiotic bacteria in the flora of the rumen,

and these bacteria produce enzymes called cellulases that help the microorganism to digest cellulose; the breakdown products are then used by the bacteria for proliferation. The bacterial mass is later digested by the ruminant in its digestive system. Horses use cellulose in their nutrition by fermentation process in their hindgut via symbiotic bacteria which produce cellulase enzyme to digest cellulose. Similarly, some termites contain in their hindguts certain flagellate protozoa producing such enzymes, whereas others contain bacteria or may produce cellulase. The enzymes used to cleave the glycosidic linkage in cellulose are glycoside hydrolases including endo-acting cellulases and exo-acting glucosidases [30]. Another process of breaking down cellulose is pyrolysis reaction by decomposition of substance at temperatures above 350 °C, cellulose undergoes thermolysis, decomposing into solid char, vapors, aerosols, and gases such as carbon dioxide [31].

2.3.4 Properties of cellulose

The cellulose from wood pulp has typical chain lengths between 400 and 1600 units while the cotton and other plant fibers as well as bacterial cellulose have chain lengths ranging from 900 to 11,000 units. Molecules with small chain length resulting from the breakdown of cellulose are known as cellodextrins. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighbor chain holding the chains firmly together side-by-side and forming microfibrils with high tensile strength. This confers tensile strength in the cell walls where cellulose microfibrils are meshed into a polysaccharide matrix. The high tensile strength of plant stems also arises from the arrangement of cellulose fibers intimately distributed into the lignin matrix. The mechanical role of cellulose fibers in the wood matrix is responsible for its strong structural resistance. Moreover, the cellulose has no taste and odorless. It is insoluble in water and most organic solvents. Cellulose fiber is a natural resource for biodegradable substance that can be applied to improve mechanical, hydrophilic properties and biodegradable properties.

2.3.5 Applications of cellulose

Recently, cellulose can be used to paper making that cellulose is the major constituent of paper because it is mainly processed to produce card stock, paperboard, and fiber that paper making needs numerous quantities. In addition, cellulose is also the main ingredient of textiles made from cotton linen and other plant fibers. Cellulose powder is used in processed cheese to prevent caking inside the package. Moreover, cellulose can be chemically converted or modified into derivative products such as cellophane and rayon. Both cellophane and rayon are known as regenerated cellulose. They can also be used for textile. They are recognized as cellulose in chemical structure which made from dissolving pulp. Other cellulose derivatives are used as adhesives, explosives, and thickening agents of food and drug tablet. Further,

its usage is seen in the pharmaceutical section as inactive fillers in drugs in the form of powdered cellulose.

Use of cellulose in renewable energy, the population of the world coupled with an exponential increase in technological advancements. The fossil fuels are being rapidly depleted. The term of sustainable development receives attention and comes into play now. Recent studies have exhibited that due to increase in demand of energy, the cost of biofuel is increasing as well as fossil fuel. Further, there is a significant reduction in the carbon emission. The bioethanol successfully obtained from cellulose used as an alternative substrate in the production of biofuel. This is a very good source for renewable energy as it is found most abundantly in stalks, leaves and branch of green plants. Cellulose as renewable material can be broken down into fermentable sugars by using the enzyme or by using acid to convert them into sugar. Another way of sugar, bioethanol fuel is mainly produced by the sugar fermentation process with yeast at suitable conditions.

Use of cellulose in consumables, cellulose has numerous applications in the field of food technology. Further, cellulose is indigestible by human beings that it tends to have zero caloric value. For food, due to its unique physical and chemical properties and its behavior in water, it is today being increasingly used a food additive to improve the bulk and fiber content of foods. It can also be used in excessive amounts in diet foods to create a sensation of fullness. Therefore, the cellulose have been used in food to serve several purposes.

Use of cellulose in biomedical and pharmaceutical applications, cellulose is extensively used in the field of biomedicine and pharmaceuticals. The price of pharmaceutical products is expansively high due to production factors such as high cost, difficulty in process of the material and complicated processing steps. These problems can be remedied by using of cellulose as filling agent. Moreover, cellulose based models in novel drug delivery systems seemed like distinctive candidates due to their projected benefits. Cellulose based drug delivery systems are considerable step in green and sustainable pharmacy which focuses on toxicity reduction, biodegradability, and less hazardous synthesis.

2.4 Green composites using NR and natural fiber reinforcements

2.4.1 Green composites using natural matrices and fiber reinforcements

The term of green composites is normally used to describe a composite material with environmental and ecological advantages over conventional composites. The green composites might contain either natural fiber reinforcements or natural matrix of polymer, or it can be a combination of natural fiber reinforcement and a biodegradable polymer matrix together. Natural rubber is a possible polymer matrix material. NR is important since it possesses the general features of other rubbers such

as high tensile strength and elongation at break. NR is produced by plants which is renewable and inexpensive. Besides, it has no health hazards. Even though NR is advantageous material in many respects, it does suffer certain disadvantages. Their strength is lower than that of other engineering polymer such as nylon and thermosets such as polyester epoxy. Hence, the products based on NR often suffer from breakage and puncture. Moreover, it possesses poor crack resistance by ozone and oil conditions. These drawbacks can be overcome by many methods such as cross-linking or vulcanization.

However, even though the natural polymer can be produced elastic products by vulcanization, their strength is low. Hence it is necessary to increase the strength further by incorporating fillers that have different physical forms. This leads to the production of a special properties of material known as composites. The fibrous reinforcing constituent of composites may consist of thin fibers or relatively short fiber segments. Thin fiber reinforced composites with high aspect ratio of length to diameter are generally required for high performance of structural applications. Depending on the fibers within the matrix of natural polymer, composites can be fabricated with structural properties specifically tailored to particular use. For example, polymers concretes are increasingly being used in buildings and other structures. They represent a new structural material with its tolerating highly corrosive environments. It can be utilized in economical and innovative structures [32].

A schematic representation of composites is given in Fig. 2.9. Fiber reinforcements represent a physical rather than a chemical feature of converting a material to proper composite. The fibers dispersed in the matrix may be continuous or discontinuous. In continuous fiber reinforcement, the transference of the load from matrix to the fibers will be comfortable and effective whereas in discontinuous fiber reinforcement, the fibers must be of sufficient length to have effective load transference that the properties of the composite vary with fiber length [12].

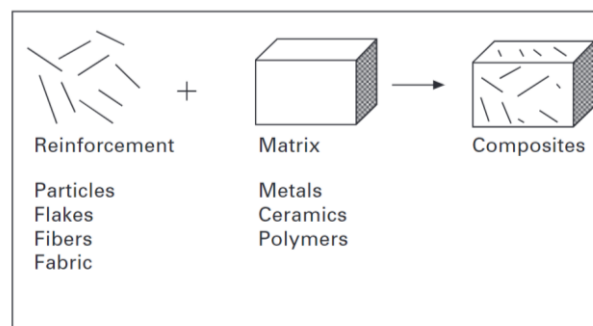


Figure 2.9 The reinforcing constituent of composites for improving properties [12].

The difficulty relating to the use of fibers in composites is the lack of good adhesion to most polymeric matrices. The hydrophilic nature of natural fibers

adversely affects adhesion to a hydrophobic matrix. As a result, strength may be lost. To prevent this reduction, the fiber surface must be modified since it can promote adhesion. Several methods to modify the natural fiber surface have been reported such as graft copolymerization of monomers onto the fiber surface. It can improve fiber–matrix adhesion. The mechanical properties of fiber-reinforced polymer composites depend not only on the properties of their constituents, but also on the properties of the region immediately surrounding the fiber, known as the interphase. Stress transfer from the matrix to the fiber takes place at the interphase and it is therefore important to characterize its properties for understanding the performance of the composite. The optimal mechanical properties in a composite depend mainly on the fiber orientation, but the adhesion between the fiber and the matrix is also important. This is especially true for short fiber reinforced composites. The fibers are loaded through the matrix for good performance, the load should be transferred effectively to the fiber so that a strong fiber/matrix bond is required. By controlling factors such as the aspect ratio and orientation of the fibers, and by establishing a high degree of fiber dispersion and fiber–matrix adhesion, reasonably good rubber products can be fabricated using short fibers.

The properties of a fiber reinforced matrix are governed by many factors including the mixing of rubber compounds, fiber dispersion, fiber orientation, fiber breakage, aspect ratio of the fiber, fiber–matrix adhesion, fiber concentration, etc. Natural fiber reinforced polymer composites are superior to synthetic fiber reinforced composites in properties such as biodegradability, combustibility, weight, toxicity, environmental pollution, cost, recyclability, etc. These advantages place natural fiber composites among the class of high performance which have both economic and environmental advantages. Reinforcement of polymers with vegetable fibers also yields opportunities for the effective utilization of agricultural products. They are combustible in the absence of production of either toxic gases or solid residues [21–24]. Short fibers can be easily incorporated into the rubber compound along with other ingredients. Mechanical properties such as specific strength and stiffness, reduced shrinkage in molded products, resistance to solvent swelling, abrasion, tear and creep resistance are greatly improved in the case of short fiber composites [12].

2.4.2 Natural rubber composites using cellulosic fiber reinforcements

The importance of natural rubber/cellulose composites, cellulose is the most widely spread organic renewable material, endowed with outstanding properties and a variety of useful applications. When the reinforcement is constituted by cellulosic materials, there are additional features like biodegradability and renewability, along with the inherent stiffness. Cellulose is also relatively inexpensive and has a much lower density than most fillers that are in use today [33, 34]. Natural rubber is an amorphous material, but a very strong matrix because of its strain-induced crystallization. Reinforcing fillers from renewable resources, such as plant-based

natural fibers, can be thought of as a potential alternative for the production. Short fiber reinforcements of rubber are a subject of interest to large number of researchers. These composites exhibit the combined behavior of the soft from elastic rubber matrix and the stiff from strong fibrous reinforcement. The use of short fibers makes it almost impossible to obtain the high level of reinforcement. Many researchers have reported the processing advantages and improvements in the mechanical properties of short fiber reinforced rubber composites.

Use of cellulose in composites, cellulose is the main component of vegetable fibers and the unit of a cellulose macromolecule contains three hydroxyl ($-OH$) groups. These hydroxyl groups form hydrogen bonds inside the macromolecule itself and between other cellulose macromolecules. These cellulose fibers can impart benefits such as low density, less machine wear during processing than is generated by mineral reinforcements, no health hazards, and a high degree of flexibility. Also, natural fibers impart high specific stiffness and strength to the composite. Most importantly, they have a low cost per unit volume.

The reinforcing efficiency of natural fiber is related to the nature of cellulose and its crystallinity, which in turn is dictated by its molecular weight. The primary effects of short fiber reinforcement on the mechanical properties of NR composites include increased modulus, decreased elongation at failure, greatly improved creep resistance over particulate-filled rubber, increased hardness and a substantial improvement in cut, damping and processing economy, tear and puncture resistance. Nowadays cellulose is also produced at a nanoscale in different ways. Such nano cellulose is typically ultra-strong and has, in addition, several other interesting properties like super-hydrophilicity and interesting rheological properties. The uses are expected to be in new lightweight composite materials to be used in transport and electronic applications. The most widely used natural fibers as filler for NR composites is a lignocellulosic fiber considered as hard cellulosic fiber because of its high tensile modulus and low elongation at break. The quality of a composite can be increased through the preservation of high aspect ratio of the fiber, control of the fiber alignment, generation of a strong interface through physical-mechanical bonding and establishment of a high degree of dispersion.

Fibers with chemical and physical surface treatments can also be obtained for improving the mechanical properties of final products. Some examples of fiber treatments are dipping, surface roughening, and chemical modification. The rubber can also be treated by mixing ingredients in the rubber that enhance adhesion or by grafting functionalities to the rubber polymer. The commonly used commercial dip is resorcinol formaldehyde latex [35].

2.4.3 Use of NR/cellulose composites in applications

For applications, numerous advantages result from the use of cellulosic reinforcements in composites with NR since both are obtained from renewable, biodegradable sources, being low cost, low density materials. Short-fiber reinforcement of rubber exhibits the combined behavior of the soft elastic rubber matrix and the stiff, strong fibrous reinforcement. Those composites are preferred in products such as V-belts and hoses because of their easy processability and high green strength, and the possibility of producing complex-shaped articles. Bagasse in natural and synthetic rubber composites showed both improved tensile strength and barrier properties and increased rate of rubber degradation in soil. Coir fiber has certain advantages over other natural fibers. It possesses high weather resistance due to its higher amount of lignin, and research has been undertaken to identify new fields of applications such as reinforcement of polymers. The advantages of nanocomposite materials when compared to conventional composites are their superior thermal, mechanical and barrier properties at low reinforcement levels as well as their better transparency [35-37].

2.5 Literature reviews

In this part, the relevant information involving NR composite sponges using cellulosic reinforcements have been provided. Furthermore, the detail about the sulfur-vulcanization process, the preparation of bio-composite sponges of NR with various compositions has been summarized.

Ab Rahman, Norfaizal, & Azura, (2019) [38] studied on the object of the influence of sago starch dispersion on mechanical properties of biodegradable natural rubber latex film. The purpose of this study focused on the effect of different types of dispersing agent; anchoid, sodium alginate and CMC to the starch dispersion on the mechanical properties and swelling index of NR films. The swelling properties and crosslink density values with different types of dispersing agent are presented in Table 2.2. Based on the results obtained, sodium alginate gave better swelling index and mechanical properties. Moreover, it is high crosslink density than CMC. The suitability of sodium alginate as dispersing agent for reinforcement dispersion can be beneficial to improve the stability and viscosity of NR latex.

Table 2.3 Swelling index and crosslink density of NR latex with different sago starch dispersion [38].

Sample	Swelling index (%)	Crosslink density (mol/cm ³)
NR + SS/An	458.82	0.0436
NR + SS/SA	449.35	0.0483
NR + SS/CMC	449.21	0.0401

Sanhawong, Banhalee, Boonsang, & Kaewpirom, (2017) [39] investigated the effect of concentrated NR latex (CNRL) on the properties and degradation behavior of cotton-fiber (C6)-reinforced cassava starch bio-foam. The cotton fiber and concentrated NR were incorporated into the bio-foam products in this experiment. Starch bio-foams without concentrated NR and cotton-fiber exhibit high moisture content because of the inherent hydrophilic nature of native cassava starch that shown in Figure 2.10. The moisture adsorption capacity of the foam decreased with increasing NR content up to 5 phr because NR latex was a hydrophobic substance as moisture resistance. As evidenced by contact angle measurements, the addition of high CNRL content in the foam increased better wetting with oil or enhanced hydrophobicity but decreased hydrophilicity of material that shown in Figure 2.11. The results are in good agreement with those obtained from moisture content measurement discussed above.

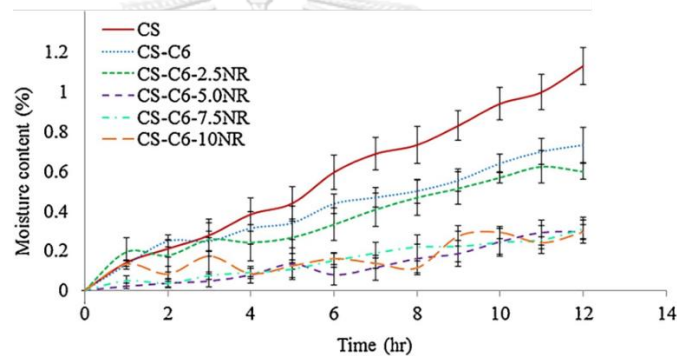


Figure 2.10 Moisture content of the starch bio-foams as a function of time [39].

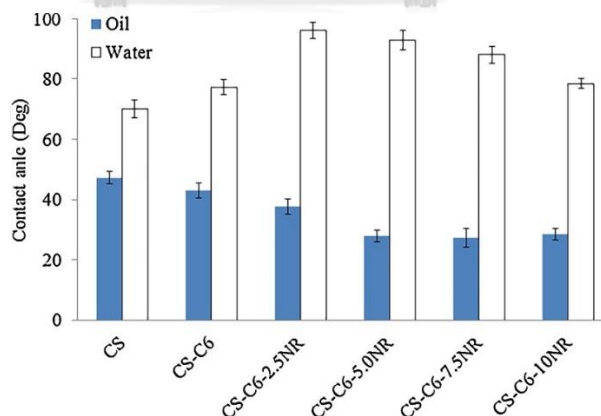


Figure 2.11 Oil and water contact angles on the starch bio-foam surface [39]

CHAPTER III

EXPERIMENTAL

The methodologies of this study, for the fabrication eucalyptus cellulose reinforced green composite sponge via Dunlop and vulcanization process, the study of the effects of cellulose fibers and sodium alginate on the porous structure and hydrophilic properties of NR-C sponges and its characterization of chemical and mechanical properties have been summarized in this Chapter. Chapter III, Experimental is divided into five topics as follows:

3.1 Materials and chemicals

The specification of raw material and chemicals used in the fabrication process could be summarized as follows. The formulation for Dunlop process consists of four fragments, latex base, foaming agent, gelling agent, and curing agent. High ammonia concentrated natural latex was purchased from Thai rubber latex that fresh rubber is obtained commercially from the sap of trees called *Hevea brasiliensis*. These trees yield a latex containing approximately 35% rubber hydrocarbon (rubber plant grown in Songkhla, Thailand) with properties of total solids contents of 62.59% and ammonia as the preservative is the basic latex base used (HA). The eucalyptus cellulose fibers with 100% of cellulose contents was kindly provided by Teppatana Paper Mill Co., Ltd, Thailand. Sodium alginate (SA) was supplied by Acros, China.

3.2 Preparation of eucalyptus cellulose

Cellulose fibers extracted from the pulp of eucalyptus trees were used as reinforcing agent in the fabrication of NR-C green composite sponges. The eucalyptus sheets received from the collaborated company were dried to discharge moisture by an oven at 60 °C and then cut into small pieces for powder preparation. The dried small pieces of cellulose fibers were grinded into powder by Ball Mill machine (Scientific Promotion Co., Ltd) and then sieved in order to obtain the smaller particles with an average size of 106 µm and then all of samples were collected in desiccator before adding with centrifuged natural rubber latex into the fabrication of NR-C green composite sponges by Dunlop process.

3.3 Fabrication of NR-C composite sponge with various compositions

Green composite sponges of natural rubber and cellulose (NR-C) with various compositions were synthesized via Dunlop process. The delayed action gelling agent by using sodium silicofluoride for setting is the essential key leading to the final production of latex foam for the Dunlop's process. The suitable formulation has selected in order to obtain a finished product in this analytic experiment that shown in [Table 3.1](#). Potassium oleate solution is used as foaming agent. This also acts as a latex stabilizer when the ammonia content of the latex is decreased for foaming. Sodium

silicofluoride dispersion (SSF) is the primary gelling agent, while a zinc oxide/ammonium acetate combination acts as the secondary gelling agent. Diphenyl guanidine dispersion (DPG) acts as the foam stabilizer. Sulphur dispersion is the crosslinking agent while zinc-diethyl dithiocarbonate (ZDEC), zinc salt of mercaptobenzthiazole (ZMBT) are vulcanization accelerators. Poly dicyclopentadiene-co-P-cresol (CPL) is the antioxidant to protect the finished product against oxidative degradation. For Dunlop process, compounding ingredients are done in two stages to obtain the optimal properties for the foam. This is because it is advisable to mature the first stage compound to get uniform distribution of ingredients and partial pre-curing. The physical properties of the foam are also improved by the maturation of the initial compound [22, 23].

Table 3.1 The formulation and function of chemical substance for Dunlop process in NR-C green composite sponges

Compounding ingredients	Function
Part A (First stage compound)	
Centrifuged natural rubber latex	natural polymer matrix
Cellulose compound	natural fiber reinforcement
Potassium oleate solution	foaming agent and stabilizer
Sulphur dispersion	crosslinking agent
ZDEC dispersion	vulcanization accelerators
ZMBT dispersion	vulcanization accelerators
CPL solution	antioxidant
Part B (During processing compound)	
DPG dispersion	Secondary gelling agent
Zinc oxide dispersion	secondary gelling agent
Ammonium acetate solution	secondary gelling agent
Sodium silicofluoride dispersion	primary gelling agent

Steps in the batch process

3.3.1 Preparation of the compound

The slurry that is a mixture of cellulose fillers and sodium alginate solution as dispersing agent was successfully prepared by mixing the various cellulose for different loading (0, 15, 30, and 45 parts per hundred rubber) and sodium alginate (SA) loading at 1 parts per hundred rubber while it was mechanically stirred by a drum shaped stirrer at 5 minutes or until a homogenous mixture was obtained under the room temperature ($\approx 25^\circ\text{C}$) before adding into the centrifuged natural rubber latex containing high ammonia as the preservative (HA). The 150 grams of centrifuged NR latex in presence of slurry were mixed with the compounding ingredients as dispersion and solution in the first stage compound formulation (Part A) that is shown in Table 3.2. The ingredients added in the first stage are soap, curing agent (sulfur and accelerator required for vulcanization), and antioxidant. The soap or potassium oleate solution could be added carefully to reduce any risk of destabilization of the latex during deammoniation. The compounding ingredients are combined with latex by

stirring with glass rod at 25°C for 10 minutes. Carefully, controlled addition of fiber fillers with appropriate stirring is essential to forestall destabilization of the local latex layers.

3.3.2 Deammoniation of latex

The ammonia content of the centrifuged NR latex must be reduced before the foaming process. The NR latex containing high ammonia as the preservative (HA) is the ordinary latex base used. For this high ammonia latex concentrate, the natural rubber latex with 0.7% of ammonia contents should be declined to 0.12-0.22%. This is successfully finished by blowing in the current of wind over the surface of latex while it is being stirred by using stand mixer (Nanotech Quality Products, NT-3050, Thailand).

3.3.3 Maturation of the compound

After the stage compound formulation in part A, the latex compound should be matured for 24 hours. This process is known to improve the uniformity and quality of the product. For commercial method and this experiment, the maturation of the compound is not done in the process.

3.3.4 Foaming (whipping)

The foaming process known as a Hobart mixer compose of a bowl in which a wire whip rotates in epicyclic motion. The latex compound was continually stirred by using stand mixer (Nanotech Quality Products, NT-3050, Thailand) at 25 °C. During whipping, the wire whip should take or move so fast that hitting of wire whip can create a void behind the latex. The void gets filled with air and thus a large bubble from the air gets trapped in the latex compound. Subsequent rotation of the whip breaks the large bubble into little ones so the whipping rotation can have various speeds. This process is continued carefully until the desired expansion is achieved. The last epicyclic motion of the whip receives a few large air bubbles, which usually operate at the surface of the compound. After whipping proceeds, the volume of the foamed latex compound spreads and passes through a maximum. Therefore, the compound contains bubble of varying rang of size in this step.

3.3.5 Refining

After the compound has achieved the volume of foamed latex at maximum expansion, the whipping speed of mixer is continually reduced. During refining process, all of the large air bubble is comminuted to little uniform size and the foam stabilizer is added.

3.3.6 Addition of gelling agent

Sodium silicofluoride dispersion performs as the primary gelling agent. It is added carefully for setting the foam before vulcanization, while combined reagent of DPG and zinc oxide dispersion acting as the foam stabilizer and the secondary gelling agent is added separately in the small air bubbles of latex compound together. The involved concentration of various formulations is presented in [Table 3.2](#). Normally, the gelling agent is added as aqueous dispersion at 20% w/w and its pH ranging is adjusted to 6-7 before addition to latex compound.

3.3.7 Pouring the sensitized compound into mould

The latex compound is immediately transferred into an aluminum mould by pouring that is designed to create the shape and size of the finished product. For standard form of designing product, mould shrinkage should be considered when ending the process. While pouring the compound into the mould, some excess compound will run over through the sides of the mould. This surplus is especially useful for checking the gelling product.

3.3.8 Gelling

After the latex compound is attached by addition of gelling agent, the rubber particles assemble to become a single existence together that is the destabilization of the colloidal phase. The gelling can be observed by checking the consistency of surplus on the sides of mould. Usually, the time required for gelling purpose is about 3-5 minutes. The gelling time depends on the quantity of gelling agent and temperature of the mould after pouring the compound foam.

3.3.9 Curing

After finished gelling step, the compound foam or gelled sponge in mould was kept in a steam chamber at 105 °C for vulcanization. The vulcanization is the process of establishment of sulfur bridges between different chains of latex molecules. The network structure formed by crosslinking condition is the key leading to modified properties. The suitable time of vulcanization depends on the thickness of the final product that varies from 20-50 minutes.

3.3.10 Removal of the product from the mould

After curing, the mould is taken out from the steam chamber. The cured product was stripped carefully from the aluminum mould.

3.3.11 Washing and drying

The finished product is successfully washed in running water by passing it through water sprays and squeeze rolls. Finally, the rubber foam is dry squeezed to remove water inside the porous structure. Washing of product removes residual

soluble substances and excessive non-reacted chemical reagents. Next, the NR-C green composite sponge was taken in circulating oven at 60-70 °C for 12-14 hours for evaporating water within the matrix of natural rubber sponges. During drying the product is usually laid on strong flat such as mesh grid without distortion to avoid permanent deformation of rubber form because slight post curing takes place during drying. After drying step, the finished product was trimmed carefully to displace some defect points and was kept in a plastic zip-lock bag before characterization.

Table 3.2 The various formulations of green composite sponge and latex chemicals filled cellulose reinforced NR bio-sponge with various compositions

Compounding ingredients	Concentration (%wt.)	Parts per hundred rubber
Part A (First stage compound)		
High ammonia natural latex	62.59	93.89
Cellulose compound	100	0,15,30,45
Sodium alginate solution	1	1
Potassium oleate solution	20.00	2
Sulfur dispersion	61.18	2.5
ZDEC dispersion	52.56	1
ZMBT dispersion	50.53	1
CPL solution	52.58	1
Part B (Processing compound)		
DPG dispersion	31.05	1
Zinc oxide dispersion	52.44	5
Sodium silicofluoride dispersion	24.70	1.5

3.4 Characterization of Eucalyptus cellulose particle

- Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a useful technique for the analysis of sample surfaces. Electrons are produced and passed through integral lenses to produce a focused beam of electrons which hits the surface of the sample. The sample is mounted on a stage in the chamber area. The scanning electron microscope (SEM) produces images by scanning the sample with a high-energy beam of electrons. The electrons in the beam interact with the sample afterwards its produce secondary electrons, backscattered electrons, and characteristic X-rays to produce various signals that can be used to obtain information about the surface images which are then displayed on the computer screen. When the electron beam hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample. Many signals are produced as a result of this interaction inside the sample.

Displayed scanning electron microscopy (SEM) micrographs were used to examine the morphologies by using model JSM-6610LV, JOEL, Tokyo, Japan. The eucalyptus cellulose particles were dried and sputtered with a nearly 200 Å layer of gold metal in a Balzers-SCD 040 sputter coater (Liechtenstein). The displayed images

were instantly observed at the magnification of 200X and accelerating voltage of 15.0 kV.

- Particle size analysis with PSD

The Laser particle size distribution analyzer (PSD), Mastersizer 3000, uses the technique of laser diffraction to measure particle size distributions from 10nm up to 3.5 mm. In a laser diffraction, a laser beam passes through a dispersed particulate sample and the angular variation in intensity of the scattered light is measured. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analyzed to calculate the size of the particles that created the scattering pattern using the Mie theory of light scattering. The particle size is reported as a volume equivalent sphere diameter.

Particle size distributions of blended cellulose particles in distilled water were investigated by laser diffraction technique using particle size distribution analyzer (Malvern Instruments, Mastersizer 3000, UK). The refractive index used for the cellulose particles was 1.47 at 25 °C

3.5 Characterization of green composite sponges

- Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) micrographs on the screen images were measured to examine the surface morphologies by using model JSM-6610LV, JOEL, Tokyo, Japan. To evaluate the morphologies, rubber/cellulose bio-foams were moderately cool in liquid nitrogen then specimens were vacuum-dried. The free surfaces of specimens were sputter-coated with a thin layer of gold metal and observed displayed micrograph. The micrographs were recorded using an accelerating voltage of 15 kV.

- Density testing

For the examination of density testing of biocomposite sponge, the test was carried out according to ASTM D 3574-95 that the square specimens (4.5×4.5×4.5 cm³) were initially dried in an oven at 50 °C to a constant weight and then each of specimens was weighed and measured the appearance. The density of biocomposite sponge was determined in grams per cubic centimeter by using equation:

$$Density = \frac{M}{V}$$

Where, M and V are the mass of dry specimen and the volume of the latex foam in g and cm³ units, respectively.

- Percent shrinkage

This determination of the shrinkage was carried out according to ASTM D 1055 that the dimension of the mould and finished foam rubber product was measured. Measurements are examined on all 3 aspects of the biocomposite foam, lateral direction, edges direction, and center direction that shown in below picture. The difference in dimension between the mould and the foam specimen was calculated as a percent shrinkage by using equation:

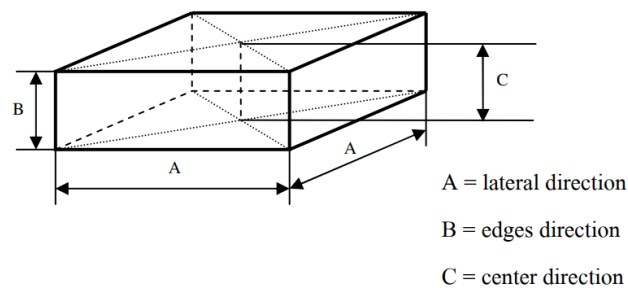


Figure 3.1 Measuring the shrinkage of biocomposite sponge

$$\text{Shrinkage (\%)} = \frac{X_{\text{mould}} - X_{\text{foam}}}{X_{\text{mould}}} \times 100$$

Where, X_{mould} and X_{foam} are the dimension of the mould and the finished product after latex compound is fabricated to biocomposite sponge in centimeter unit, respectively.

- FTIR spectroscopy

Fourier Transform Infrared Spectrometer (FTIR spectrometers) uses the technique of IR radiation to identify different chemical structures. When IR beam is passed through a sample, some radiation is absorbed by the sample and some passes through (transmitted). The detector is a spectrum representing a molecular of the sample at different spectral regions. The usefulness of infrared spectroscopy can use to identify or quantify the material. Moreover, it is utilized for determine bonding mechanisms in the samples.

FTIR spectrum representing of the Rubber/cellulose bio-foams were measured under condition by using wave numbers ranging from $4,000 \text{ cm}^{-1}$ to 400 cm^{-1} at a resolution of 4 cm^{-1} with Nicolet (US) SX-170 FTIR spectrometer.

- Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) is analytical method of material's thermal stability in which the mass of a residue sample is measured over time as the temperature changes for decomposition process. Fraction of volatile components by monitoring the weight change that occurs as a sample is heated. The thermogravimetric analysis was performed on thermogravimetric analyzer Q50 V6.7 Build 203. Universal V4.5A TA Instruments, equipped with platinum cell. TGA curves were drawn from scanning range of temperature at 50-800 °C, TA instruments with a heating rate of 10 °C/min under nitrogen atmosphere condition.

- Water absorption and swelling test

The water absorption of NR and NR-C sponges was carried out according to ASTM D471 using rectangular samples ($2 \times 2 \times 2$ cm³). The samples were initially dried in an oven at 50 °C to a constant weight and then each of specimens was measured the weight about 0.2 gram. The dried sponges were immersed in distilled water under room temperature (≈ 28 °C) for 6 days. At regular time intervals, each specimen was moved out; excess liquid surrounding the samples was quickly removed by using blotting paper and subsequently weighed. The degree of swelling was calculated by using Equation:

$$\text{Degree of swelling (\%)} = \frac{W_h - W_d}{W_d} \times 100$$

Where, W_d is the weights of dry samples and W_h is the weights of the hydrate samples after the immersion. The specimen was placed back in the water after each measurement.

- Biodegradation by soil test

For the examination of biodegradation behavior of rubber/cellulose bio-foam composites, the square specimens ($4 \times 4 \times 4$ cm³) were buried into flowerpots containing the unspecified soil at approximately depth 10 cm from soil surface under environmental condition. The soil pH and temperature of the soil were 5-6 and 20-40 °C, respectively. The water humidity was controlled at 30-60 % throughout the trial that everyday water was added for 2 months. Each two weeks, the samples were carefully collected then washed with running water and dried at 45 °C for 2 days. Finally, the test specimens were immediately weighed and taken digital photographs.

The biodegradation rate of rubber/cellulose bio-foam composites was calculated in time course experiment by following this equation:

$$\text{Biodegradation (\%)} = \left(\frac{W_i - W_r}{W_i} \right) \times 100\%$$

Where W_i is the initial dry weight of the samples and W_r is the weight of dried residual sample after degradation process in soil test.

- Compressive stress

Compressive stress is the force in one direction that is responsible for the deformation of the material such that the volume of the material reduces. High compressive stress leads to failure of the sample due to tension. It is the measurement of mechanical properties. For the compressive stress testing of NR-C sponges, NR-C sponges were carried out according to the specimens with dimension of 5×5×5 cm. It was cut without any skin layer exists on the bottom of the rubber sponges. Next, the square specimens were tested by using Instron Calibration Lab machine with system number 5569P1384. In this test, the head speed is 10 mm/min downward to measure its compressive stress. Its mathematical representation is given below. The compressive stress was calculated by using Equation:

$$\text{Compressive stress } (\sigma) = \frac{F}{A}$$

Where, σ is the compressive stress, F and A are the compressive force applied on the object and the unit area of cross-section of the object in N/m^2 or Pa, respectively.

For Young's modulus or modulus of elasticity, it is the measurement of material's elasticity. When under the stress, materials will exhibit elastic properties because the stress causes them to deform and return to previous state. The modulus of elasticity was determined by using Equation:

$$\text{Modulus of elasticity } (E) = \frac{\sigma}{\varepsilon} = \frac{F/A}{\Delta L/L_0}$$

Where, stress (σ) is the force divided by the specimen's cross-sectional area and strain (ε) is the change in length of the sponge divided by the material's original gauge length. The unite of modulus of elasticity is N/m^2 or Pa.

- Compression set

The finished products were cut for square specimens without any skin layer existed on the top and the bottom of sample foam. For the examination of compression set of green composite sponge was carried out according to ASTM D 395 using dimension of sample 5×5×5 cm. It is put through the compression device consisting of two flat steel plates that specimen is placed between spacers and in the compression device. Then, they are compressed until 25% and 50% of their original

thickness, using spacers to accurately measure the compression. Next, the sample is left in this condition for 30 minutes before the compression device was placed in an oven with the temperature of 70 °C for 22 hours. At the final step of the test period, the specimens were moved out of the device. After removing the sample from the oven, the specimen is allowed to cool for 30 minutes at room temperature before measuring the final thickness. The percentage of the compression set is then calculated using the equation below.

$$\text{Compression Set (\%)} = \left(\frac{t_0 - t}{t_0} \right) \times 100\%$$

Where t_0 is the original specimen thickness and t is the specimen thickness after compression set testing.



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of the eucalyptus cellulose filler

4.1.1 Scanning electron microscopy (SEM)

Cellulose fibers were used as reinforcing agent in the fabrication of green composite sponges that filler was sieved after physical processing in order to obtain the particle size with a smaller average size of 106 μm . The cellulose filler materials were characterized by SEM micrographs as shown in [Figure 4.1](#). The micrographs were used to obtain information about the surface images and the morphologies of the cellulose extracted from the pulp of eucalyptus tree. The displayed images were observed at the different magnification of 200X and 1000X with accelerating voltage of 15.0 kV. The SEM images indicate that the surface possesses level of dissimilar shapes and sizes as represented in below picture. The cellulose filler demonstrated smooth cylindrical fibers. From the picture below, the longest side of the cellulose shapes as length was 80-120 μm that was determined by red line in the [Figure 4.1 \(A\)](#) and the shortest side of the shapes as width was 20-50 μm . The obtained values that the length and width of sample were high variability.

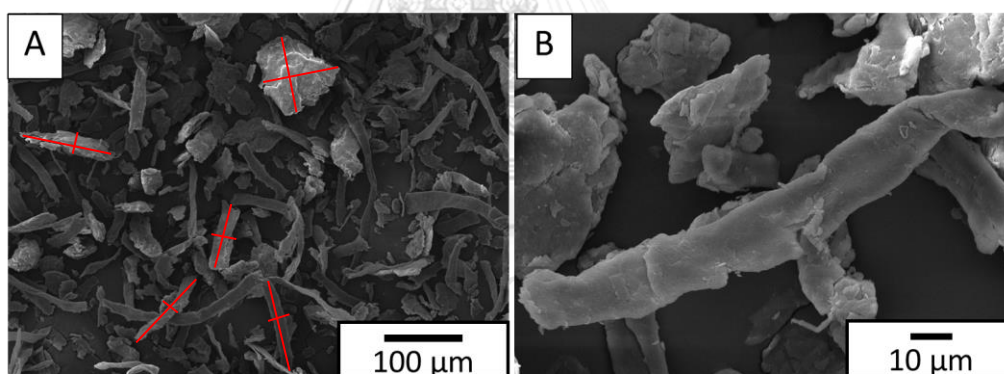


Figure 4.1 SEM micrographs of the surface and size morphology of cellulose filler after physical processing, magnified 200X (A) and 1000X (B)

4.1.2 Particle size analysis with PSD

Particle size distributions of cellulose fibers after physical processing for obtaining the smaller particle size that were investigated by laser diffraction technique in distilled water using Mastersizer 3000 Instruments. The refractive index used for the cellulose particles was 1.47 at 25 °C. The frequency particle size distribution was demonstrated as percentage of the total volume of particles involved by a given size fraction or diameter. The average size of cellulose by number distribution was 57.9 μm , that shown in [Figure 4.2](#). The size of cellulose filler was varied from 1-126 μm .

After comparing with the average diameter in SEM micrograph, the size of particles is larger than their exact diameter.

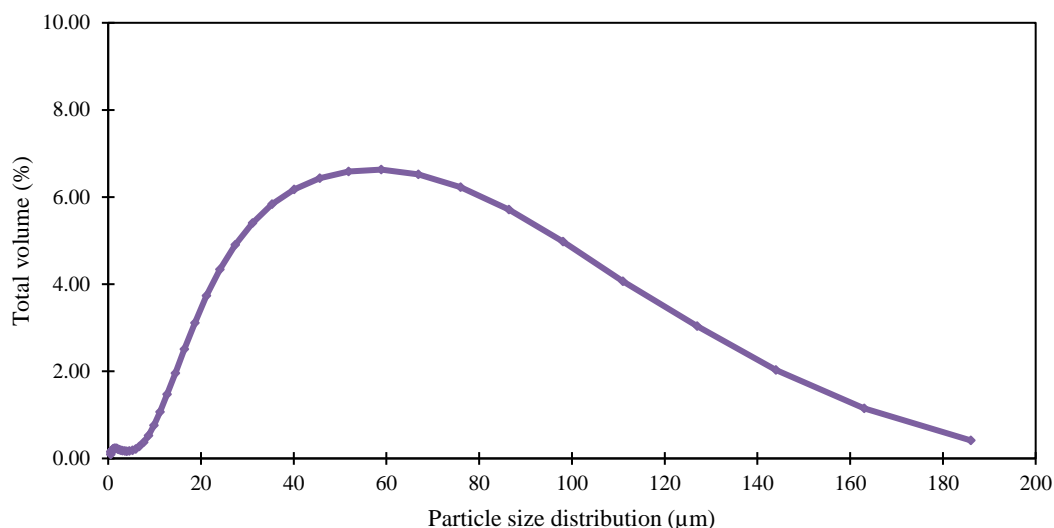


Figure 4.2 Particle size distribution for eucalyptus cellulose after physical processing

4.2 Characterization of NR-C composite sponge with various compositions

4.2.1 Scanning electron microscopy (SEM)

For Dunlop processing, the latex compound is immediately transferred into a mould that is made from aluminum plate and is designed to create the shape and size of the finished product. The NR-C green composite sponges were moderately cooled in liquid nitrogen then the specimens were vacuum-dried to evaluate the surface morphologies. The micrographs were recorded by using an accelerating voltage of 15 kV. The displayed images were observed at the magnification of 50X and 100X. SEM micrographs of the NR-C sponge show the characteristics of morphologies with pore size and pore volume in NR matrix.

Morphologies, microstructure, and cell size distribution of NR-C composite sponges are presented in [Figure 4.3](#), [Figure 4.4](#), and [Figure 4.5](#). A difference in pore size was clearly observed in cross-section views as shown in [Figure 4.3](#). [Figure 4.3 \(A\)](#) exhibited pure NR sponge without the addition of cellulose and sodium alginate (SA). The NR sponge had the porous structure with the small pore size diameter around 150-250 μm., which were considered to be smaller in comparison to those NR sponge with the addition of cellulose filler and SA substance. [Figure 4.3 \(C, E, and G\)](#) demonstrated the effect of addition cellulose fibers without SA as dispersing agent on the porous morphologies of the sponges. Particularly, [Figure 4.3 \(E, and G\)](#) indicated porous structure with the pore diameter around 300-400 μm., which were evaluated to be the bigger pore and exhibited interconnected foam network in those images. On the other hand, image C showed the porous structure with smaller pore size that is similar

to be the pure NR while its cell wall seems to be thinner structure. The thinner cell wall can be deformed faster than the bushy wall by force effect. According to the cross-section views, all bubbled foams possessed spherical cell structure with interconnected foam network while the pore sizes of the composite sponge were enhanced by the adding cellulose content that increased the pore volume of material. The larger pore size could be improved by the formation of highly connected macropore distributed throughout the sponges.

In addition, it was found that the addition of cellulose filler with the adding of SA substances resulted in the pore size. After loading SA as dispersing agent at 1 phr, no substantial transformation in the pore size and pore volume was observed from the addition of cellulose filler up to 30 parts per hundred rubber that shown in [Figure 4.3 \(B, D, and F\)](#). For cellulose loading at 45 parts per hundred rubber with SA, it shown the lower pore size compared to other formulations because cellulose fibers might be tightly combined with NR in matrix of materials that latex compound cannot completely create a void behind the latex by agitation in foaming and refining process. The results demonstrated that SA could be used as dispersing agent and pore controller for cellulose substances in NR-C green composite sponges with the addition of cellulose at 0-30 parts per hundred rubber together with 1 parts per hundred rubber of SA, the stable consistency in pore size and pore volume could be obtained by Dunlop process in this experiment.

In case of surface morphologies, SEM micrographs of the surface outer of composite sponge shown the surface characteristics with smooth and rough covering. For the surface that is on the same side as the mould, the smooth surface of pure NR sponge was noticed that shown in [Figure 4.4 \(A\)](#). As a result of [Figure 4.4 \(A, C, and E\)](#) has the smoothest surface when comparing with other composite sponges. After loading cellulose at 45 phr, the rough area in surface of NR-C composite sponges was clearly observed that presented in [Figure 4.4 \(G\)](#) hence roughness effect of cellulose loading was distinctly observed when adding cellulose fibers more than 45 phr. The higher cellulose content in NR matrix was suggested to arise the rough area due to the high cylindrical shape as well as polarity of filler material that is the cause of the reduction of the compatibility and filler dispersion. Moreover, [Figure 4.4 \(B, D, F, and H\)](#) demonstrated the effect of addition SA at 1 phr with/without cellulose filler on the surface morphologies of the composite sponges. For mould-side surface, these images were clearly observed the rough area and deep pore which had similar surface appearances at various concentrations of cellulose by using 1 phr of SA. In accordance with the surface views, the rough area of the green composite sponges could be enhanced by adding SA together. In addition, the addition of SA in latex compound had the tendency to create deep pore on surface of the green composite sponges. During the fabrication of 3D structural NR sponge by the Dunlop process, the formation of deep pore might be as a result of SA substitution of NR in the

colloidal suspension or latex before the coagulation process. For drying the final sponges in the oven, resulting in solution of SA dehydrated and then created the gap among the surface morphologies.

For the surface at air-side, cell size distribution of composite sponges were detected by SEM micrographs at the magnification of 100X that shown in [Figure 4.5](#). The pure NR, NR-C15, and NR-C30 exhibited spherical cell shape and crack-free. In contrast, after the composite sponges were enhanced cellulose content at 45 phr, spherical cell shapes were transformed to ununiform shape that can be seen in [Figure 4.5 \(G\)](#). Its different shape of cell might occur from abundant cellulose in matrix of NR sponge which obstruct the latex compound to complete products by creating a void inside the matrix due to the cylindrical shapes of cellulose. Furthermore, the sizes of cell for each NR-C composed of SA at 1 phr were similar throughout the specimens that is smaller than NR-C without SA. It might be determined that the smaller cell sizes at the surface of air-side could be improved by adding sodium alginate substances that decreased the bubbled foam in matrix materials.

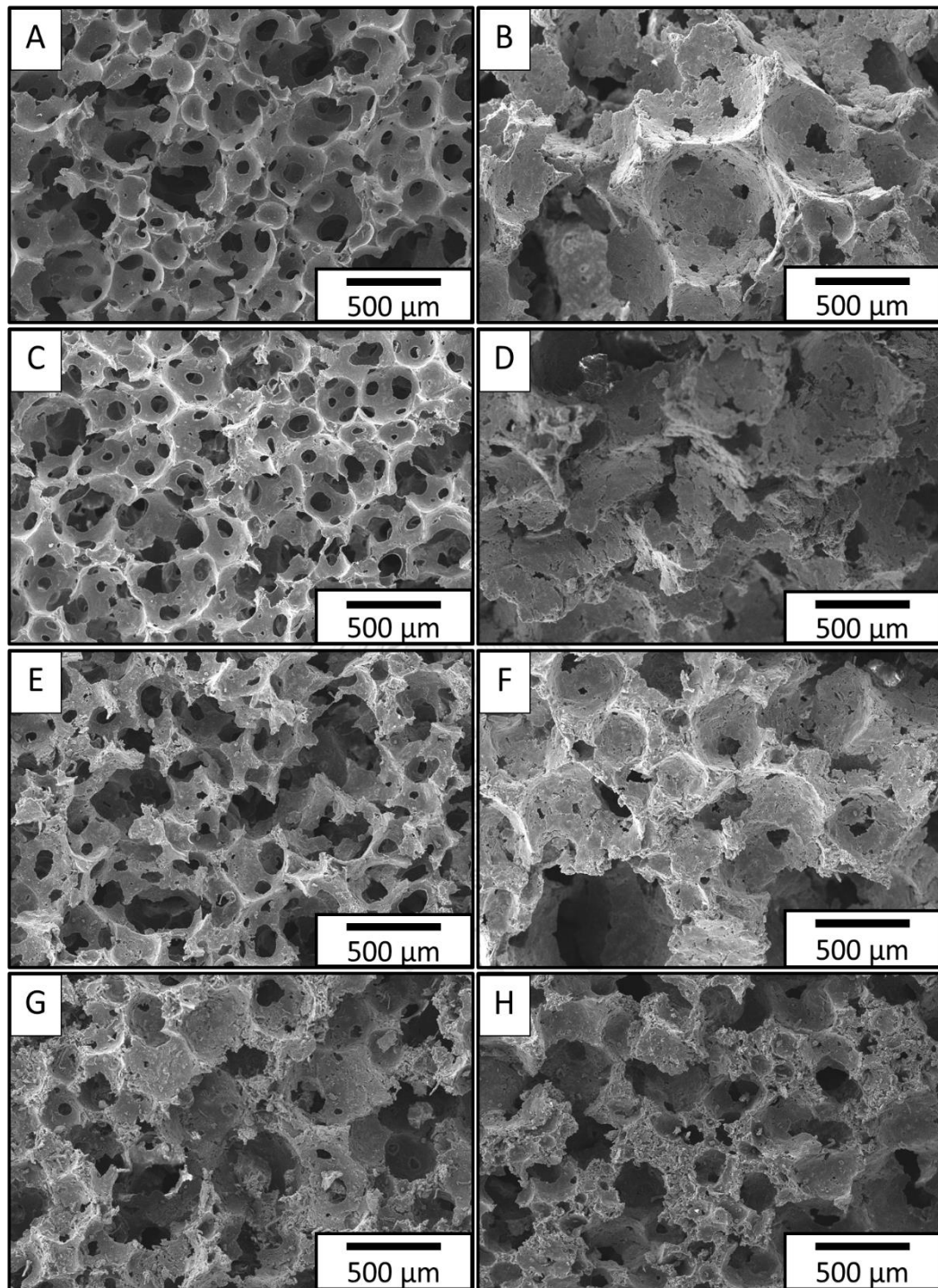


Figure 4.3 SEM micrographs of composite sponges of NR and cellulose with various compositions (NR-C) for porous characteristics by cross-section views: (A) NR; (B) NR composed of 1 phr SA; (C) NR composed of 15 phr cellulose; (D) NR composed of 15 phr cellulose and 1 phr SA; (E) NR composed of 30 phr cellulose; (F) NR composed of 30 phr cellulose and 1 phr SA; (G) NR composed of 45 phr cellulose; (H) NR composed of 45 phr cellulose and 1 phr SA

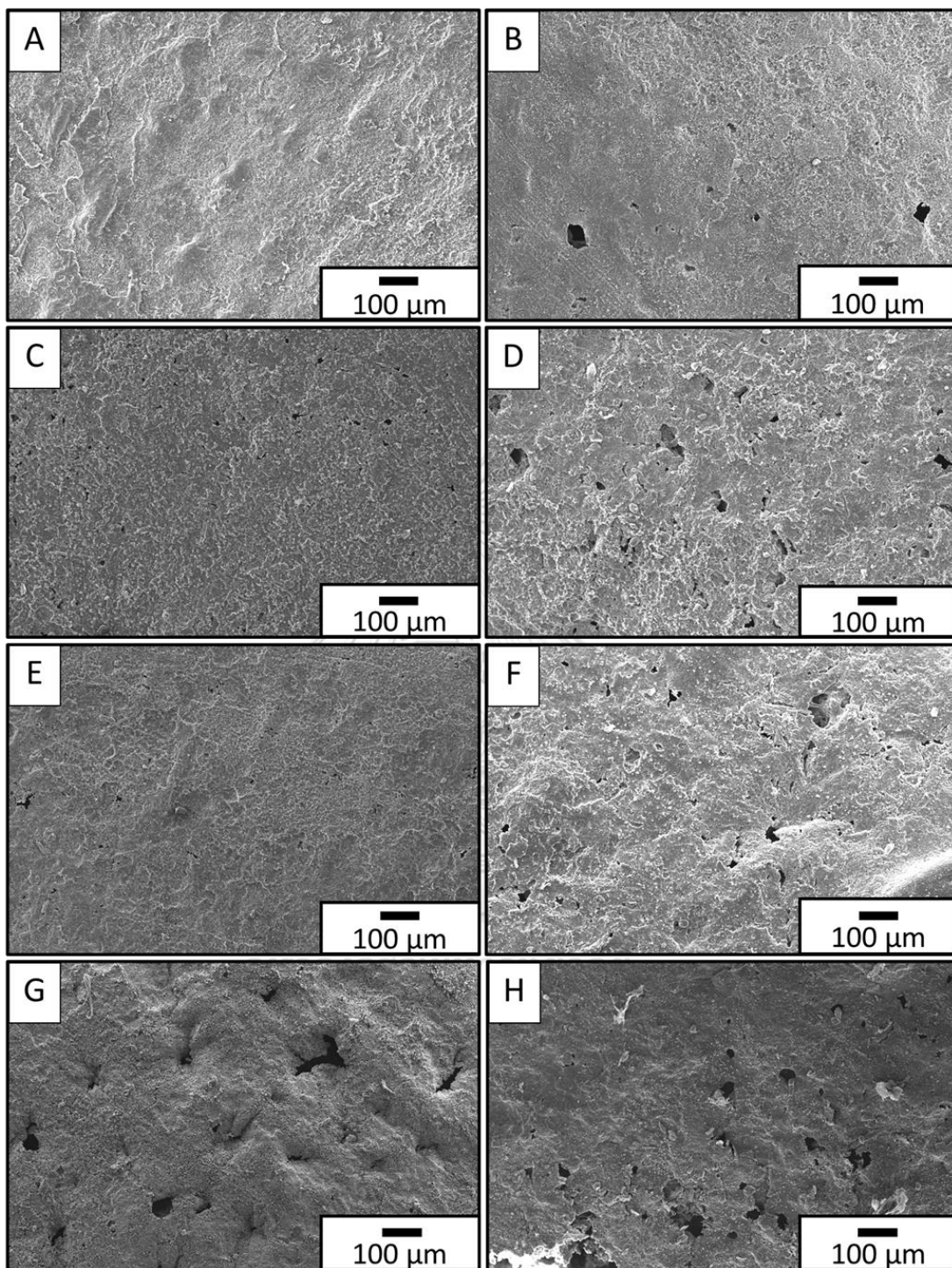


Figure 4.4 SEM micrographs of composite sponges of NR and cellulose with various compositions (NR-C) for surface morphologies at mould-side: (A) NR; (B) NR composed of 1 phr SA; (C) NR composed of 15 phr cellulose; (D) NR composed of 15 phr cellulose and 1 phr SA; (E) NR composed of 30 phr cellulose; (F) NR composed of 30 phr cellulose and 1 phr SA; (G) NR composed of 45 phr cellulose; (H) NR composed of 45 phr cellulose and 1 phr SA

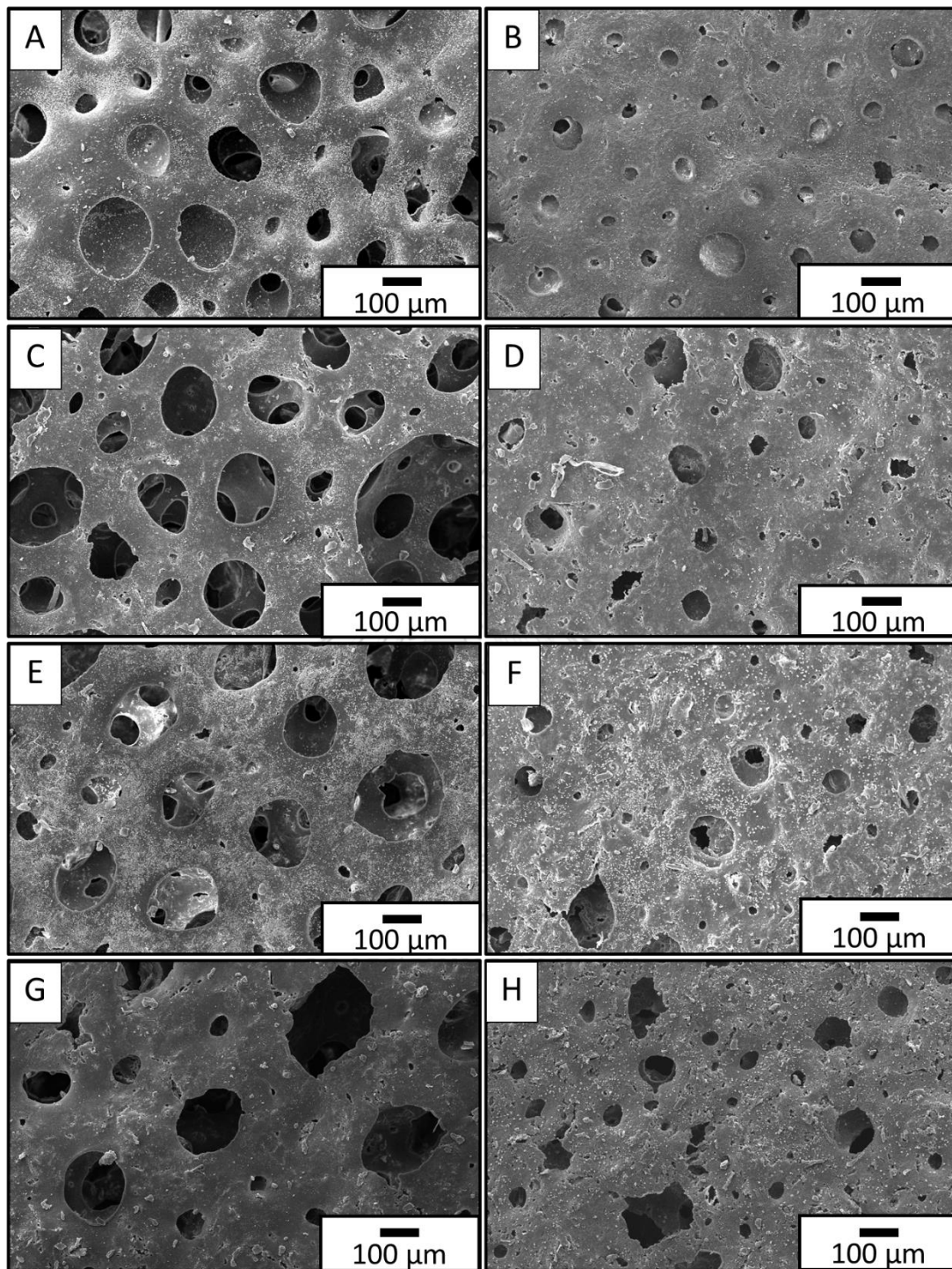


Figure 4.5 SEM micrographs of composite sponges of NR and cellulose with various compositions (NR-C) for surface morphologies at air-side: (A) NR; (B) NR composed of 1 phr SA; (C) NR composed of 15 phr cellulose; (D) NR composed of 15 phr cellulose and 1 phr SA; (E) NR composed of 30 phr cellulose; (F) NR composed of 30 phr cellulose and 1 phr SA; (G) NR composed of 45 phr cellulose; (H) NR composed of 45 phr cellulose and 1 phr SA

4.2.2 Density testing

The density of the green composite foam was usually controlled by the amount of air introduced into the latex through mechanical agitation. The density of the final product was then determined. In general, the different densities of foam were fabricated to study their properties for different applications. The density of NR-C composite sponges for the NR, NR+SA1, NR-C15, NR-C15+SA1, NR-C30, NR-C30+SA1, NR-C45, and NR-C45+SA1 were 0.14, 0.14, 0.14, 0.16, 0.17, 0.20, 0.18, and 0.26 g/cm³, respectively that shown in Figure 4.6. The densities of the foams produced in this study were within the range of 0.14-0.18 g/cm³ for the cellulose loading foams and between 0.14-0.26 g/cm³ for the cellulose loading with SA foams. The density is proportional to the cellulose and sodium alginate loading. The pure NR possessed lower density than the NR-C composite sponges. This is because higher density of matrix materials is formed when higher concentration of cellulose is applied so the density increased with the enlarged cellulose. It is worth to note that, NR sponge with the addition of SA at 1 phr can be fabricated for the highest density together with cellulose loading. Figure 4.7 was demonstrated that the maximum value of density testing was 0.26 g/cm³ at 45 phr cellulose filler and 1 phr SA. Based on the obtained results, the difference in density of sponge when the cellulose and SA were adjusted suggests an advantage that density can be adjustable for excellent physical and mechanical properties. Moreover, when the porous structure or cell size in matrix of rubber material increases, it also causes the expansion ratio of the foam. As a result, enhanced specific volume of sponge and hence lower density of the composite sponge.

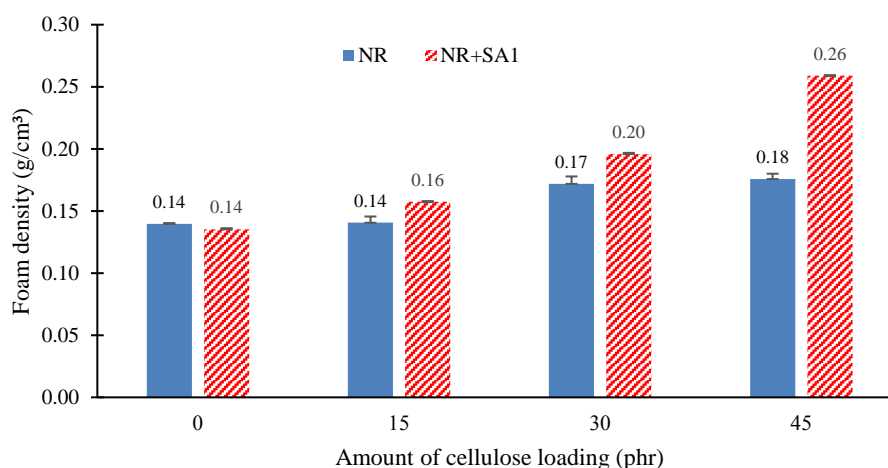


Figure 4.6 The densities of composite sponges of NR and cellulose with various compositions (NR-C)

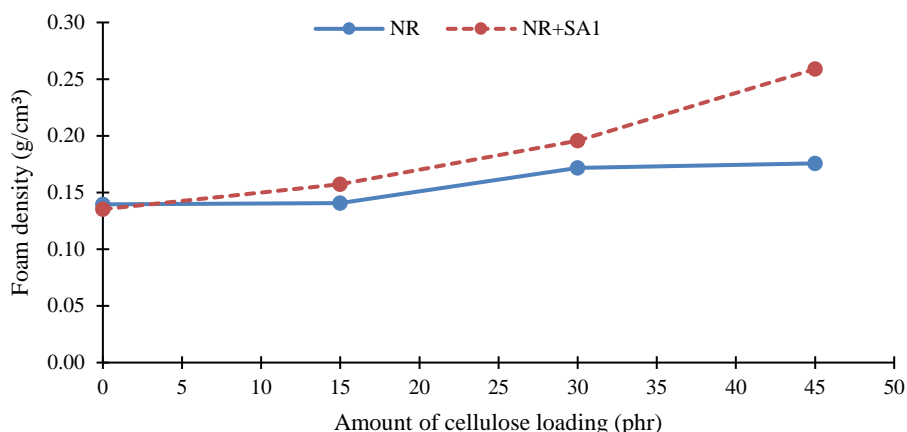


Figure 4.7 The densities of composite sponges of NR and cellulose with various compositions (NR-C) as a function of cellulose content at room temperature ($\approx 25^{\circ}\text{C}$)

4.2.3 Percent shrinkage

The shrinkage is important characteristics in latex foam technology as it determines the size of the finished product of the composite sponge. It is noted that shrinkage is regular occurrence for foam to shrink during the molding process or post molding. The percent shrinkage of the green composite sponges in this study is shown in [Figure 4.8](#), [Figure 4.9](#) and [Figure 4.10](#) that was different ratio of cellulose with/without SA. The shrinkages of the finished product produced in this experiment were with the range of 8.20-18.00% for the cellulose loading only and cellulose loading together with SA. It was demonstrated that the maximum shrinkage was 18.00% of the center direction of composite sponge at 0 phr cellulose filler and 1 phr SA while the smallest value of percent shrinkage was 8.20% of edges direction of pure NR sponge.

In addition, the higher value of percent shrinkage of the sponge seen in [Figure 4.8](#) which is NR-C sponges with SA loading can be reduce to the greater shrinkage by addition of cellulose content that the gelation time of these conditions was noticeably shorter than the NR-C sponge without SA substance. This converted time might have contributed to the shrinkage in any manner. For magnitude of shrinkage, it is important that many variables such as the water content of the latex compound and the speed of gelation time in gelling step are adequately controlled [40]. To achieve the desired size, it is necessary to increase the size of the mould cavity to compensate for such dimensional variations for an artifact because shrinkage of rubber product always come out of the mould that smaller than the cavity.

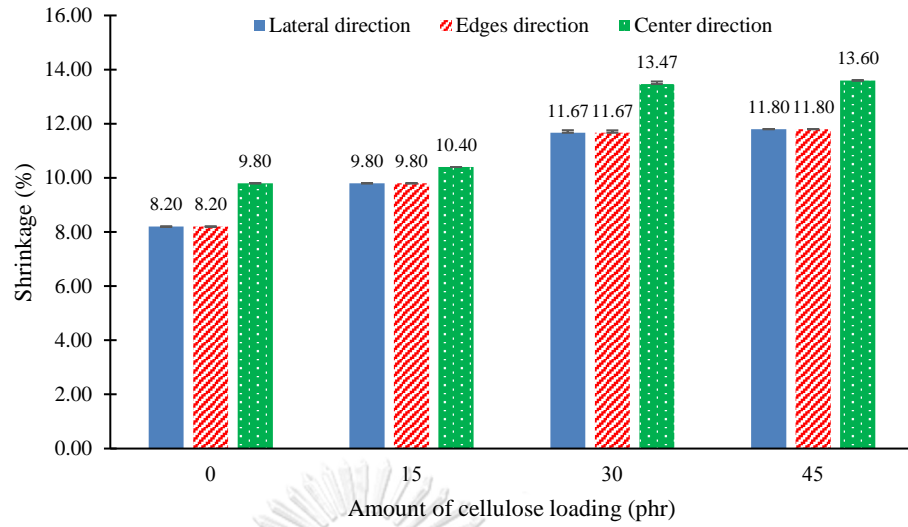


Figure 4.8 The shrinkage characteristics of the NR-C composite sponges with various compositions; no addition of SA substance

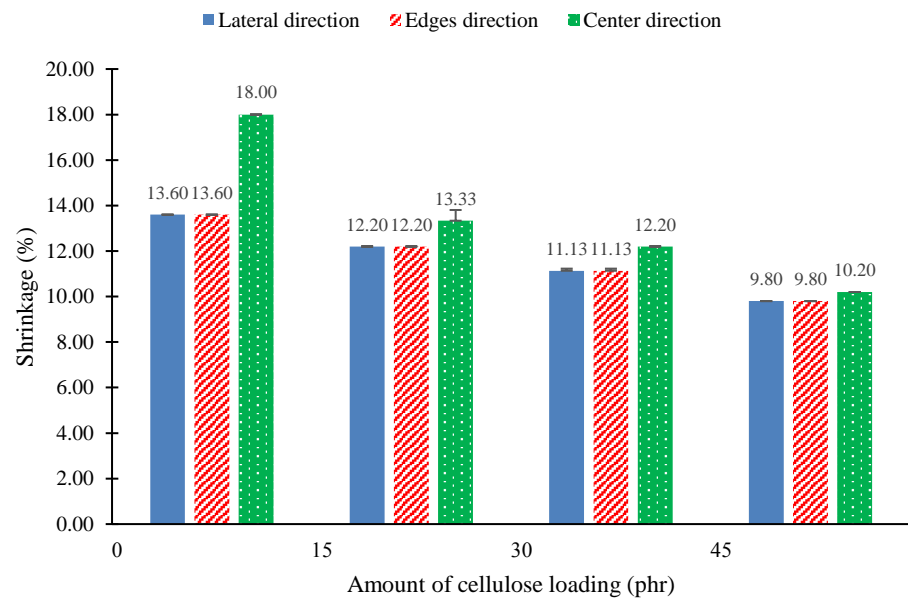


Figure 4.9 The shrinkage characteristics of the NR-C composite sponges with various compositions; addition of SA substance at 1 phr

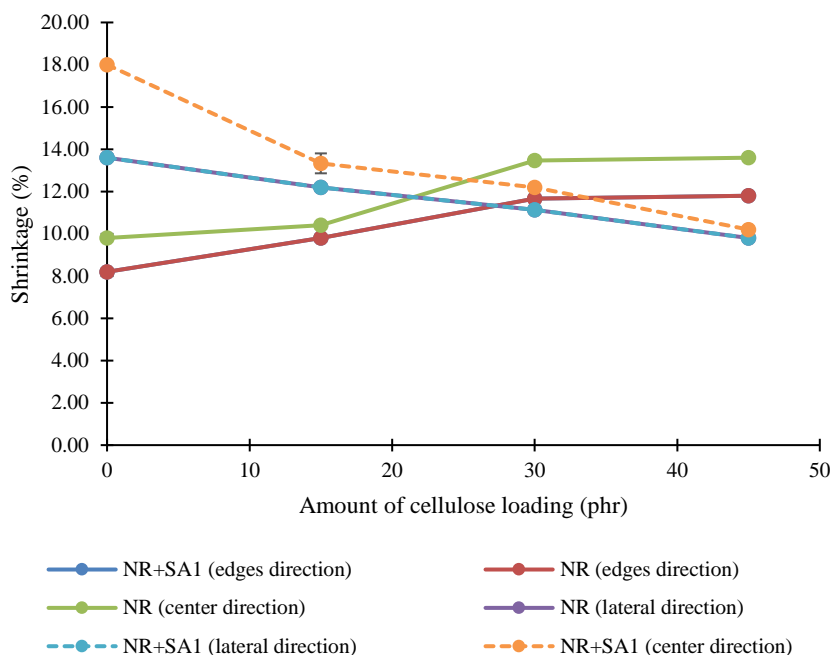


Figure 4.10 The shrinkage characteristics of the NR-C composite sponges for different ratio of cellulose with/without SA

4.2.4 Water absorption and swelling test

The effects of the addition of cellulose filler and SA for the fabrication of NR-C sponges on the swelling behavior in water and the maximum water absorption are shown [Figure 4.11](#) and [Figure 4.12](#), respectively. It was revealed that the initial water absorption rate increased with the addition of cellulose filler and SA owing to the hydrophilic properties of cellulose and SA substances. Especially, cellulose consist of polar molecules which allowed it to easily absorb water into the rubber matrix. From the observation after 96 hours of water absorption process, the maximum value of swelling degree of NR-C sponges in water for the NR, NR-C15, NR-C30, NR-C45, NR+SA1, NR-C15+SA1, NR-C30+SA1, and NR-C45+SA1 were 224.03, 268.57, 305.90, 355.79, 234.73, 354.01, 406.73, and 395.66%, respectively that shown in [Figure 4.11](#). The highest value of swelling degree in this study was 406.73% at 30 phr cellulose filler and 1 phr SA, which was about 1.81 times that of normal NR sponge (224.03%).

In comparison to NR-C sponge, no significant improvement in the maximum values of swelling degree after the immersion in water for 4 days was observed with the addition of only cellulose or the addition cellulose together with SA because those sponges might have total pore volume limiting; thus the water holding capacity were almost the same as the NR-C30+SA1 and the NR-C45+SA1 sponges. However, it was demonstrated that the water adsorption rate and the adsorption capacity of NR-C green composite sponges were enhanced by the addition of cellulose filler together

with SA substance. As a result, it directly affects the absorption due to higher hydrophilic properties in cellulose and SA. It was shown that the hydrophilic properties could be improved by adding of hydrophilic substances that increased the polarity of material and the maximum absorption capacity could be enhanced by the formation of highly connected macropore distributed throughout the green composite sponges.

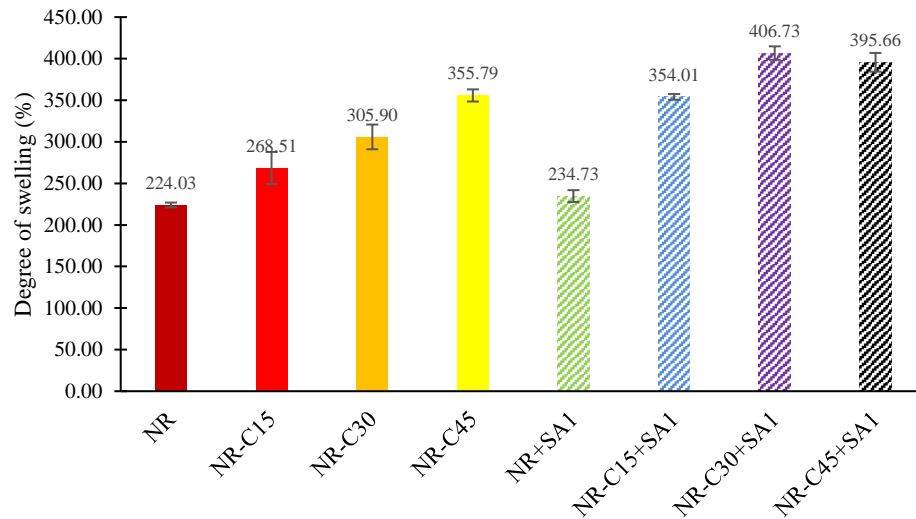


Figure 4.11 The maximum degree of swelling of NR-C and NR-C+SA1 sponges in water

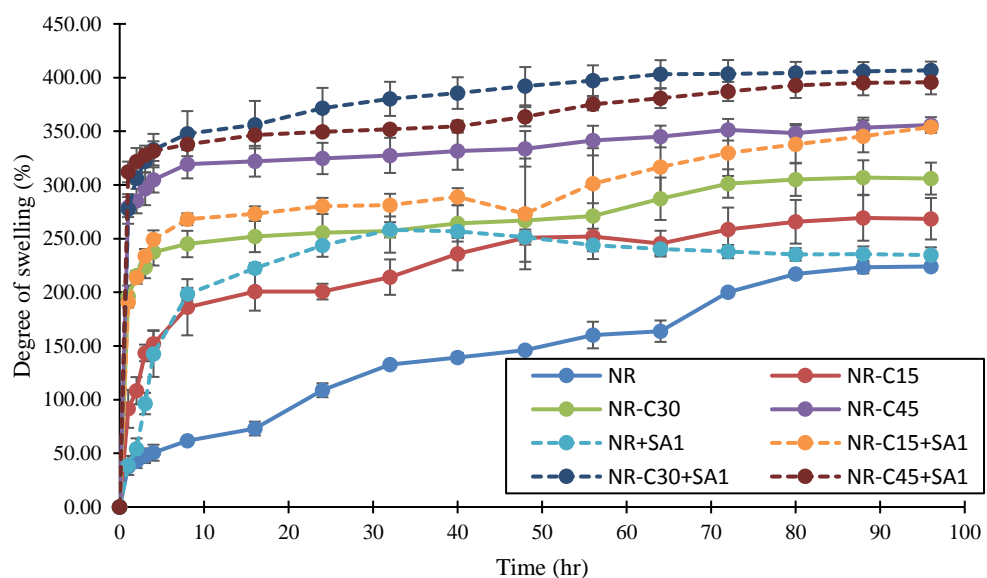


Figure 4.12 Evolution of the swelling kinetic behaviors of NR and NR-C sponges as a function of time at room temperature ($\approx 25^{\circ}\text{C}$)

4.2.5 Biodegradation by soil test

The degradation behavior of NR green composite sponges decomposed by the soil burial test was investigated. Biodegradable properties are important requirement in the area of green materials. A graphical representation of this occurrence can be seen in [Figure 4.13](#) and [Figure 4.14](#). In this work, the experimental conditions were operated closely the environment as well as the humidity and the temperature change with the variation of the weather. Daily weather reports of testing days (2020, July 18 – 2020, August 31) were referred in the appendix. The burial environmental parameters such as temperature, soil pH moisture, nutrition, and amounts of microorganisms considerably affected the biodegradation rate of materials [39, 41]. Result in [Table 4.1](#) display that after adding cellulose of composite sponges, the biodegradation of sponge dramatically increased with increasing the cellulose contents. Moreover, the rate of biodegradable of NR-C green composite sponges with SA as dispersing agent was faster than that of NR-C sponges with only cellulose due to cellulose and SA substances were greatly degraded by bacteria and fungi in soil activated by moisture and heat. On the other hand, virgin NR sponge containing high molecular weight composed of cis-1,4-polyisoprene were responsible for the more difficult biodegradation[42]. In the many previous work presented that NR can be slowly degraded in natural soil by microorganisms [39]. Those bacterial strains are able to utilize decomposed the rubber as the essential carbon and energy sources for living.

[Figure 4.13](#) and [Figure 4.14](#) presented the visual analysis of NR-C sponges with a different cellulose filler loading after 45 days of biodegradation. NR-C sponges with cellulose demonstrated more appearance signs of biodegradation scattered on the surface sponges compared to virgin NR sponge that can be observed the black and yellow spots on the surface morphology. It was an excellent indicator that the cellulose substances and SA has dispersed and then decomposed well in the green composite sponge which efficiently increased the rate of biodegradation process of NR-C sponges. Based on the obtained results, the higher rate of degradation of NR-C green composite sponges within 45 days was affected due to the high amount of cellulose and SA in matrix polymer of sponges.

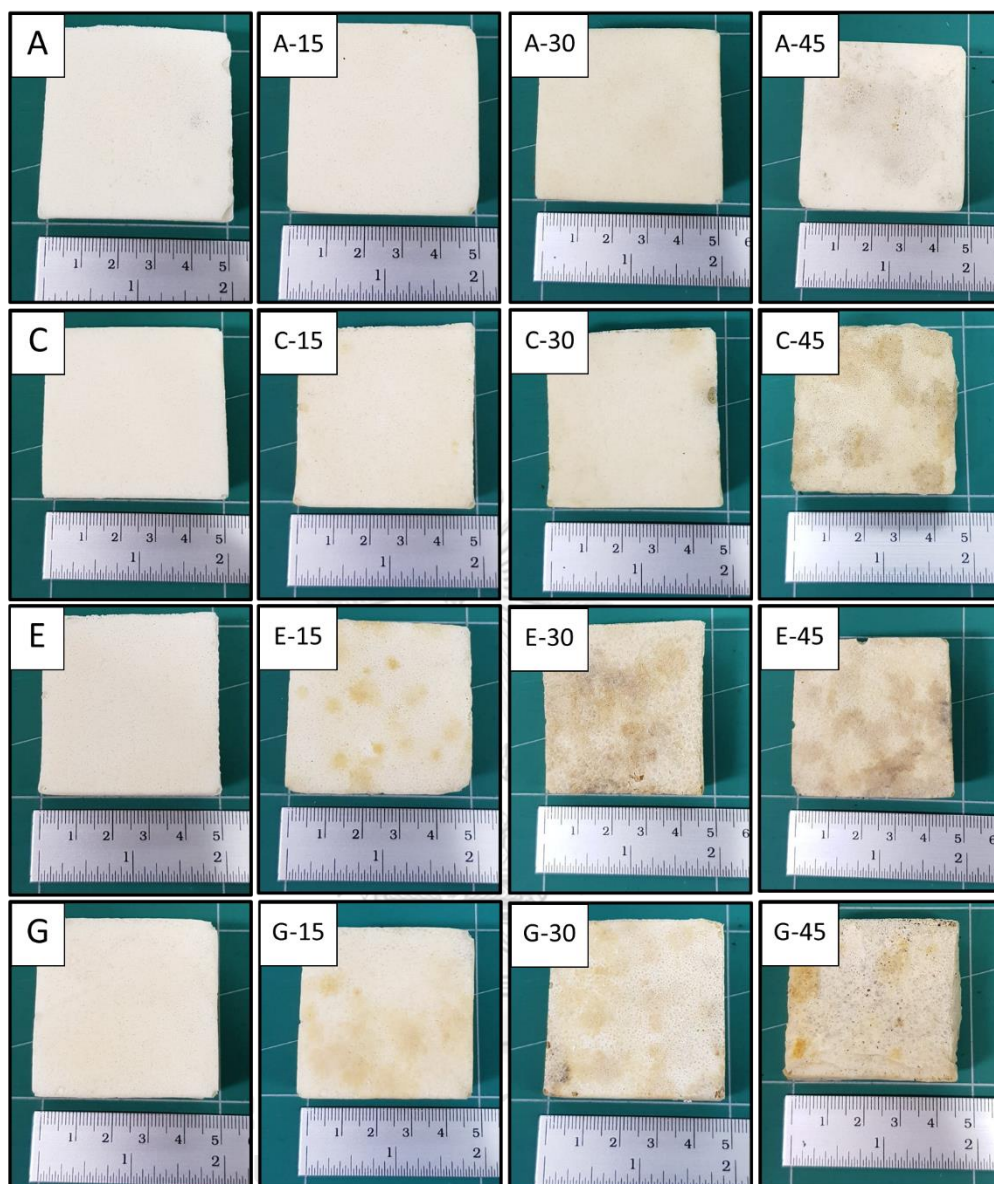


Figure 4.13 Digital photographs showing the degradation behavior of green composite sponges of NR and cellulose with various compositions (NR-C) as function of time: (A) NR; (C) NR composed of 15 phr cellulose; (E) NR composed of 30 phr cellulose; (G) NR composed of 45 phr cellulose within 45 days

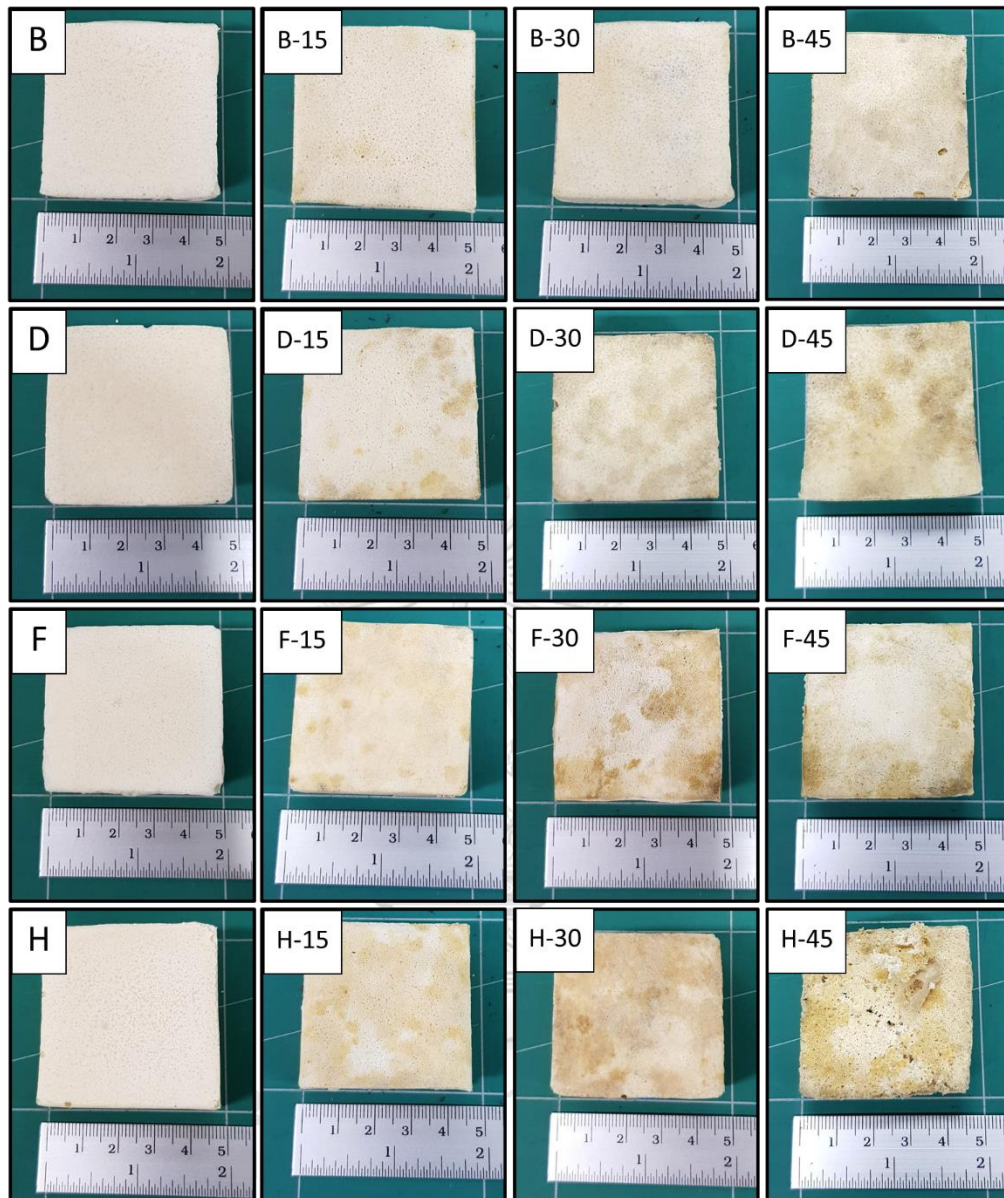


Figure 4.14 Digital photographs showing the degradation of green composite sponges of NR and cellulose with various compositions (NR-C) as function of time: (B) NR composed of 1 phr SA; (D) NR composed of 15 phr cellulose and 1 phr SA; (F) NR composed of 30 phr cellulose and 1 phr SA; (H) NR composed of 45 phr cellulose and 1 phr SA within 45 days

Table 4.1 Weight loss of NR, NR-C, and NR-C with SA composite in soil burial test

Rubber sponges	Weight loss (wt.%)		
	15 days	30 days	45 days
NR	0.48	1.99	2.67
NR-C15	2.28	3.02	4.52
NR-C30	2.16	4.05	5.79
NR-C45	5.46	5.49	8.90
NR+SA1	4.51	5.32	5.56
NR-C15+SA1	6.02	7.51	9.08
NR-C30+SA1	6.35	10.86	11.64
NR-C45+SA1	6.92	14.41	16.94

4.2.6 Compressive stress

The compressive stress is the results from the shortening in one dimension of an elastic material due to oppositely directed forces tending to crush or deform it that force causes a material to deform to occupy a smaller volume. The green composite sponges can be responsible by the force that the deformation of sponges such the volume of material reduces. The effects of the addition of cellulose filler and SA for the fabrication of NR-C sponges on the compressive stress at 25% and 50% strain rate are shown [Table 4.2](#). Based on the obtained results, it is discovered that the compressive stress is increased with raising content of cellulose and SA. The highest values of compressive stress at 25% strain rate in this study was 46.05 kPa by adding cellulose 45 phr with SA 1 phr. Also, the highest values of compressive stress at 50% strain rate was 133.52 kPa by the same condition as shown in [Figure 4.15](#). As a result, compressive stress could be able to improve by adding of cellulose and SA substances that increased the strength of matrix in material. Hence, the maximum value of NR-C sponge is also obtained from the maximum filling of cellulose.

In general, the pore morphology changes, the sponge will also present different value of compressive stress. The thinner cell wall or larger pore size will decrease the resistant towards shortening of dimension so bigger cell will undergo microscopic deformation faster than the smaller cells. As a consequent, it is observed that NR-C green composite sponge fabricated with 15 phr of cellulose displayed the lowest value compared to other formulations at 25% and 50% strain rate together. The difference in compressive stress of NR-C15 was demonstrated because its cell wall is extremely thin compared to other formulation that resulted in the collapse of the matrix in polymer. Also, its bigger pore size of NR-C15 can be easy to force that it uses less pressure than other conditions. [Figure 4.3](#) shown that the cell wall thickness and pore size of all condition in this experiment.

A drastic change in the compressive stress value for the sponge is caused by the effect of compressive force on the matrix rubber so density of rubber foam can also be influenced to stress by the component in the matrix phase. With a rise in the density, it can be observed that the compressive stress increased [\[43, 44\]](#).

Table 4.2 Data of compressive stress and modulus of elasticity for different amount of cellulose with SA substance.

NR-C sponges	Compressive stress at 25% strain (kPa)	Compressive stress at 50% strain (kPa)	modulus of elasticity (kPa)	modulus of elasticity (kPa)
NR	9.16	19.71	32.67	39.42
NR-C15	5.38	15.81	19.76	31.62
NR-C30	8.14	26.19	31.55	52.38
NR-C45	36.38	122.84	140.99	245.68
NR+SA1	9.67	31.80	28.45	63.61
NR-C15+SA1	8.72	26.81	33.81	53.62
NR-C30+SA1	21.10	60.58	73.32	121.15
NR-C45+SA1	46.05	133.52	152.35	267.04

Modulus of elasticity is the measurement of material's elasticity. When under stress for first state, materials will exhibit elastic properties because the stress causes them to deform but the materials will return to its previous state after the stress is removed. Since both stress and strain are normalized measurement, modulus is a consistent material property that can be compared between specimens of different sizes. Modulus is defined as being the slope of the straight-line portion of a stress and strain curve. A large sponge specimen will have the same modulus as a small sponge specimen, although the large specimen will require higher maximum force to deform the material, the cross-sectional area of large specimen will also be bigger. In the table above, modulus is reported as stress at 25 and 50 strain.

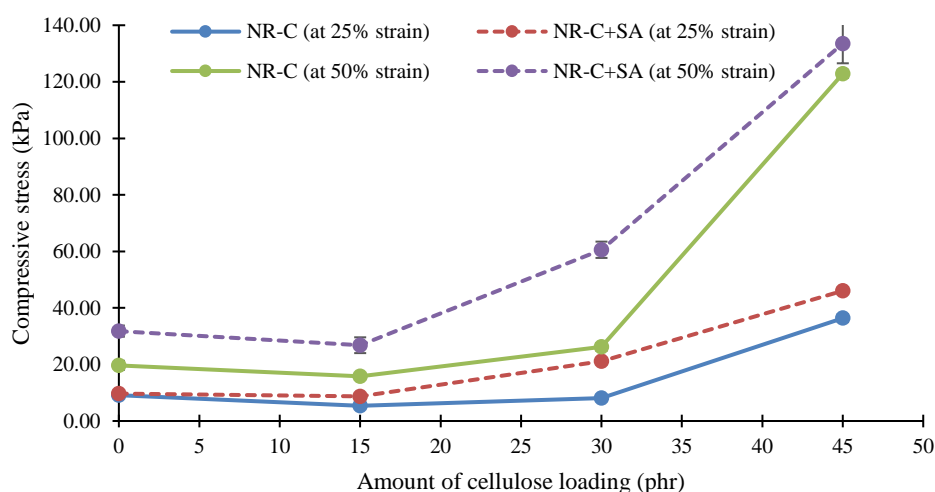


Figure 4.15 Compressive stress of NR-C composite sponges as a function of cellulose content at room temperature (25 °C)

4.2.7 Compression set

Compression set testing, it used to purpose the ability of elastomeric materials to maintain elastic properties after prolonged compressive stress. The test measures the permanent deformation of the specimen after it has been successfully exposed to compressive stress for a set time period by measuring the final thickness. This test is particularly useful for many applications in which elastomers would be in a constant pressure state.

In general, its physical properties of NR-C sponges or foam will direct or indirectly affect the foam mechanical properties. From the observation of compression set at 25% of their original thickness, the value of NR-C sponges for the NR, NR-C15, NR-C30, NR-C45, NR+SA1, NR-C15+SA1, NR-C30+SA1, and NR-C45+SA1 were 6.07, 10.28, 12.74, 13.35, 12.04, 12.59, 12.36, and 12.56%, respectively. From the observation of compression set at 50%, the value of NR-C sponges was 11.12, 11.12, 15.09, 16.07, 20.29, 16.54, 18.28, and 20.84%, respectively that shown in [Figure 4.16](#). As for compression set, it can be determined by addition more cellulose fibers after that results are observed the higher value of compression set with higher cellulose. For compression set with addition of SA, the value unchanged significantly to increasing amount of cellulose. It can be clearly seen in [Table 4.3](#). These scenarios are caused by the average cell sizes are getting bigger with increasing amount of cellulose loading to microscopic deformation when the sponges are exposed to heating and compression.

The compression set value of the NR-C composite sponges shows an actual increase compared to the pure NR sponge. Also, the NR-C composed of SA composite sponges indicated a lower ability to recover from deformation as shown in [Figure 4.16](#). This might be attributed to the overall structure of the sponges which can be together observed in the SEM micrograph. The morphologies of pore size and pore volume in the NR matrix of material that was characterized by SEM micrographs play an important role in compression set testing. Ordinarily, the bigger pore size will be destroyed first rather than the smaller ones due to macroscopic deformation so that bigger pore sizes are inclined to undergo deformation rather than the smaller size but the results are in reverse direction as shown in [Figure 4.16](#). However, in the results in this experiment, it is possible that during the compression set testing the bigger cells were not damaged and then recovered to give a better recovery [43].

Table 4.3 Data of compression set at 25% and 50% of their original thickness for various compositions of cellulose fibers

NR-C sponges	Compression set at 25% of the original thickness	Compression set at 50% of the original thickness
NR	6.07	11.12
NR-C15	10.28	11.12
NR-C30	12.74	15.09
NR-C45	13.35	16.07
NR+SA1	12.04	20.29
NR-C15+SA1	12.59	16.54
NR-C30+SA1	12.36	18.28
NR-C45+SA1	12.56	20.84

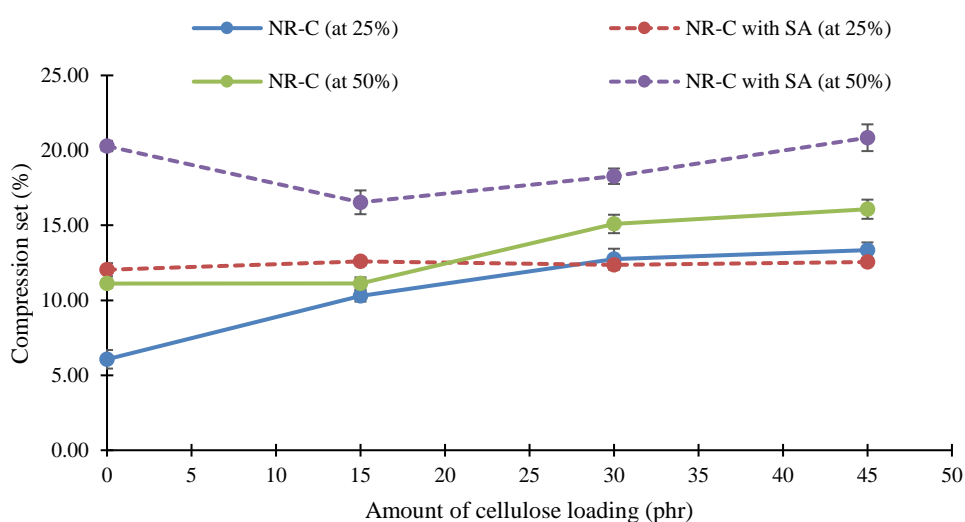


Figure 4.16 Compression set percentage for different amount of cellulose fibers content of NR-C composite sponges

4.2.8 Analysis of FTIR spectra

The rubber molecule can be considered to be polyisoprene, in which individual isoprene molecules are joined by 1,4-addition. They are possible to represent this polyisoprene in *cis* and *trans* isomeric forms. This hydrocarbon polymer consists of 97% *cis*-1,4 units, 1% *trans*-1,4 units and 3% 3,4 units in a head-to-tail structure. The characterization and attribution peaks of FTIR spectra of NR are listed in below table [45]. It can be seen from Table 4.4 and Figure 4.16 that the difference of FTIR behavior of the sponges is obvious. The FTIR spectra of green composite sponges were recorded in the regions of 4000-600 cm^{-1} . The infrared spectroscopy offers unique information about many characteristics such as identification,

composition, structural information, and conformation. FTIR spectra of green composite sponges were compared with variable cellulose content that shown in Figure 4.17. Both the NR-C and NR-C composed of SA substance spectra showed the same band in the 3100-2500 cm^{-1} and 1500-600 cm^{-1} domains. The common vibrational bands were attributed to carbon-carbon and carbon-hydrogen bonds of the macromolecules. Also, the 840 cm^{-1} band of the NR spectra was attributed to the C-H out-of-plane bending of the *cis*-1,4 addition.

Table 4.4 The explanation of absorption peaks of FTIR spectrum of polyisoprene [45]

Wavenumber (cm-1)	Attribution	Wavenumber (cm-1)	Attribution
3080	-C-H stretching vibration of C=C in 1,2-unit	1375	Scissoring vibration of CH ₃ in <i>cis</i> -1,4-, 3,4- and 1,2-unit
3070	-CH ₂ stretching vibration of C=C in 3,4-unit	1325	Scissoring vibration of CH ₃ or CH in <i>trans</i> -1,4-unit
3035	-CH stretching vibration of C=C in 1,4-unit or 1,2-unit	1311	Scissoring vibration of CH ₃ or CH in <i>cis</i> -1,4-unit
2727	Sympathetic vibration	1150	Stretching vibration of CC main chain in <i>trans</i> -1,4-unit
1663	C=C stretching vibration of 1,4-unit	1140	Stretching vibration of CC main chain in <i>cis</i> -1,4-unit
1644	C=C stretching vibration of 3,4- or 1,2-unit	843	Out-of-plane bending vibration of C-H in the -CH=CH- group of <i>trans</i> -1,4-unit
1383	Scissoring vibration of CH ₃ in <i>trans</i> -1,4-unit	837	Out-of-plane bending vibration of C-H in the -CH=CH- group of <i>cis</i> -1,4-unit

According to the FTIR spectra, pure NR as polyisoprene only adsorbed at 2912 and 2928 cm^{-1} are assigned to asymmetric stretching vibration of methyl group (-CH₃). Moreover, it is shown a peak of symmetric stretching vibration of methylene (-CH₂) at 2850 cm^{-1} and a peak of C=C stretching appeared at 1662 cm^{-1} . For a case of cellulose substance, cellulose was successfully analyzed as FTIR spectroscopy by many reports. There is the absorption of the band of O-H stretching assigned to the hydroxyl group at 3000-3500 cm^{-1} , symmetric stretching vibration of methylene (-CH₂) appeared at 2866 cm^{-1} , C-O-C pyranose skeletal vibration at 1035 cm^{-1} . Also, it is shown the band intense of C-O symmetric stretching of primary alcohol appeared at 996 cm^{-1} . The signal at 1061 cm^{-1} is assigned to -C-O group of secondary alcohols and ethers functions existing in the cellulose chain backbone. Bands at 2906 and 1373 cm^{-1} are assigned to stretching and deformation vibrations of C-H group in glucose unit. The absorption band at 898 cm^{-1} is characteristic of β -glycosidic linkage between glucose units. For stretching vibrations of sodium alginate, its stretching vibrations of O-H bonds of SA appeared in the range of 3000-3600 cm^{-1} .

For the NR-C composite sponges, their FTIR spectra exhibited the consisting of pure NR and cellulose peaks which were including at 2912, 2928 and 1662 cm^{-1} are

correspond to $-\text{CH}_2$, $-\text{CH}_3$, and $\text{C}=\text{C}$ stretching, respectively. In addition, there are the peak of cellulose component that exhibited the O-H stretching at $3000\text{--}3500\text{ cm}^{-1}$. For the NR-C composed of SA composite sponges, it has the closely identical pattern with NR-C but peak area of O-H groups at $3000\text{--}3600\text{ cm}^{-1}$ is larger than NR and NR-C conditions because its stretching vibrations of O-H bonds of SA altogether appeared in the range of $3000\text{--}3600\text{ cm}^{-1}$ together.

It can be seen that the absorption band or peak area of O-H groups were enhanced with the increase of cellulose fiber content and SA whereas peak areas of methyl and methylene groups were slightly decreased from peaks of pure NR sponge that can be implied some interactions without chemical reaction between cellulose fibers and NR molecules. Nonetheless, it might be takes place the interaction between NR matrix and cellulose substances such as hydrogen bond that the FTIR spectroscopy cannot find out the detection.

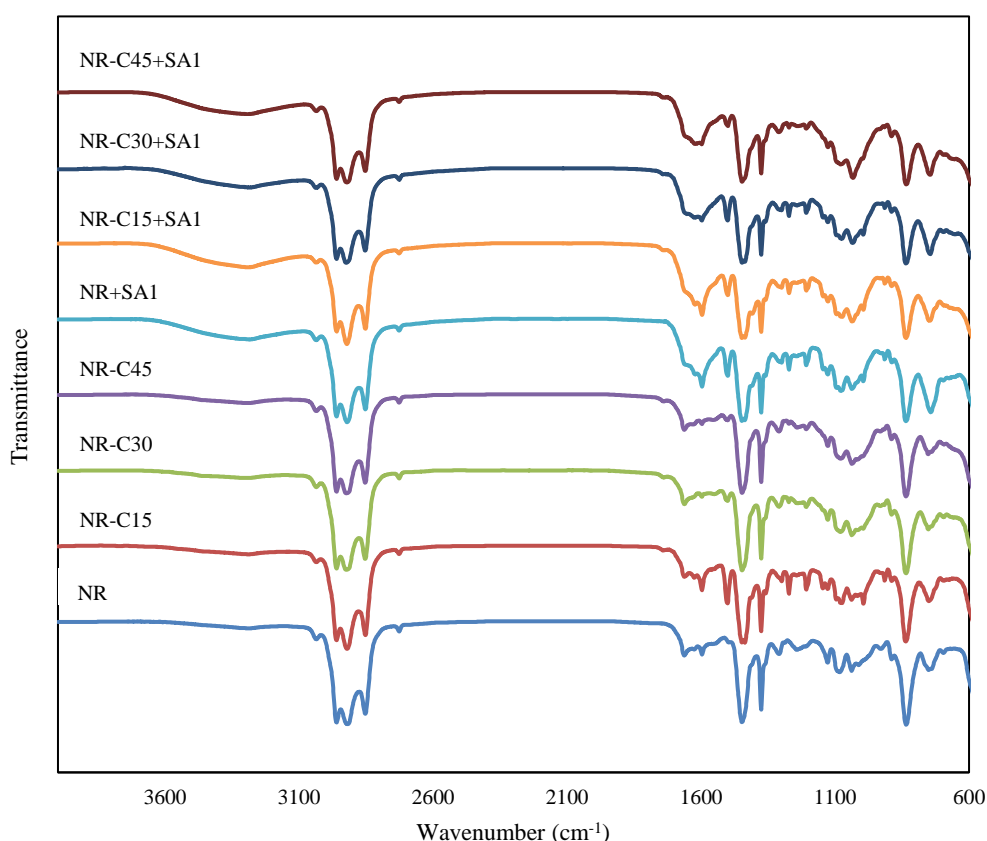


Figure 4.17 FT-IR spectra of NR, NR-C, and NR-C composed with SA sponges

4.2.9 Thermal Gravimetric Analysis (TGA)

The TGA curves of NR-C and NR-C with SA composite sponges were shown in [Figure 4.18](#). The thermal degradation of the NR, NR-C and NR-C composed of SA sponges have been investigated in term of percentage weight loss with temperature.

All of the prepared composite sponges showed single-stage degradation behavior similar to the many previous reports. The thermal decomposition of sponges take place in a single step with temperature of 250-450 °C. The initial weight loss around 80-100 °C was due to the evaporation of moisture from the sponges because when the sponges were heated at lower temperature, volatile components such as moisture or solvent would evaporate first. After heating up, the polymer part would degrade and converse into gaseous products. Finally, the heating will remove all organic matter. For this experiment, the main degradation occurs between 200-450 °C in all the sponges was due to the chain scission and cross-link breakage.

By the addition of cellulose fibers, the sponges increased degradation by temperature that clearly observed at 300-400 °C. This indicates the effectiveness of cellulose substance in raising the thermal degradation of NR sponges. The decomposition of NR-C sponge result in the formation of volatiles and char. These residues act as a protective barrier to both mass and energy transports from the burning surface to the attached polymeric materials. The temperature at which 50% degradation occurs (T_{50}) of NR, NR-C15, NR-C30, NR-C45, NR+SA1, NR-C15+SA1, NR-C30+SA1, and NR-C45+SA1 was found to be 378.3, 377.2, 372.4, 374.7, 378.7, 376.6, 374.8, and 375.0, respectively. The thermal analysis explicitly clarifies that the decrease in the thermal stability of cellulose fibers reinforced NR composite sponges was associated with the substances that were added into the matrix of NR. Moreover, the high crystallinity index of eucalyptus cellulose fibers might also play a important key role in effectiveness the thermal stability of composite sponges. The residue at 750 °C of all NR-C composite sponges for NR, NR-C15, NR-C30, NR-C45, NR+SA1, NR-C15+SA1, NR-C30+SA1, and NR-C45+SA1 were found to be 5.61, 8.89, 0.56, 8.34, 6.59, 8.26, 8.18, and 11.38%, respectively. It was observed that the residue content at 750 °C of composite sponges increased with an addition of cellulose fibers and SA as dispersing agent. This suggests that the cellulose was successfully introduced into NR sponge for improving the lower thermal degradation by heating. Moreover, the improvement of degradation temperature of composite sponges is also reduced by the well dispersed particles of cellulose fibers with SA.

The DTG curves of NR-C composite sponges are shown in [Figure 4.19](#). From the DTG curve, the temperature at which maximum degradation occurs (T_{max}) is pure NR and is 372.3 °C. The degradation of pure NR was started at about 220 °C and then was completed at 450 °C. The major products of thermal degradation of NR are isoprene, di-pentene and p-methene. It might be due to the fact that cellulose filler presented in the material is more prone to thermal degradation.

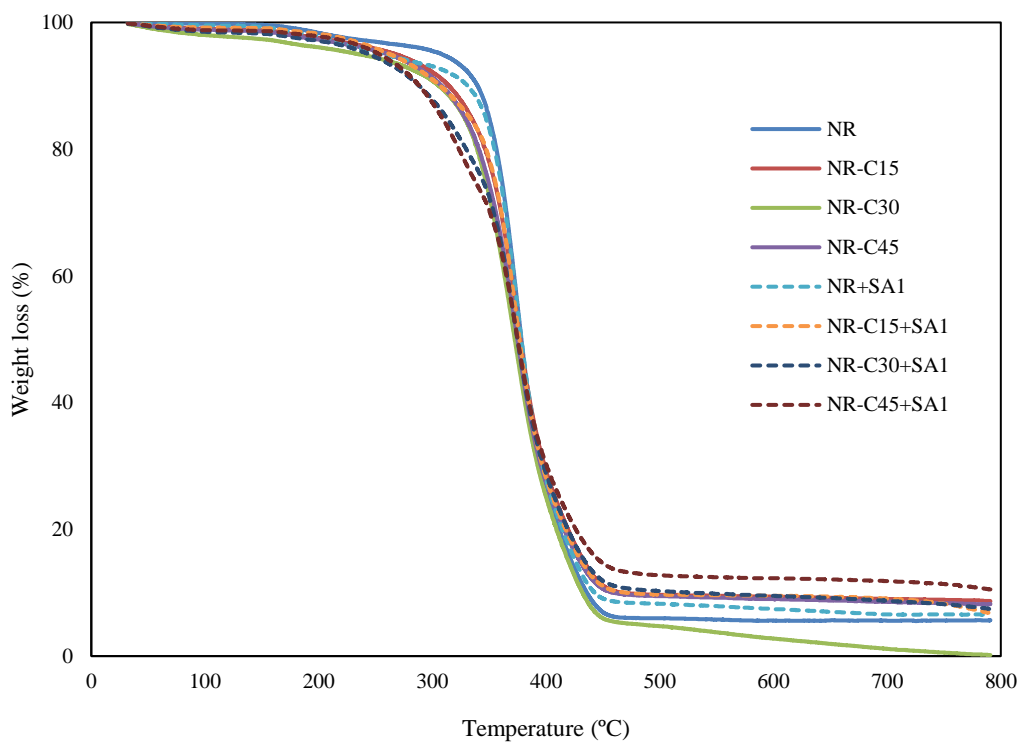


Figure 4.18 The TGA curves of NR, NR-C, and NR-C composed of SA composite sponges in term of percentage weight loss

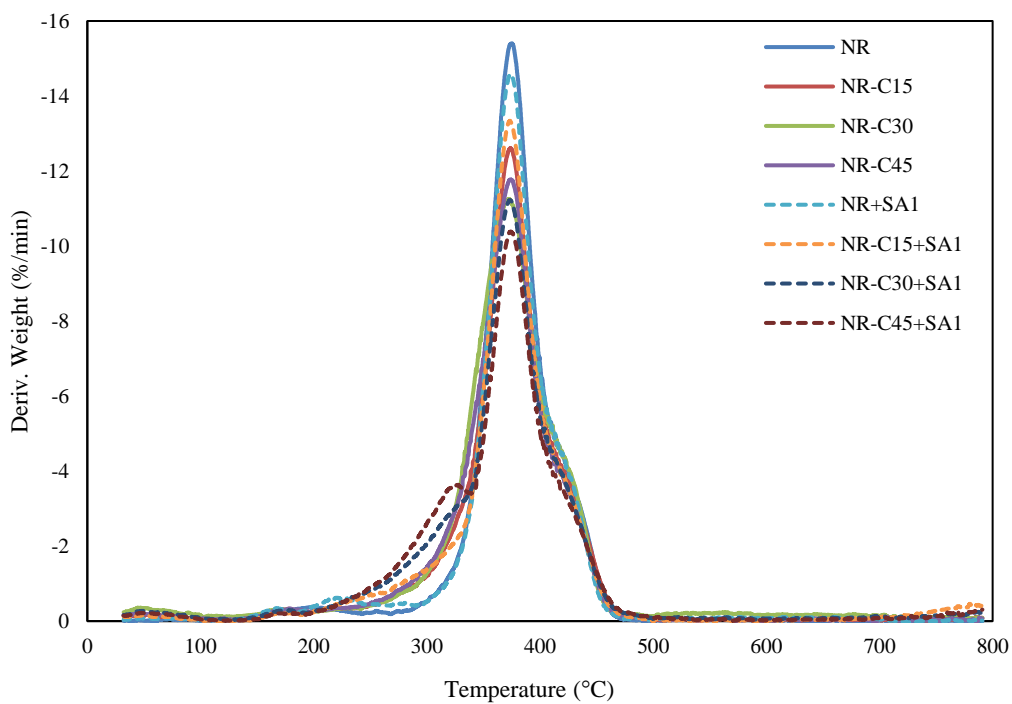


Figure 4.19 The DTG curves of NR, NR-C, and NR-C composed with SA sponges

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the green composite sponges of natural rubber and cellulose (NR-C) with various compositions were successfully synthesized via Dunlop and vulcanization process. The cellulose fibers extracted from the pulp of eucalyptus trees were used as reinforcing agent and sodium alginate was used as a dispersing agent for developing the hydrophilicity to improve absorption rate and water holding capacity inside the matrix of NR-C sponges. The hydrophilicity and pore size of NR-C sponges increased with the addition of cellulose and SA. By using this method, the absorption rate and water holding capacity of NR-C sponge was enhanced with the addition of cellulose fibers together with SA. The maximum values of swelling degree possessed sponge at 30 parts per hundred rubber (phr) of cellulose fibers and 1 phr of SA, which was about 1.81 times higher than that of pure NR sponge. In water surrounding, the swelling ratio of the NR-C composite sponges increased as function of cellulose due to hydrophilic behavior of cellulose fibers incorporation in NR matrix. In addition, a void behind the latex compound that gets filled with air trapped in the composite sponges by agitation becomes the pore volume inside the structural sponges. It directly effects to water holding capacity of green NR-C sponges that the structure of finished NR was confirmed by SEM micrographs.

For mechanical properties, the compressive stress of NR-C sponge in presence of cellulose content at 45 phr was the highest value compared to other conditions and the compression set was higher than that of pure NR sponge when the NR-C sponge was increased the cellulose fibers. Also, the thermal stability of NR composed of cellulose content was little bit lower than pure NR, which was confirmed by TGA. After NR-C sponges added with 1 phr of sodium alginate, it can lead the excellent dispersion between cellulose and NR molecules therefore the hydrophobic groups of NR were reduced to improving the compatible substance that were incorporated in the matrix of composite polymer so SA could be used as dispersing agent for cellulose fiber dispersion in NR composite sponges. The NR-C displays the good physical properties that the sponge exhibited upon the application of forces and easily degraded in the natural environment, which was achieved degradation behavior by burial soil test. The eucalyptus cellulose reinforced green composite sponge can be used as an alternative technique for improving hydrophilicity of green composite sponge production. This novel NR-C product with a good absorption and water holding capacity could be especially useful for agricultural and horticultural options in many applications.

5.2 Recommendations

The higher loading of cellulose fibers can be obtained failed product because of the change of viscosity and foam creating that is the result of mechanical agitation in the presence of many cellulose fibers in matrix composite sponge

As evidence by swelling test which shown that absorption behavior and water holding capacity could be noticeably increased from hydrophilic substances that was added by general method in fabrication of composite production. For the future focus, novel product not only was added the hydrophilic substances but also converted some molecules in NR polymer chains to polar molecules by holding hydrophilic molecules with polyisoprene by chemical reaction that might also enhance more efficiency in the water absorption.



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