

วัสดุที่ประกอบจากยางธรรมชาติและแป้งข้าวเหนียว



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COMPOSITE MATERIAL FROM NATURAL RUBBER AND STICKY RICE FLOUR



Miss Supanee Chantippimarn

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วัสดุที่ประกอบจากยางธรรมชาติและแป้งข้าวเหนียวได้ศึกษาและตรวจสอบถึงความสัมพันธ์ระหว่างโครงสร้างและสมบัติกายภาพ สำหรับกระบวนการผลิตเริ่มจากการผสมยางธรรมชาติและแป้งข้าวเหนียวและส่วนผสมต่างๆด้วยเครื่องบดแบบสองลูกกลิ้ง หลังจากนั้นนำแผ่นยางผสมที่ได้เข้าเครื่องอัดเพื่อทำให้เกิดโครงสร้างโฟม ในการศึกษาด้านโครงสร้างโฟมได้ตรวจสอบด้วยกล้องจุลทรรศน์ และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด เพื่อดูผลของการกระจายตัวและขนาดของเซลล์ ส่วนการศึกษาสมบัติกายภาพจะตรวจสอบความหนาแน่น การดูดซึมน้ำและน้ำมัน และเวลาที่ยางคงรูป สมบัติของโฟมจะแปรผันตาม ปริมาณแป้ง ปริมาณสารเชื่อมขวาง อุณหภูมิที่ให้ความร้อน และสารอื่นๆ ผลจากการศึกษาพบว่า ความหนาแน่น จะลดลงเมื่อเพิ่มปริมาณแป้ง เพิ่มอุณหภูมิที่ให้ความร้อน หรือลดปริมาณสารเชื่อมขวาง การดูดซึมน้ำจะลดลงเมื่อลดปริมาณแป้ง อุณหภูมิที่ให้ความร้อน หรือลดปริมาณสารเชื่อมขวาง ส่วนการดูดซึมน้ำมันจะลดลงเมื่อลดอุณหภูมิที่ให้ความร้อน ลดปริมาณสารเชื่อมขวาง หรือปริมาณแป้งที่น้อยกว่าร้อยละ 40 ทั้งนี้สมบัติกายภาพที่เหมาะสมของวัสดุผสมขึ้นอยู่กับความต้องการที่นำไปประยุกต์ใช้

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จุฬาลงกรณ์มหาวิทยาลัย

หลักสูตร...ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์...

สาขาวิชา...ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์...

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Composite foam made from natural rubber (NR) and sticky rice flour blends has been investigated to establish a relationship between the structure and physical properties. The blends of NR, sticky rice flour and other ingredients were prepared by mixing on a two-roll mill. Subsequently, foam structures of the blends were obtained by compression molding. The foam structure was inspected with an optical and also a scanning electron microscopy for the distribution and average cell size. The physical properties studied were density, water absorption, oil absorption and cure characteristics. Results indicated the influences of foaming process variables, i.e. sticky rice flour loading, cross-linking agent loading, molding temperature and other ingredients added. It was found that density decreases with increasing flour loading, molding temperature and low cross-linking agent loading. Water absorption decreases with decreasing flour loading, molding temperature and cross-linking agent loading. Oil absorption decrease with decreasing molding temperature, cross-linking agent loading, and with flour loading less than 40%. A suitable physical properties can thus be achieved for particular applications of the composite material.

Program...Petrochemistry and Polymer Science..... Student's signature.....

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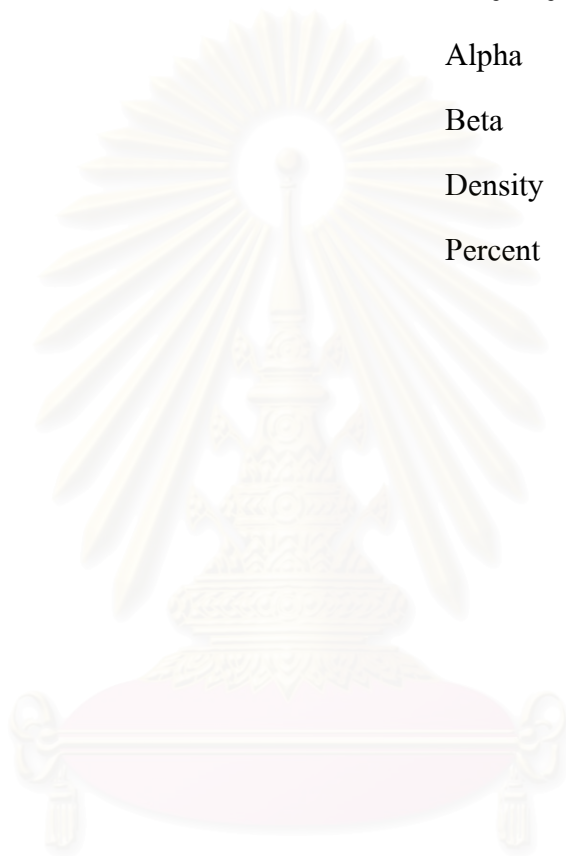


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ABBREVIATIONS

Å	Angstrom
ADS	Air dried sheet
AGU	Anhydroglucose unit
°C	Degree Celsius
cm	Centimeter
Ca	Calcium
CBS	Cyclohexylbenzoyl sulphenamide
g	Gram
hr	Hour
HA	High ammonia
HDPE	High density polyethylene
Kg	Kilogram
LA	Low ammonia
LDPE	Low density polyethylene
m	mass
m ³	Cubic meter
min	Minute
mm	Millimeter
M	Mega
Mpa	Megapascal
MNR	Maleated natural rubber
NR	Natural rubber
phr	Part per hundred of rubber
PVOH	Poly (vinyl alcohol)
RSS	Ribbed smoked sheet
sp.gr.	Specific gravity

SEM	Scanning electron microscope
$t_c(90)$	Optimum cure time
W	Weight
Zr	Zirconium
ZnO	Zinc oxide
ZMBT	Zinc mercaptobenzothiazole
α	Alpha
β	Beta
ρ	Density
%	Percent



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CHAPTER 1

INTRODUCTION

1.1 Scientific rationale

The world consumption of natural rubber has increased at an average rate of 3.74 percent over the five years period (1994-1998) [1], in 2000, the world consumption was 7.35 million tons. Asia in general is the center of production, accounting for 95 percent of world production of natural rubber. The three largest world producers are Thailand, Indonesia and Malaysia. Natural rubber is one of the most important agro-industrial products of Thailand. The preliminary survey of natural rubber and its application according to the Rubber Research Institute of Thailand (RRIT) reported that, in 2000, Thailand produced 2,346,487 tons, exported 2,166,153 tons and consumed 242,549 tons of natural rubber [2]. Thailand is poised to be a dominant force in the rubber market in the future. The global natural rubber production is expected to grow reaching about 8.535 million tons in 2010 [3].

The increase of world synthetic rubber consumption has an immense impact on the future of natural rubber. The choice of raw material is steadily increasing, new polymers and compounding ingredients jostling for a place among those already established and requiring critical evaluation before their worth or be assessed. Therefore, the application and development of a new material is required to produce more advantage and value.

This research work concerns the study of composite material made from natural rubber and sticky rice flour. Natural rubber is abundantly available and not expensive, the same can be said for sticky rice flour. In addition, starch is carbohydrate or polysaccharide that is a natural product, biodegradable and derived from an annually renewable source [4]. It is therefore another choice for better environment in place of plastic made from petroleum. The foam making process for plastics is complicated and the product is generally expensive.

Starch is known to explode into foam when heated to exceed certain temperature. It is therefore a convenient material for the intended composite which is not only a flexible but also a lighter material than rubber alone. The composite will be useful for construction, however, the low oil resistance of rubber and the affinity to water of the starch can be a limiting factor in its applications. The investigation into the foam forming during molding and the physical properties of the resulting material will reveal its usefulness.

1.2 Objectives of the research

- 1.2.1 To determine the appropriate ratio between natural rubber and sticky rice flour for foam forming.
- 1.2.2 To set conditions for required foam structure of the composite material by varying temperature of curing.
- 1.2.3 To observe the influence of sulphur, maleic anhydride and benzoyl peroxide addition on composite material.

1.3 Scope of the research

The research involves the development foam making process for the starch and NR blends and the study of the physical properties of the composite. Followings are work plan:

- 1.3.1 In-depth study of the production method.
- 1.3.2 The composite material with varying content of sticky rice flour (10%, 20%, 30%, 40%, 50% and 60%) is produced for evaluation of the physical properties.
- 1.3.3 The effects of added sulphur, maleic anhydride and benzoyl peroxide is studied.
- 1.3.4 The foam structure formed by compression molding at different temperatures (170°C , 180°C , 190°C and 200°C) is studied.

- 1.3.5 The surface and properties of the composite material is observed:
- a. the surface of composite material by scanning electron microscope (SEM) and optical microscope;
 - b. density, water absorption, oil absorption and cure characteristics.
- 1.3.6 Summation of the results.



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CHAPTER 2

THEORETICAL BACKGROUND

2.1 Natural rubber latex

Natural rubber (NR) latex is obtained directly from the *Hevea brasiliensis* rubber tree, of the family *Euphorbiaceae* by tapping and collecting the fluid [5]. NR latex exudes as thick, white liquid and is called “ fresh or field latex ”.

Normally, fresh latex has the rubber content of around 25-40% by weight. This material is not utilized in its original form due to its high water content and susceptibility to bacterial attack. It is necessary both to preserve and concentrate it, so that the end product is stable and contains 60% or more of rubber [6].

2.1.1 General properties

Natural rubber latex is anionic having isoelectric point between 4-5 pH range [5]. The chemical composition of fresh latex is complex, when compared to synthetic latex. It is known that Hevea latex contains, in addition to rubber hydrocarbon, small amounts of protein, lipids (notably phospholipids), carbohydrates, free amino acids, other organic acid, metals in various chemical combination and inorganic cations. The composition of typical fresh latex is shown in Table 2.1.

It is an established fact that the physical and chemical properties of preserved latex, as received in the consumer countries, differ from those of the freshly tapped latex due to changes which occur during collecting, preservation, concentration and subsequent storage during shipment. The nature and extent of these changes are influenced by many factors, including the composition of latex.

Table 2.1 Composition of latex sap [7].

Constituent	% Composition
Total solid	36
Dry rubber	33
Proteinaceous substances	1-1.5
Resinous substances	1-2.5
Ash	Up to 1
Sugar	1
Water	Add to 100

2.1.2 Stability of natural rubber latex

It has been postulated that the non-rubber constituents, protein-lipid complex, are associated with the rubber particle. As a consequence of the addition of ammonia to preserve the latex concentrate, the lipid materials are believed to hydrolyze slowly, releasing fatty acid soaps which themselves become adsorbed onto the particle surface [8] as an adsorbed layer as shown in Figure 2.1. The variability in composition of both the lipid and soap-protein layers obviously influences colloidal stability.

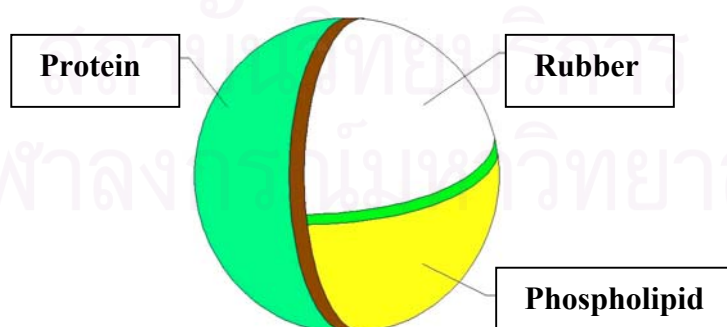


Figure 2.1 Rubber Particle [9].

At present the detail information on the exact nature of the adsorbed layer is not readily available because any attempt to remove the layer results in immediate coagulation of the latex. When fresh latex is concentrated latex having ca. 60% dry rubber content (DRC), it can be preserved in two ways. One is known as low-ammonia (LA) preservatives (0.2% w/w), and the other is high-ammonia (HA) preservatives (0.7% w/w).

In addition, after ultra-centrifugation, fresh latex can be separated into four major components as shown in Figure 2.2.

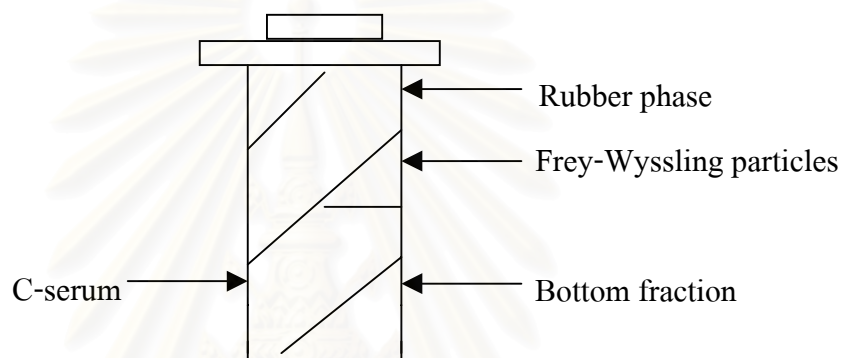


Figure 2.2 Fraction of fresh latex after ultra-centrifugation [10].

Rubber Phase, the white upper layer, consists of rubber hydrocarbon particles stabilized by an adsorbed layer of proteins and phospholipids.

C-serum, the serum comprises mostly soluble substances such as amino acid, proteins, carbohydrates, organic acid, inorganic salts, and nucleotidic materials.

Frey-Wyssling particles, the particles comprise 2-3% of latex volume. It is spherical with encapsulation by two carotenoid layers, which make rubber dark yellow.

Bottom fraction, or lutoid consists largely of the lutoid particles and non-rubber particles.

2.2 Natural rubber

Natural rubber, while at room temperature having considerable strength and appreciable elasticity and resilience, is sensitive to hot and cold and is liable to oxidise to a sticky product [11]. Rubber is a material that is capable of recovering from large deformations quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent, such as benzene, methyl ethyl ketone, and ethanol toluene azeotrope. A rubber in this modified state, free of diluents, retracts within one minute to less than 1.5 times its original length after being stretched at room temperature (18 to 20 degree celsius) to twice its length and held for one minute before [12].

2.2.1 Composition and structure of natural rubber

Natural rubber is commonly obtained from the latex of *Hevea Brasiliensis*. Natural rubber is a high molecular weight polymer composed of isoprene unit (Figure 2.3), C_5H_8 .

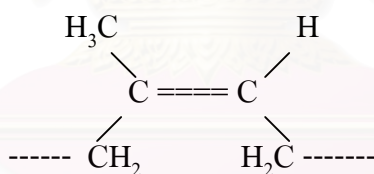


Figure 2.3 Isoprene unit.

The length of the chain is given by interpretations of osmotic pressure data, viscosity of dilute solutions and ultra-centrifuge data. It is thought to be about 350,000 composed of 5,000 isoprene unit [13].

The rubber molecule was a long chain polymer of isoprene arranged in a head-to-tail fashion (Figure 2.4).

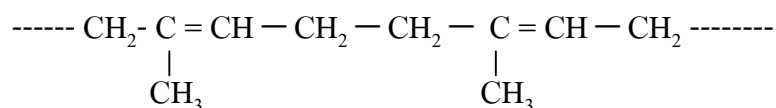


Figure 2.4 Arrangement of isoprene units in head-to-tail fasion [14].

Infra-red studies have indeed shown for a long that natural rubber at least 97% *cis*-1,4-polyisoprene [15] and H-NMR techniques have been used to be establish the structural purity of the *cis*-1,4-polyisoprene. *Trans*-1-4 content is less than 0.2% and 3-4 addition units are present to less than 0.1% [11].

In admixture with naturally occurring resins, proteins, sugars, etc. The composition of the non-rubber depends on the coagulation procedure used and in addition varies somewhat between clones, some high yielding types tending towards higher acetone extract and nitrogen (protein) content.

2.2.2 General properties [11].

The specific gravity of raw natural rubber at 20°C is 0.934, and it increases somewhat, if the rubber is either frozen or stretched. The heat of combustion at constant volume is 44.16 kJ/g, and the specific heat at 20°C is 0.502. Natural rubber, which is purified after extraction with acetone, has a reflective index at 20°C of 1.5212 to 1.5238. Thin film of natural rubber start to absorb light with a wavelength of shorter than 3100 Å, and below 2250 Å, there is complete absorption. The electrical properties of natural rubber are determined by its water soluble impurities. For instance, the specific resistivity of sheets is $1 \cdot 10^{15}$ and that crepe is $2 \cdot 10^{15}$ ohms-cm.

2.2.3 Types of natural rubber [11]

1. Ribbed smoked sheet (RSS)

Prior to coagulation (but after addition and distribution of coagulant) aluminium partitions are inserted vertically into the coagulating tanks so that sheets of coagulum are

produced. These are floated into even-speed rolls provided with water sprays and adjusted to give progressively tighter nips and faster speeds. The last pair of rolls impresses a grooved pattern, and sometimes the producer's identification mark. Drying is in a smokehouse or tunnel at a temperature gradient of 43-60°C, so that the smoked sheets become completely dry within 2 to 3 days.

2. Air-dried sheet (ADS)

For air-dried sheet the RSS procedure is followed but the sheets are dried in hot air without smoking (and no bleaching agent added). The high quality, light-brown coloured grades, which are practically odour free, are characterized by a high degree of purity and their vulcanizates have properties of a high level.

3. White and pale crepes

The natural colour of crepe is pale yellow, mainly owing to its content of β -carotene. To produce the palest crepes, the β -carotene is removed by fractional (two-stage) coagulation of the latex and/or the latex is bleached by the addition of xylyl mercaptan (0.05% max. on rubber). In addition, sodium bisulphite suppresses any tendency towards darkening due to polyphenol oxidase. The coagulum is machined eight or nine times between grooved differential-speed rollers with liberal washing.

For sole crepe (for footwear), a number of plies of thin crepe are laminated to the required thickness, consolidated first by hand-rolling and finally through even-speed rolls.

4. Brown crepes, blanket and compo crepe, flat bark, etc.

The source materials are the field coagula, pre-coagulated lump, cup lump (latex which has continued to flow after collection and has dried on the tapping cup), tree lace (latex which has dried on the tapping cut), earth scrap recovered from the ground. These materials are cleaned by washing and milling in the presence of ample water and the final crepe dried.

2.2.4 Chemical modification of natural rubber

The objectives of chemical modification of natural rubber are two folds, *i.e.*, to improve the behaviour of natural rubber during the manufacture of rubber articles and the performance of these articles in service and to alter the properties of natural rubber in such a way that it could compete in areas of application outside its traditional ones. It should be noted that the backbone unsaturation in natural rubber facilitates certain types of chemical modification to yield a range of modified natural rubber polymers. In natural rubber the all-*cis*, trialkyl-substituted double bond is electron-rich *via* both hyperconjugative and inductive effects, but is also somewhat sterically hindered.

The modification of natural rubber by chemical method can be made in different ways. Some types of the more important modified rubbers are as follows:

1. Changes which result simply from bond rearrangements in the natural rubber molecule (without the introduction of new atoms), *e.g.*, carbon-carbon crosslinking, cyclization, *cis*, *trans*-isomerization and depolymerization.
2. Functionalization by attachment of new chemical groups to the rubber chains through addition or substitution reactions at the olefinic double bonds, *e.g.*, epoxidation, sulphur vulcanization.
3. Grafting of chains of a second polymer to the natural rubber backbone *e.g.*, Heveaplus-MG. A graft copolymer of natural rubber and poly(methyl methacrylate), commercial thermoplastic rubber.

It is useful to remark that chemical reaction such as vulcanization and grafting directly on natural rubber latex or on dry rubber is influenced by the presence of non-rubber contaminants such as proteins. These substances, for example, can act as catalyst inhibitors and influence the course of free-radical reaction [16].

2.3 Starch

2.3.1 General characteristic

Starch is one of the most important polymeric in the plant world. Since it constitutes the chief source of carbohydrate in human nutrition, it is a considered in reserve polysaccharide of the vegetable kingdom, being stored as minute white granules in the roots, bulbs, tubes, seeds, pith, and fruit of plants.

Starch is extracted by grinding with water, filtering, centrifuging, and drying, a process which yields starch in a granule form [17]. The granules, which vary in size (from about 0.005 to 0.02 mm across, with some up to 0.15 mm in length), have a concentric layered structure and are often very distinctive in shape.

At room temperature natural starch is insoluble, but when heat but some fifteenfold its weight of water to 65-85°C it forms viscous dispersions that may set to gels when cold [18].

2.3.2 Structure and composition of starch

Chemically, starch is a polymeric carbohydrate consisting of anhydroglucose units (AGU) linked together primarily through α -D-(1 \rightarrow 4) glucosidic bonds. While the detailed fine structure has not been fully elucidated, it has been established that starch is a heterogeneous material consisting at the extremes of two major types of polymers, namely amylose and amylopectin, and also contain moisture, lipids, proteins and mineral ions either present discretely in the matrix of the starch granule or as a specific complex with the starch polymer.

1. Amylose

Amylose is essentially a linear polymer in which the anhydroglucose units are predominantly linked through α -D-(1 \rightarrow 4) glucosidic bonds (Figure 2.5). Its molecular size varies depending upon the plant source and processing conditions employed in extracting the starch. It may contain anywhere from about 200 to 2000 AGU [19].

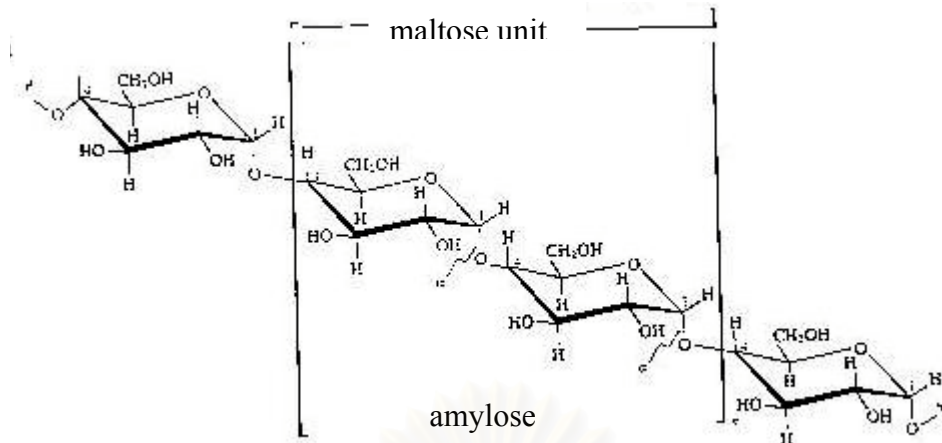


Figure 2.5 Structure of of the amylose fraction of the starch [21].

2. Amylopectin

Amylopectin is a branched polymer containing, in addition to anhydroglucose units linked together as in amylose through α -D-(1 \rightarrow 4) glucosidic bonds, periodic branches at the carbon-6 positions. These branches are linked to the 6 carbon by α -D-(1 \rightarrow 6) glucosidic bonds (Figure 2.6). Each branch contains about 20 to 30 AGU [19]. Besides, amylopectin is the crystalline part of starch particle, so if there is only amylopectin, starch can exist itself. Moreover, most of various starch also amylopectin more than amylose [20].

3. Moisture

The moisture content of starch will vary depending on the surrounding conditions in which it is placed. Moisture contents are usually quoted at 5.5% relative humidity and 20°C, typical ambient conditions. The ability of starch to gain and lose large quantities of moisture is utilised in confectionary in starch-depositing processes [22].

4. Lipids

Lipids are of importance in the starch since they can form complexes with the starch polymers and make a significant contribution to the behavioural characteristic of starch.

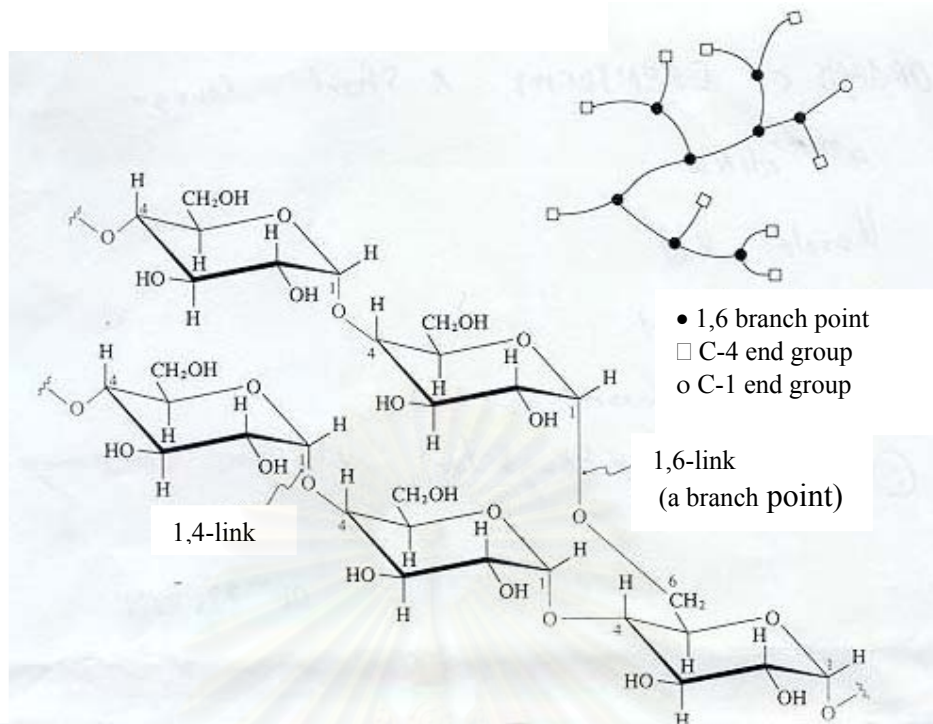


Figure 2.6 Structure of the amylopectin fraction of the starch [21].

5. Proteins

The proteinaceous matter is more important in a food starch application than in glucose syrup manufacture due to off-taints that may develop. Since the protein and peptides have surface activity, of far more significance is the problem of foaming caused by these residues. If not removed they can contribute to unacceptable levels of browning and foaming during concentration or during subsequent use. These residual proteins can be reduced to acceptable levels through the correct use of enzymes and refining techniques [22].

6. Ash

All starches contain mineral ions. The cations are mainly sodium, potassium, and magnesium but calcium, aluminium, and iron are also found.

2.3.3 General properties

1. Swelling and gelation of starch

The swelling and gelatinization behaviour of natural starches varies considerably according to the source and previous history of the samples. The gelatinization temperature range varies with starch species as shown in Table A2 [23] in the Appendix A. However, most starch follow the same general pattern of behaviour. In cold water most starches are insoluble and swell only to a limited extent. On heating, little further swelling occurs until the temperature reaches about 60°C when the granules start to swell vary rapidly with increasing temperature.

The temperature at which swelling starts is called the initial gelatinization temperature. Apart from swelling, a number of other changes occur. The granules begin to lost their birefringence the solubility of starch increases due to the loss of low-molecular-weight amylose from the granules, and the solution becomes viscous and sticky. If the solutin of gelatinized starch is sufficiently concentrated it will set to a rigid gel on cooling to room temperature [24].

2. Retrogradation

Retrogradation is a term given to the changes with occur in a starch paste or gel an aging. Solutions of low concentration (approximately 2% or less) become increasingly cloudy due to the progressive association of starch from solution takes place, and it was because the precipitated starch appeared to be reverting to its original condition of cold-water insolubility that the term retrogradation was used for these phenomena. Pastes of higher concentration on cooling set to a gel, which on aging becomes steadily firmer due to increasing association of the starch molecule [24].

2.4 Polymer blends

2.4.1 The Importance of blending [25-26]

The reason for blending are mainly the following points:

1. Incorporate the ingredients and ancillary substances necessary for vulcanization.
2. Adjust the hardness and modulus of the vulcanised product to the value required.
3. Detection and role of phase boundaries and their influence on compatibility.
4. Cost savings for expensive engineering materials.
5. Increase size stability.
6. Improved fire retardancy and corrosion protection.
7. Improved electrical properties and reduction of dielectric constant .

2.4.2 Factors affecting blend properties [25]

The normal considerations of compounding a vulcanizate of a single elastomer for a particular use such as filler type and loading, type of cure system and level, and antidegradants. There are a number of factors which arise in blends of elastomers, primarily because these almost always have more than one polymer phase. These factors may be summarized as:

1. Polymer ratio, the relative amounts of each elastomer, is readily controlled and is often dictated by the end use in mind.
2. Phase morphology, control of phase size is more complicated and obviously the conditions of preparation of the blend have a major influence. In general, the higher the shear used in mixing, the smaller the phase size attained, although some elastomers undergo chain scission during mixing and there can be an optimum degree of mixing before phase size increase again.
3. Interfacial adhesion/crosslinking, Interfacial tension imposes a limit on the phase size which can be attained under a given shear regime. The lower the interfacial tension also plays a role in the control of the interfacial adhesion and crosslinking between

the two elastomer. High interfacial tension means little mixing of the two elastomers at the interface.

4. Distribution of the filler.

2.4.3 Processing of the rubber compounding

In many cases, polymer composite processing utilizes the same technique as polymer processing which include injection molding, compression molding and extrusion. There are other techniques which are unique only to polymer composite processing, the operational conditions can be very different; thus, it is important not to directly transfer knowledge without careful consideration.

1. Two-roll mills [26]

The mixing of compounds on open mills proceeds as follows:

The rubber is first worked on the mill until a coherent band is formed on the mill rolls. Subsequently, those chemicals are added which are difficult to mix, and which are used in small quantities only, namely protective agents and accelerators, so that they will be well dispersed during the mixing cycle. Next, part of the filler is added, together with stearic acid, if required. On adding softeners, the band will be generally split, and it has to heal before additional fillers are added to the compound. Finally, the sulfur is mixed in, if no ultrafast accelerators are present. Otherwise, the sulphur is added on the warmup mill before processing. During the mixing process, the band must not be cut, and only after all ingredients have been incorporated in the compound, the band is cut and folded, that is, the compound is homogenized. When the mixing cycle is completed, the compounds is cut from the mill.

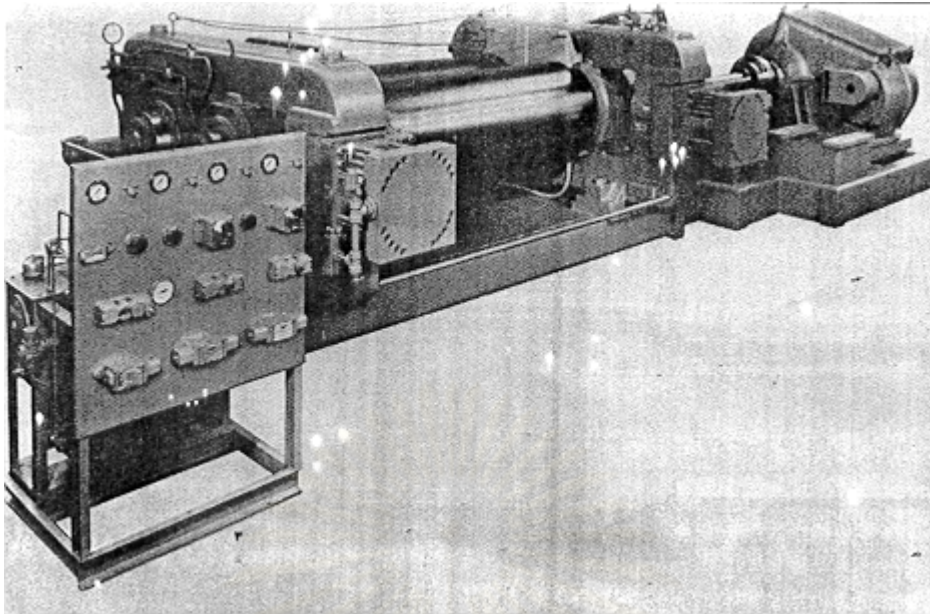


Figure 2.7 Two-roll mill compounding machine.

2. Compression molding, Transfer molding and Resin transfer molding [26]

Compression molding uses a press to compress either a dough of resin and fiber mixture, on the layers placed by a hand lay-up method or mechanical means, typically at an elevated cure temperature. With the compressive force, the void content is lower than the ordinary atmospheric pressure processing method.

A matched die mold allows shaping of the composite precursor into reproducible shapes. Although a compression molding machine is used, it is still a labor intensive method as the dough or layed-up materials must be weighed and hand-fed into the mold.

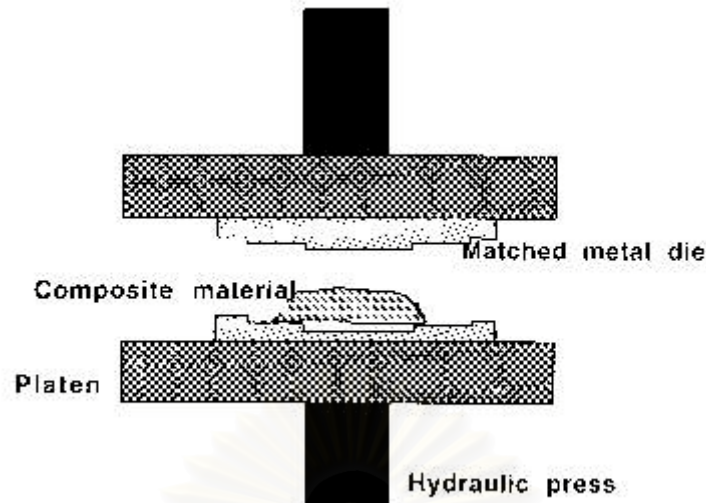


Figure 2.8 Schematic diagram of compression molding press [26].

Transfer molding is the improved version of compression molding from the material metering point of view as the fiber/resin mixture is transferred from the reservoir into the mold cavity by the press. However, a long-fiber reinforced composite cannot be made. This method is nearly identical to a plunger-type injection molding operation based on the material flow. The term “transfer molding” is used for a compression press operation while plunger-type injection molding is obviously carried out in an injection molding machine.

Resin transfer molding is the same as the ordinary transfer molding except that only the resin is transfer molded into the mold cavity where fabrics are placed beforehand. Preforms of glass fibers and other reinforcements can be made with short fibers and sometimes continuous fibers. Preforms must be made to withstand the pressure if resin injection in order to avoid compression of the fibers during mold filling which would lead to inhomogeneous fiber distributions in the final part. Curing proceeds typically after filling at an elevated temperature.

3. Injection molding [26]

Injection molding is probably the most extensively used method for processing short fiber reinforced thermoplastics. The fiber/resin mixture, whether it is preblended or fed as a physical mixture, is fed into the hopper and transferred into the heated barrel. The material softens by the heat transfer from the barrel wall. At the same time, the screw rotates to apply high-shear process to further heat the material and fill the barrel. The molten material is collected in front of the screw by the rotation of the screw, and the injected with a high pressure into the mold cavity through the runner and the gate. The mold is cooled below the solidification temperature of the resin in case of thermoplastics composites. The level of automation of this method is the highest among many processing methods. Due to the intensive mixing with high-shear and passage through a narrow gate, extensive fiber damage occurs, therefore, injection molding for composite materials is suitable only with short fiber reinforced or particulate-filled polymers.

4. Reaction injection molding [26]

Reaction Injection Molding (RIM) is one of the newest processing methods. Instead of using already polymerized materials as matrices, highly reactive monomeric or oligomeric ingredients are placed into the tanks which are then quickly mixed by impingement, and injected into the mold cavity. As soon as the two materials are mixed, chemical reaction begins to form a polymeric matrix, which completes typically within 5-30 seconds. Thus, the major portion of the RIM machine is a higher pressure pump and a metering system. Again, with high intensive shear, only short fibers and fillers can be used as reinforcements. However, RIM utilizes low viscosity chemicals and this allows the preplacement continuous fiber-woven fabrics in the mold in the same as resin transfer molding. Distinction is made between these two methods based on the preparation on the resin precursor. When the resin formulation is already made, the method is called resin transfer molding while if the resin is prepared in-situ by an impingement or static mixer, the method is termed RIM.

5. Extrusion [27]

Extruders are machines which force rubber through a nozzle or die to give a profile strip of material. They fall into two types: those in which the pressure is produced by a ram, and those in which the pressure is produced by a screw. The later is the type of machine most generally used in the industry and is known as an extruder, forcing machine, or tuber, whereas the ram extruder is a more specialised machine for short runs.

Extrudate swell is an important characteristic of polymers, since it determines the geometrical dimensions of the final extruded product.

6. Pultrusion [28]

Pultrusion is a process used for making continuous filament reinforced composite extruded profiles. Reinforcing filaments, such as glass fiber roving, are saturated with catalyzed resin and then pulled through an orifice similar to an extrusion die, polymerization of the resin occurs to continuously form a rigid cured profile corresponding to the die orifice shape. The material are pulled through the die rather than being pumped. Although the primary resins used are of the thermosetting type such as polyester, vinyl ester, and epoxy, thermoplastic resins can be utilized in the same process. The major design consideration for thermosetting systems consist of the dispersion of the resin in the reinforcement and the conditions for complete cure of the resin.

2.5 Cellular rubber

Cellular rubber products are probably more varied than another rubber product. In addition to the natural technological differences between one rubber formulation and another, the degree of expansion causes significant changes in the properties and these is further varied by the cellular structure, which may be opened or closed.

Classes of cellular rubber

Cellular rubber is defined as a mass of cells in which the main is rubber. The three mains classes of cellular rubber are:

1. Foam rubber

Foam rubber is particularly defined as a product made from liquid starting materials; the best sample is latex foam, in which the cellular structure is intercommunicating [29].

The production of a foamed latex depends upon the inclusions, the latex, of gas bubbles which are initially discrete and non-communicating to enable an increase in volume to take place but which, in the end product, are open and interconnecting and give the resulting.

The process most used today is called the Dunlop process. It consists of adding a slight excess of soap, over and above that needed to stabilize the latex, and of beating air into the latex with a whisk. The latex froths up to something like 10 times its original volume, depending on how much air is beaten in. The more air the lighter the foam and the softer final product. In the latex stages of foaming a delayed action coagulant is added and when the mixture has the consistency required it is poured quickly into a mould. The latex then coagulates and at the same time the foam structure changes. The individual air spaces become interconnecting. Vulcanization takes place in the same mould and is effected by steam. The mould is then opened and the steaming article removed, washed through in water and dried. Much of the water can be squeezed out by hand; this is supplemented by centrifuging the article, which removes more water, and finally by drying in hot-air chambers. The foam rubber thus made has a permanent structure of interconnected air spaces so that rubber is porous [30].

2. Sponge rubber

Sponge rubber is made directly from solid starting materials. The production method for sponge rubber give rise to an open or intercommunicating structure.

Sponge rubber production fallows normal mixing particles except that the highly plasticised formulations create sticking problems. Mixing in internal mixer is preferred to open mill mixing, and peptisation is commonly adopted to reduce cycles to an economic level. This procedure, however, creates some problems because of the difficultly of obtaining precise controll over the level of viscosity required [29].

Sponge products include carpet underlay, industrial sheet, moulding, soleing, and automobile sealing strips. The mixed batches are processed on extruders or calenders to give the required section or sheet stock from which the blank is prepared. In applications requiring a tough outer skin, such as door seals or slipper soleing, a mix without blowing agents in calendered sheet form is applied to the sponge profile [11].

The curing and blowing of the sponge is carried out either freely or in a mould which is only partially filled with the moulding compound. In the free blow method, the section is hot air or steam cured and the resultant product usually shows considerable dimensional variation. In the moulding operation, a trial and error procedure is adopted to determine the mould volume loading necessary to produce a product with the desired prsperties. Sponge compounds are not usually highly blown, and a volume loading of 40-60% is common. Adequate venting of the mould and liberal use of tale or other dusting agent enable air to escape freely from the surface of the matrix and so avoid the formation of surface blister.

3. Expanded rubber

Expanded rubber is made from solid starting materials same sponge rubber but the term “expanded rubber” is applied to those materials which have a substantially closed cellular structure.

Another important manufacturing process is that in which inert gas such as nitrogen and carbon dioxide are used as sponging agents. Usually the compound rubber is put into containers, which in turn are placed in a heat chamber, the temperature being such that only slight vulcanization can take place. Inert gases are then forced into the ensure that the gas is uniformly dispersed throughout the rubber. The pressure is released, and the containers colled, and as a result the gas expands the rubber to about five or six times the original volume. This expanded rubber is then built up to the usual manner. As additional expansion takes place during final vulcanization the compound must be less in volume than the mould. This is the principle employed in making hard rubber sponge [13].

Unicellular rubber fabrication is characterized by the need for achieving at least partial cure before extension below occurs and by the three-dimension involved (compared with primarily unidirectional expansion of open cell sponge) with reduced heat transfer and consequently long cure times.

2.6 Literature reviews

S. Thiebaud, et al. [31] studied the starch esters were mixed with low density polyethylene (LDPE) at various propotions in Haake Rheometer (ester group was found to act like an internal plasticizer). It can be seen that tensile strength decreases and the elongation at break increases with an increasing degree of substitution, this is because starch with higher content of fatty ester groups becomes more plasticized and also loses its crystallinity. The water absorption decreases these increases are higher when the carbon chain length is longer and the degree of substitution of starch ester is higher. Also, the tendency of starch to swell in water is eliminated by the chemical modification. The addition of starch esters to LDPE led to a very slow rate of biodegradation of these blends.

S. Kiatkamjornwong, S. Thinakorn, and P. Tasakorn [32] studied the foaming process of high density poethylene (HDPE) and natural rubber (NR) blends, using azodicarbonamide as a chemical blowing agent (It was found the hardness, tensile

strength, tear strength, flexural strength, and elastic modulus decrease with increasing weight of blowing agent). The blends were prepared on a two-roll mill at 150°C. Subsequently found structures of the blends were obtained by a single stage compression moulding at 170°C. It was found this foaming process variables, *i.e.* heating time, blowing agent loading, and ratio of HDPE/NR at a fixed crosslinking agent loading.

R. L. Shogren, et al. [33] studied starch-poly (vinyl alcohol) foamed articles prepared by a baking process. It was found the starch component was gelatinized (melted) during baking while the PVOH component crystallized to a high degree during baking. Scanning electron micrographs of the surface of the foams revealed a phase-separated morphology in which swollen starch granules were embedded in a matrix of PVOH. The improvement in strength at low humidity was greater for partially (88%) hydrolyzed PVOH while strength at higher humidities improved most with fully (98%) hydrolyzed PVOH and foam flexibility increased with higher PVOH molecular weight. Crosslinking agents such as Ca and Zr salts were added to starch batters to give further increases in water resistance (Bake foams prepared from starch and PVOH have mechanical properties that are adequate for use as packaging containers over a wide range of humidity).

H. Kakinoki, et al. [34] patented the granular material prepared by mixing 3-60% of rubber latex, starch and water, wherein the starch contains 10-25 weight % of water. These granular material is packed in a mold and heat to a temperature within the range 100-250°C thereby form a foam-expanded materials, the material expands to 3-4 times its original volume. The foam-expanded material has biodegradability, and suitable for use as a shock absorber that prevents environmental pollution.

C. Bastioli, et al. [35] patented a method for producing biodegradable foamed articles by agglomeration of foamed particles having composition comprising a

thermoplastic starchy material or a thermoplastic natural polymer capable for absorbing water when converted into the thermoplastic state, a thermoplastic polymer and water. Biodegradable foamed articles having density comprised from 5-300 kg/m³.

C. Nakasorn, et al. [36] studied rheological (and curing behaviour) of reactive blending interaction maleated natural rubber (MNR) and cassava starch. It was found that the pure MNR gave the lower apparent shear stress, shear viscosity than did those of the blends with cassava starch. The rheological data of the MNR blends increased with increasing quantity of cassava starch. Furthermore, rheological properties increased with increasing the levels of compatibilizer (MNR). The curing curve of pure MNR without cassava starch gave the long delayed onset on vulcanization (10 min), but it was shortened by adding the cassava starch.

H. Shirato, et al. [37] patented shape-recoverable resin foamed product. These resin foamed product was foamed of a resin, which was natural resin, synthetic resin, thermoplastic resin, thermosetting resin, or as a mixture of two or more of thereof. It was found the resin with the closed cells therein has a shape-recoverable property at ambient temperature, a closed cell rate higher than 30% and a compression permanent set lower than 10% (Thus, when contraction takes place in the resin with the closed cell, after a predetermined time has passed without providing an outer stimulation to the resin, a shape of the resin foamed product formed of the resin with the closed cells is automatically recovered at least in one direction without equally expanding in all direction).

J. J. G. Van Soest, et al. [38] studied the mechanical properties of the thermoplastic waxy maize starch. Granular waxy maize starch was plasticized by extrusion with water and glycerol. It was found the amorphous rubbery materials are soft and weak with moduli of 0-10 MPa and tensile strength of 0-2 MPa. The materials are viscoelastic, resulting in high values of elongation (500%) and the initial increase in modulus, tensile

strength, and relaxation time is the result of the lower mobility of the amylopectin molecules and the reinforcement of the network by physical crosslinking.

A. Roberta, I. Salvatore, and N. Luigi [39] studied the synthetic and characterization of starch-based polyurethane foams, which were synthesized by reacting a mixture of starch and polycaprolactone triol with an aliphatic diisocyanate, in the presence of water as blowing agent. Starch-based polyurethanes show higher glass transition temperature and lower thermal stability.



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CHAPTER 3

EXPERIMENTAL METHOD

3.1 Material and equipment

3.1.1 Chemicals

1. Ribbed smoked sheet.
2. Sticky rice flour (Erawan Brand) with physical properties of sticky rice flour listed in Table 3.1.

Table3.1 Physical properties of sticky rice flour

Properties	Value(s)
Moisture (%)	12
pH	6.5-7.0
Ash (%)	0.3
Viscosity (B.U)	280-300
Colour	White

3. Sulphur powder (analytical grade) from S.R. Lab. Co., Ltd.
4. Maleic anhydride (analytical grade) from A.C.S. Xenon Limited Partnership.
5. Cyclohexylbenzoyl sulphenamide (commercial grade) from Cosan (Thailand). Co., Ltd.
6. Lowinox (commercial grade) was obtain from Cosan (Thailand). Co., Ltd.
7. Stearine (commercial grade) was purchase from K. H. Co., Ltd.

3.1.2 Equipment

1. Two-roll mill compounding machine for mixing and compounding the rubber.
2. Compression molding machine model Labtech LP 20 (Labtech Engineering Co., Ltd.).
3. Rheometer model MDR 2000 (Monsanto Co., Ltd) for determining optimum cure time [$t_c(90)$].
4. Densitometer model Densitech II (Tech pro Co., Ltd.) for determining density.
5. Scanning Electron Microscope model JSM 5800LV (JEOL Co., Ltd.) for analysis the surface of composite material.
6. Optical Microscope model Olympus BS 60 (Olympus Co., Ltd.) for determining distribution of starch.

3.2 Experimental methods

3.2.1 Rubber/sticky rice flour mix sheet production

Ribbed smoked sheet was mixed with chemicals with compositions given in Table

- 3.2. The mixing was carried out on a two-roll mill at room temperature, in three stages:
- 1) rubber, steryl alcohol and stearine were mixed first,
 - 2) zinc oxide, lowinox and CBS were added next,
 - 3) sulphur and ZMBT were added last.

Table 3.2 Composite material formulation

Ingredients	Part per hundred of rubber (phr)
Ribbed smoked sheet rubber	100.0
ZnO	5.0
Stearine	2.0
Stearyl alcohol	1.0
Lowinox	1.0
CBS	1.5
ZMBT	0.7

The mixture was passed through two-roll mill with a gap setting of 1.5×10^{-3} m then the gap was set at 1.0×10^{-3} m for further addition of sticky rice flour. The ratio of rubber to sticky rice flour chosen is shown in Table 3.3. The compound was made into sheet. Furthermore, some specimens were mixed with dye to test colouring of the compounds.

In addition, the effect of cross-linking agent on composite properties is investigated by using two types of cross-linking agent with ratio given in Table 3.4.

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Table 3.3 Formulation of composite materials of NR-sticky rice flour

Test Series*	% of sticky rice flour	Sulphur (phr)	Temp (°C) / time 15 min
A	10	2.5	180 °C
	20	2.5	180 °C
	30	2.5	180 °C
	40	2.5	180 °C
	50	2.5	180 °C
	60	2.5	180 °C
B	60	2.5	170 °C
	60	2.5	190 °C
	60	2.5	200 °C
C	60	0	180 °C
	60	5	180 °C
	60	20	180 °C
	60	45	180 °C

* Series A is for effect of sticky rice flour / NR compound ratio, B is for effect of molding temperature and C is for effect of sulphur loading

Table 3.4 Cross-linking agent loading.

Flour*/NR Compound	Sulphur (phr)	Benzoyl Peroxide (phr)
60/100	----	2.5
30/100	----	2.5
30/100	2.5	---

* containing 10% maleic anhydride (part per hundred of flour)

3.2.2 Rubber / sticky rice flour foam and flatten sheet production

Rubber compound was vulcanized and foam formed during compression molding at a temperature given in Table 3.3. The specimen was then flatten out by pressing at room temperature.

3.3 Composite material properties testing

1. Density [40]

The specimen was hooked on the balance, and it was weighed in air and in distilled water at standard temperature ($27^{\circ}\text{C} \pm 2^{\circ}\text{C}$). For a density of more than 1 it was determined from Equation 3.1 and For density less than 1 it was determined from Equation 3.2.

$$\rho = \frac{m_1}{m_1 - m_2} \quad (3.1)$$

where ρ is the density of rubber (Mg/m^3)

m_1 is net mass of rubber (Mg)

m_2 is mass of rubber less mass of an equal volume of water, determined by weighing in water (Mg)

$$\rho = \frac{m_1}{m_1 + m_2 - m_3} \quad (3.2)$$

where ρ is the density of rubber (Mg/m^3)

m_1 is net mass of rubber (Mg)

m_2 is mass of rubber less mass of an equal volume of water, determined by weighing in water (Mg)

m_3 is mass of sinker and rubber less mass of a volume of water equal to their combined volumes, determined by weighing in water (Mg)

2. Starch distribution using optical (visible light) microscopy

A sample of thin starch/rubber compound was treated with iodine to develop the typical blue-violet complex. This is one of the oldest and best known reaction of starch. It was then placed on a slide with cover slip and inspected on a cavity microscope.

3. Inspection of foam by scanning electron microscopy

The samples were mounted on aluminium stubs with graphite-filled tape and vacuum-coated with gold-palladium to prevent the build-up of a primary electron negative charge on otherwise nonconductive starch.

4. Water sample absorption

A round sample was cut from a vulcanized piece to a size of 1.1×1.1 cm. Water absorption was measured by placing the sample in a petri dish containing distilled water. The dish with sample was then placed in an oven kept at 75°C . At a regular time intervals of 1, 2, 4, 8 and 24 hr, the sample was removed from the dish, wiped excess water on surface with blotting paper, and subsequently weighed to determine water uptake. The sample was then placed back into the water after each measurement. The water absorption was calculated as the weight difference and reported as percent using Equation 3.3.

$$\text{Absorption percentage} = \frac{W_t - W_i}{W_i} \times 100 \quad (3.3)$$

Where W_t is weight of sample after uptake solvent

W_i is initial weight of sample

5. Oil absorption

A round sample was cut from a vulcanized piece to a size of 1.1×1.1 cm. Oil absorption was measured by placing the sample in a petri dish containing lubricating oil. The dish with sample was then placed in an oven kept at 75°C . At a regular time intervals of 1, 2, 4, 8 and 24 hr, the sample was removed from the dish, wiped excess oil on surface with blotting paper, and subsequently weighed to determine oil uptake. The sample was then placed back into the oil after each measurement. The oil absorption was calculated as the weight difference and reported as percent using Equation 3.3.

6. Cure characteristics [41]

The cure characteristics of compound rubber was determined for finding the condition of rubber vulcanization. The specimen was cut into 0.03 m in diameter and 13×10^{-2} m in thickness, it was then placed on the top of the oscillating disc before closing of die. The specimen was heated at 150°C until it reached optimum cure or 90% cross-linked time.

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CHAPTER 4

RESULTS AND DISCUSSION

The hypothesis of this research is that starch granules mixed into natural rubber will act as blowing agent generating foam network throughout the mixture. If our assumption is true, structure of the cell network will depend on the distribution of starch particles in the rubber. As a result the new composite material will have less density (and lighter) than normal rubber due to the porous structure. The presence of starch will allow this material to have higher water affinity than traditional vulcanized natural rubber making it environmental friendly as it is likely that this new material is biodegradable. Moreover, we predict that adding starch to natural rubber will increase its oil resistance property. Unlimited practical applications can be derived, combining good oil resistant property with foam texture, from the new composite starch/natural rubber material.

4.1 Density of composite material

Studies were done to compare densities of the original NR/starch mixtures to those of the corresponded composite materials made by vulcanization process. The results are as followed:

4.1.1 Effect of sticky rice flour content on density

Since the density of starch is higher than rubber, we expect the density of starch/NR mixture to increase with increasing amount of starch content as shown in Figure 4.1. When the mixture is heated and vulcanized at a temperature high enough for starch to explode forming foam, the density of the new material decreases with increasing starch content. This can be explained that a mixture containing higher concentration of starch have higher porosity and therefore less dense. The results at this stage indicated that glutinous rice starch is a very good blowing agent for our purpose.

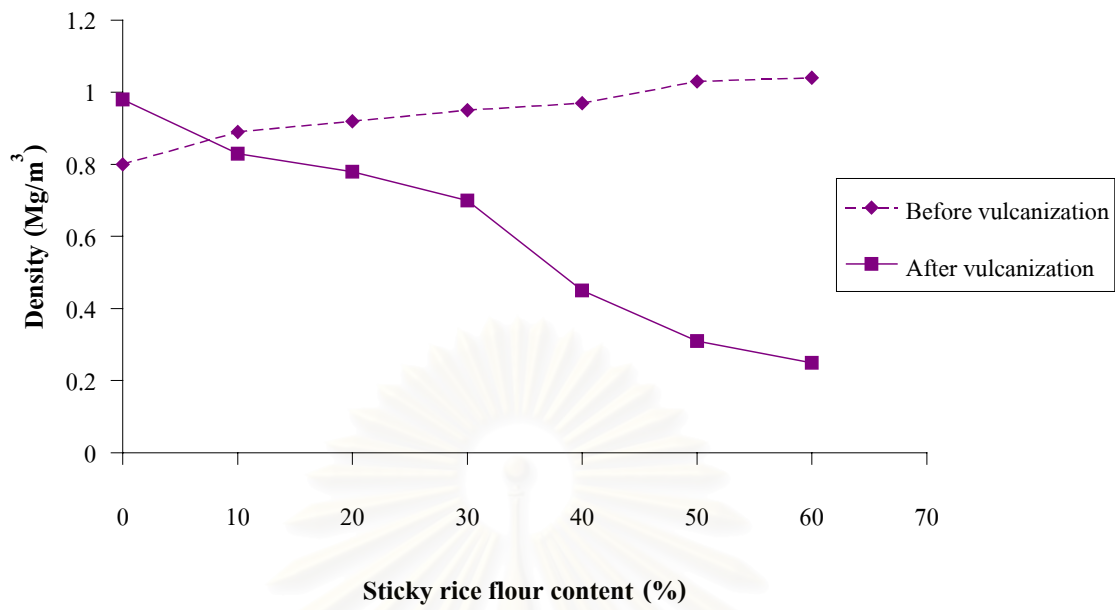


Figure 4.1 Effect of sticky rice flour content on density of composite material.

4.1.2 Effect of sulphur content on density

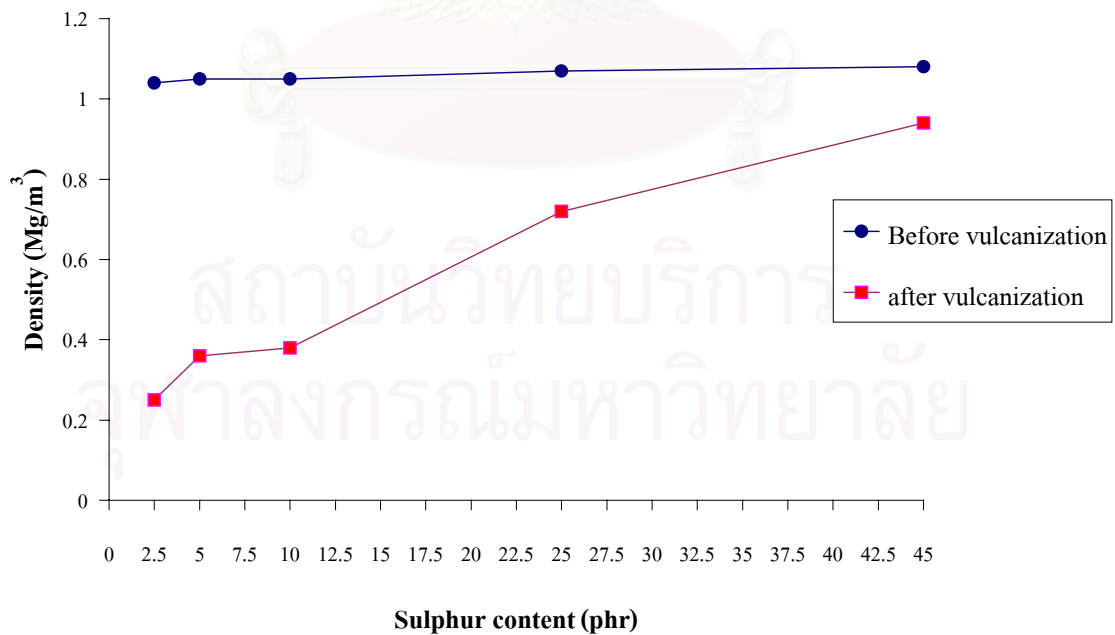


Figure 4.2 Effect of sulphur content on density of composite material.

Only small amount of sulfur is used as a vulcanizing agent, therefore, we did not expect its amount to influence on the density of our composite material (specific gravity: sulfur 1.97, rubber 0.95). However, during vulcanization process when cross-linking between rubber chains occur via sulfur bridges, mixture with higher amount of sulfur can not flow freely and as a result become less porous than mixture containing lesser amount of sulfur. This explains why the density of vulcanized material increases as percent sulfur increases as shown in figure 4.2. Further evidence also indicates smaller cells in material containing higher amount of sulfur supporting our hypothesis.

4.1.3 Effect of molding temperature on density

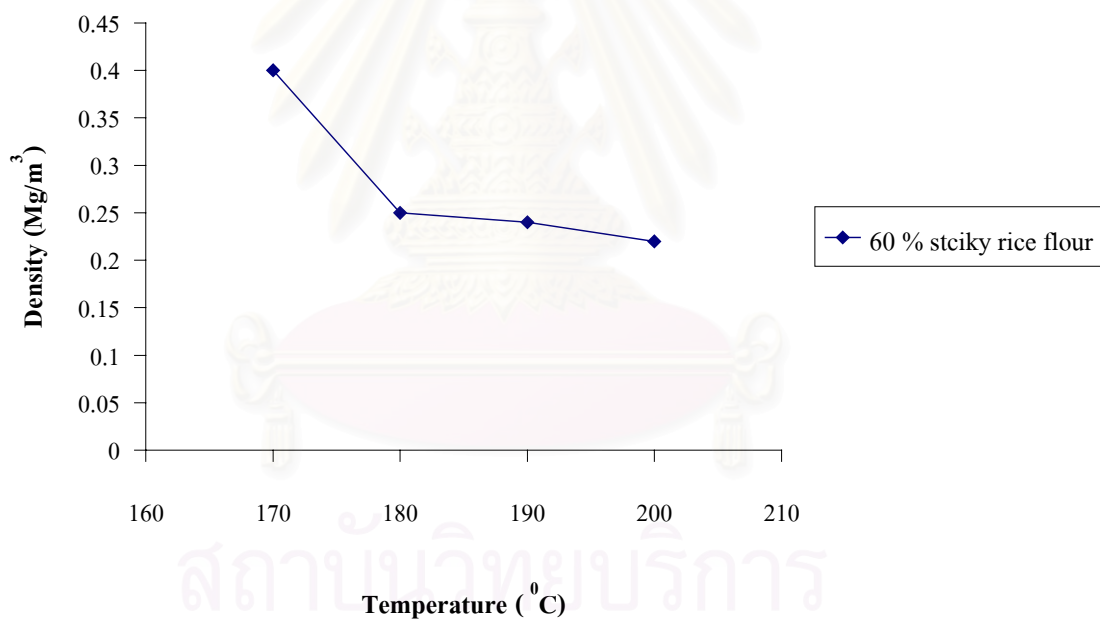


Figure 4.3 Effect of molding temperature on density of composite material.

Figure 4.3 shows effect of molding temperature on density of composite material. The graph indicates lower density at higher molding temperature. At higher temperature starch paste dries rapidly and cannot gel to form the normal starch network throughout the mixture. Also at higher temperature water in dried starch paste vented out rapidly creating

large void volume within. Thus result in decreasing of density as the molding temperature increases.

4.1.4 Comparison of the effect of cross-linking agent on density

Table 4.1 Comparison of cross-linking agent on density of composite material

Cross-linking agent	Density (Mg/m ³)	
	Before vulcanization	After vulcanization
Sulphur	0.95	0.70
Sulphur+maleic anhydride	1.01	0.65
Benzoyl peroxide+maleic anhydride	1.02	0.79

Three systems of vulcanization were studied as listed in Table 4.1. It was found that the density of material vulcanized in the system of benzoyl peroxide and maleic anhydride is the highest. The data indicated better vulcanization than the normal sulfur process. This is because in the presence of benzoyl peroxide, the cross-linking process occurs via free-radical mechanism. Homolytic decomposition of benzoyl peroxide by heat produces two free radicals as shown in Figure 4.4.

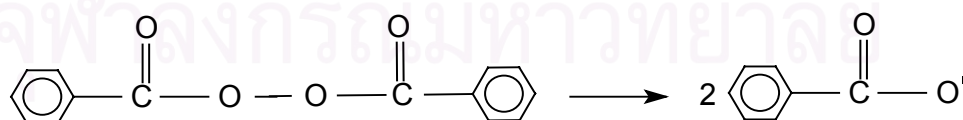


Figure 4.4 Peroxide curing process for benzoyl peroxide produces two radicals.

The free radical can react at the double bond to form a polymer radical that in turn combines with additional polymers to give multiple crosslink bonding.

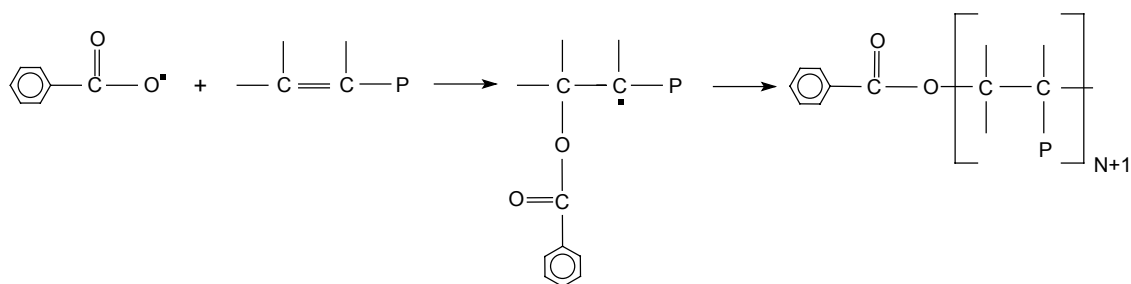


Figure 4.5 Multiple crosslink bonding in polymer radicals.

Certain side reactions can occur with peroxides that lead to degradation of polymer. Many compounding ingredients, such as oils and antioxidants, react with the radicals formed on peroxide decomposition, and these reactions can dilute the crosslinking effect.

In addition, benzoyl peroxide can react with maleic anhydride to form a free radical that is highly reactive. This radical can initiate polymerization process of isoprene unit leading is multiple crosslinks as shown in Figure 4.6.

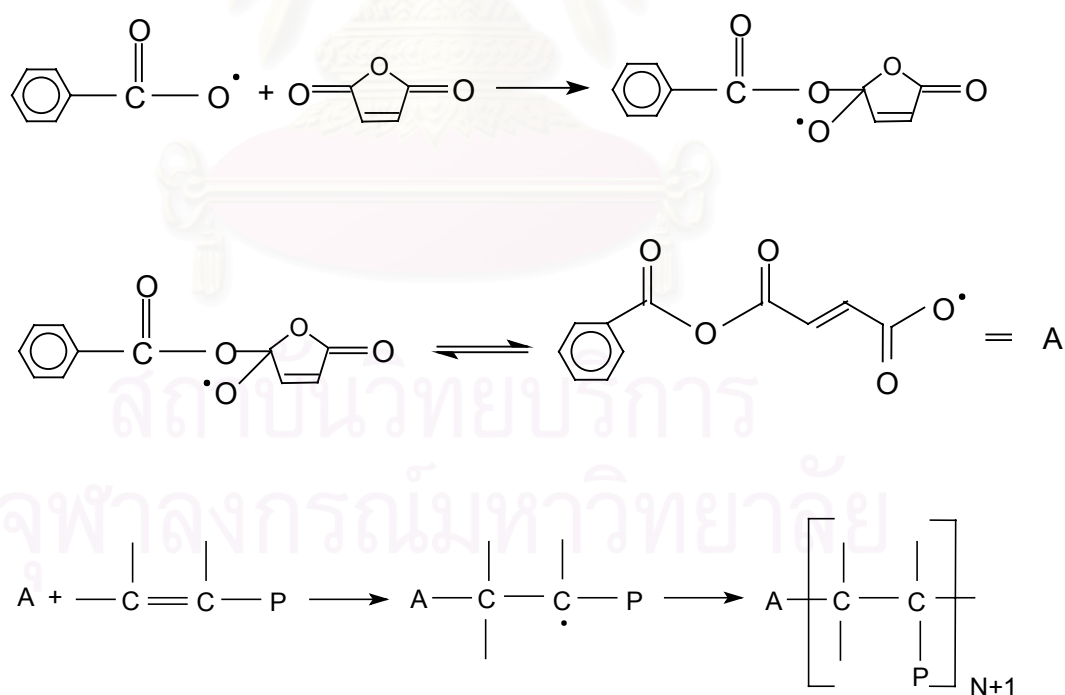


Figure 4.6 Mechanism of maleic anhydride 'free radical' curing process.

4.2 Distribution of starch granules

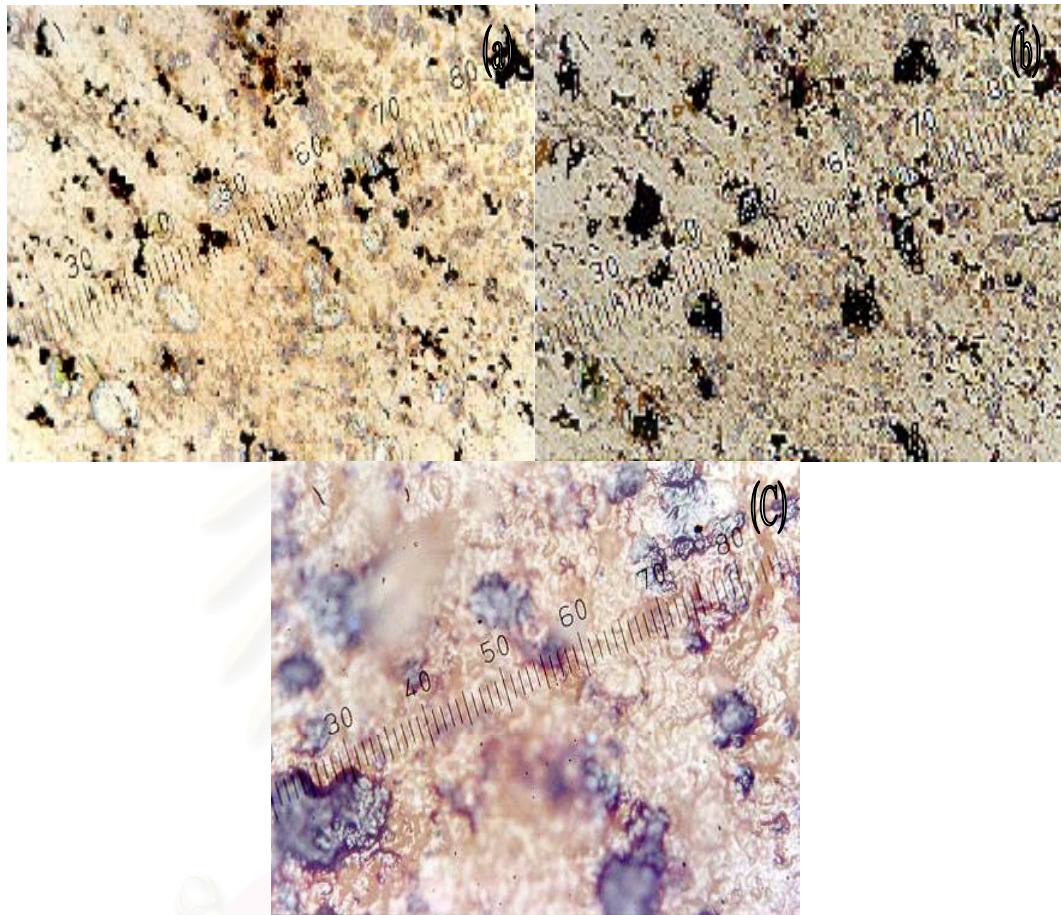


Figure 4.7 Optical micrographs of surfaces of NR/starch mixture of (a) 20% flour, (b) 40% flour and (c) 60% flour.

It can be seen from Figure 4.7 that starch has been evidently distributed in a matrix. Therefore foam forming is expected to occur evenly.

4.3 Foam structure of composite material

4.3.1 Effect of sticky rice flour content on the foam structure

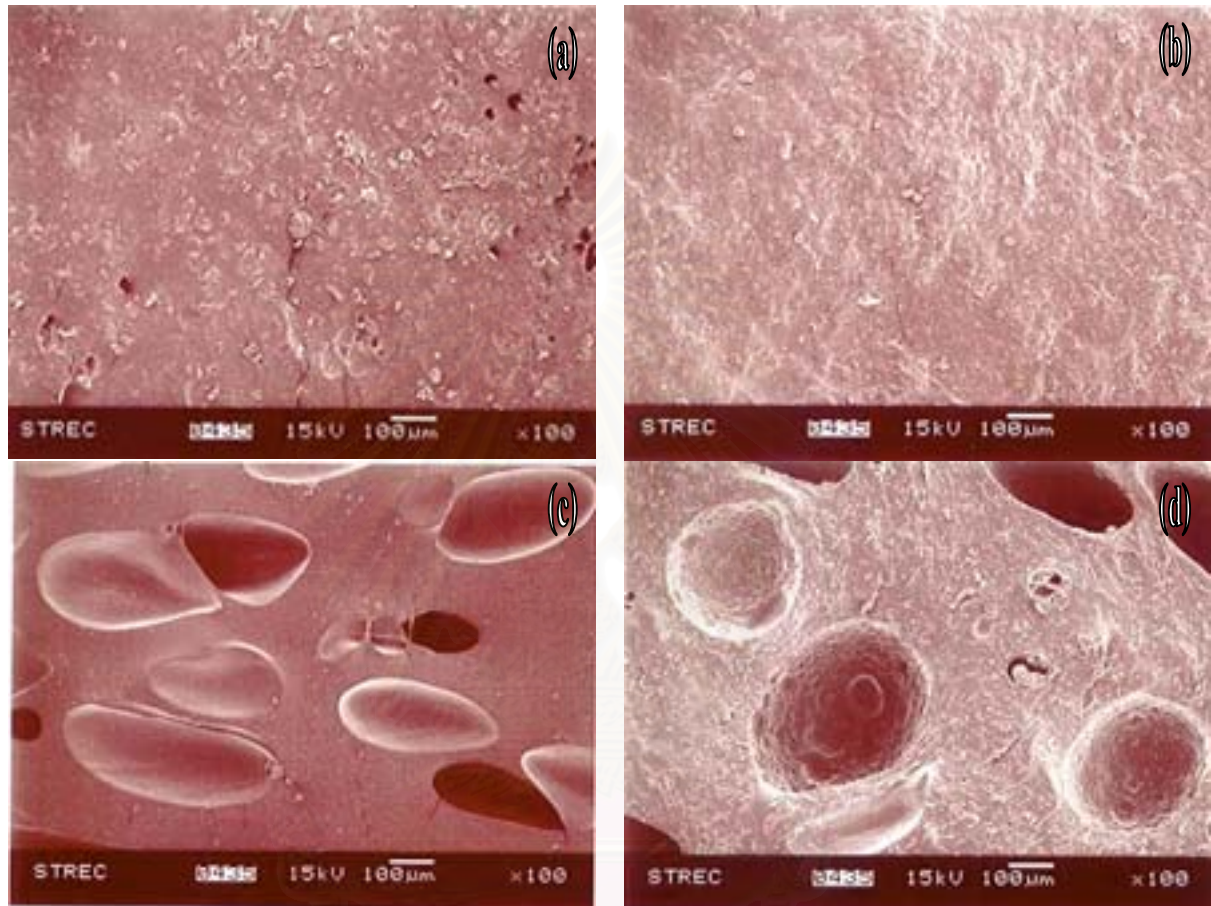


Figure 4.8 Scanning electron micrographs of surfaces of (a) non-starch content, (b) 20% starch content of NR/starch mixture and cross sections of (c) non-starch content and (d) 20% starch content of composite material.

Scanning electron micrographs of NR/starch mixture and composite material are shown in Figure 4.8. The cross section of the foam formed is shown in Figure 4.8 (d) supports the idea that starch is the blowing agent and it has an effect on the density.

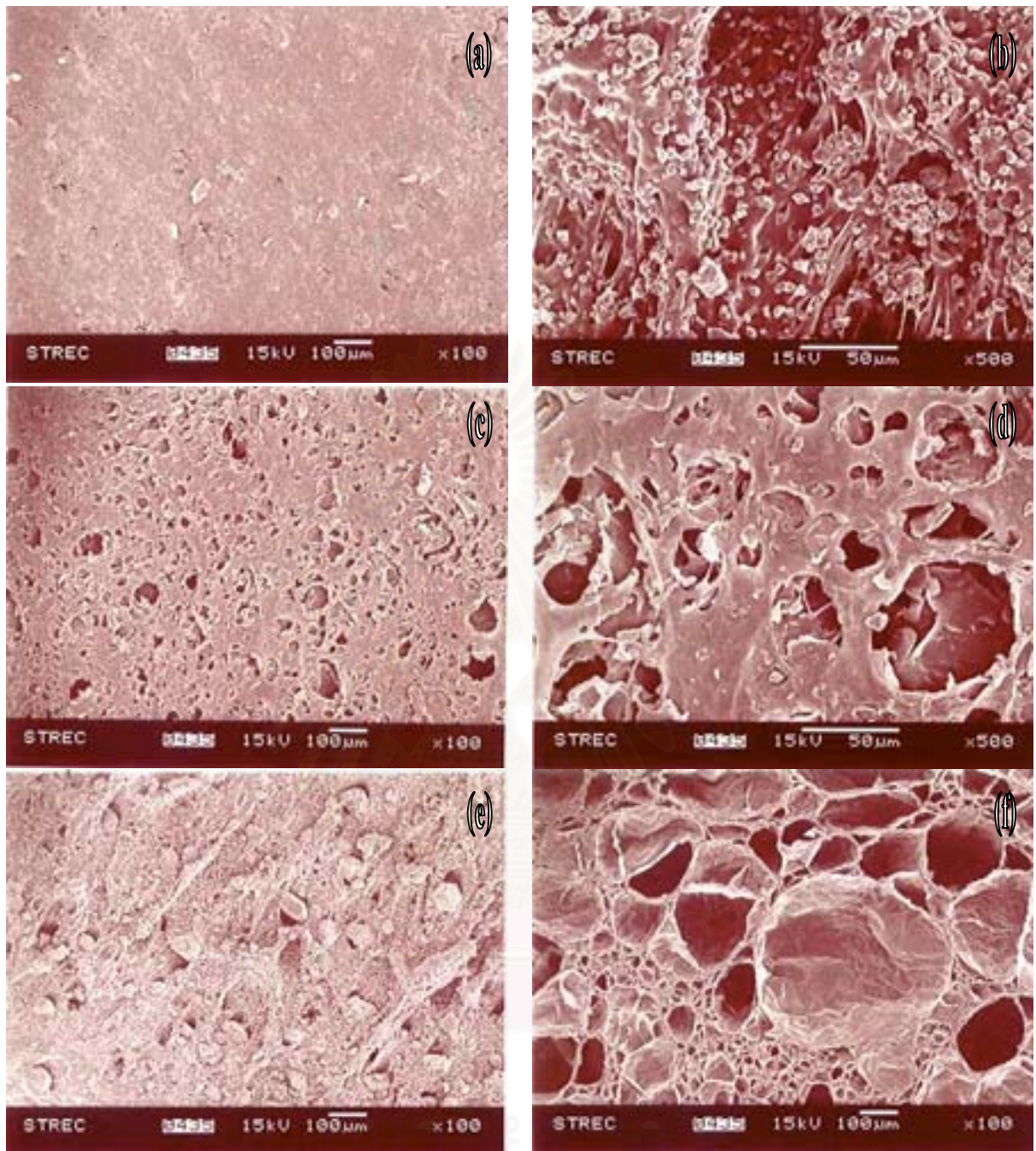


Figure 4.9 Scanning electron micrographs of surfaces of (a) and (b) 60% starch content of NR/starch mixture, (c) and (d) 60% starch content of composite material and cross sections of (e) 60% starch content of NR/starch mixture and (f) 60% starch content of composite material.

Scanning electron micrographs of a sample with 60 % starch content are shown in Figure 4.9. Cross-sectional views [Figure 4.9 (e)] show that foams have dense outer skins with small cells and less dense interiors with large cells. The outer skin is more dense because it is close to the hot mold. The starch paste dries rapidly and therefore cannot expand to its fullest. The interior of the foam contains mostly large, open cells due to the large amounts of steam venting outside the mold and consequently causing cell rupture. Starch near the surface of the mold dried up rapidly so that there is less time for starch gelatinization and granule fragmentation to occur, while granular swelling in the interior is more extensive. Some remnants of swollen starch granules can be seen on the surfaces of the foams [Figure 4.9 (b-d)]

4.3.2 Effect of sulphur content on the foam structure

Scanning electron micrographs of NR/starch mixtures and composite materials are shown in Figure 4.10. The cross section of the foam formed is shown in Figure 4.10 (d) supports the idea that starch acts as the blowing agent affecting the density of new material.

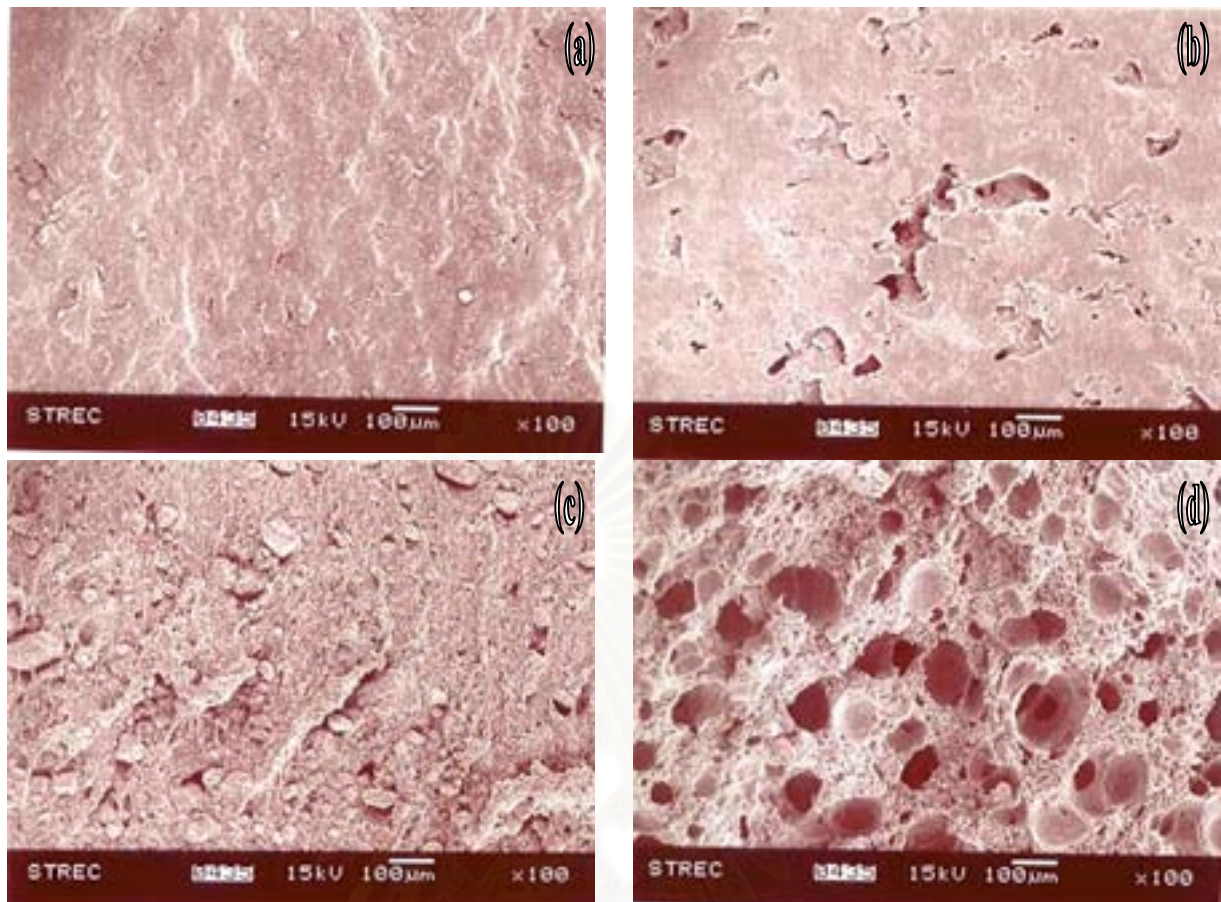


Figure 4.10 Scanning electron micrographs of surfaces of (a) and (b) 45 phr of sulphur content of NR/starch mixture and composite material, respectively and cross sections of (c) and (d) 45 phr of sulphur content of NR/starch mixture and composite material, respectively.

4.4 Water absorption of the NR/starch and composite material

Determination of swelling by water absorption was carried out in triplicate and the values averaged. There are two sets of values for water absorption, before and after vulcanization.

4.4.1 Effect of sticky rice flour content on water absorption

The water absorption property increases with increasing starch content as can be seen in Figure 4.11. When the mixture is heated, the rubber is vulcanized and foamed.

Starch granules contain hydroxyl groups which capable of forming hydrogen bonding and are responsible for the structural integrity of the granule. At high temperature the hydrogen bonding is weakened, allowing the penetration of water and hydration of the linear segments of amylopectin. The exposed amylopectin moiety resulted in greater water adsorption as shown in Figure 4.12.

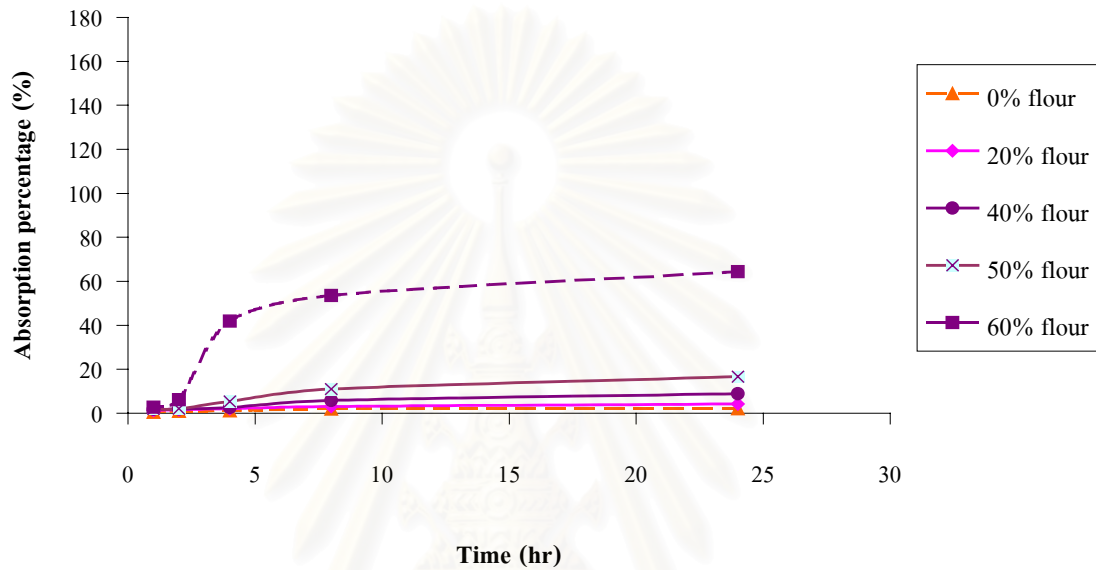


Figure 4.11 Effect of sticky rice flour content of NR/starch mixture on water absorption.

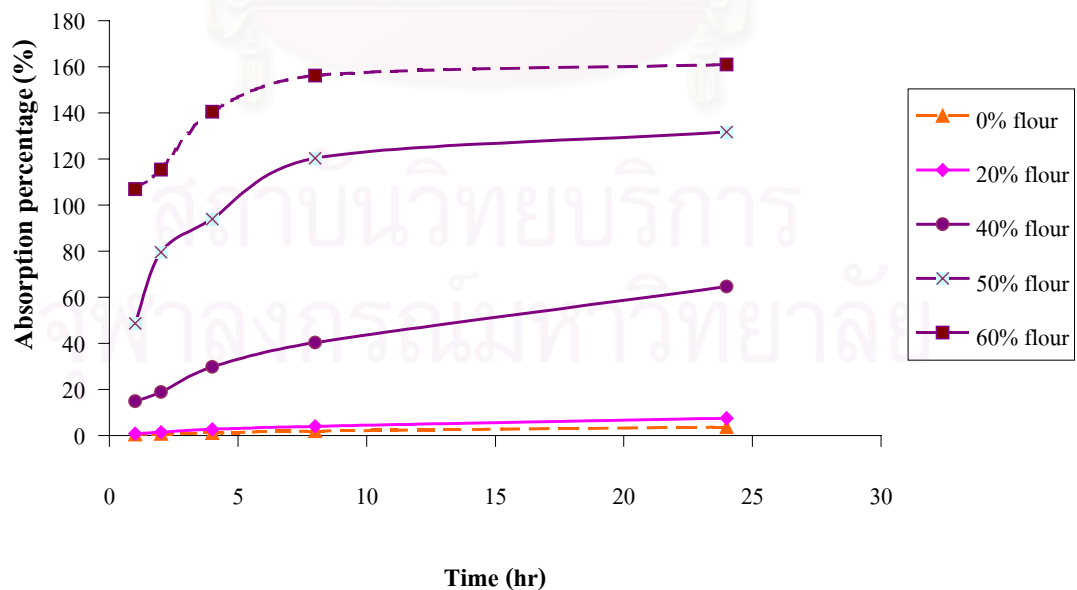


Figure 4.12 Effect of sticky rice flour content of composite material on water absorption.

4.4.2 Effect of sulphur content on water absorption

The effect of sulfur content on water absorption of NR/starch mixture is shown in Figure 4.13 where the water absorption property increases with decreasing sulfur content. Figure 4.14 illustrated the effect of sulfur content on water adsorption of composite material. When the sulfur content is high, water absorption property drastically reduced. This is because the growth of foam is restricted with increasing sulfur loading. As more crosslinking occurs, the penetration of water becomes more difficulty.

4.4.3 Effect of molding temperature on water absorption

It can be seen in Figure 4.15 that water adsorption increases at higher molding temperature due to enhancement of water penetration into the cellular network of the starch granules. The structure of composite material of higher porosity is formed at high molding temperature and contains mostly large free volume. Therefore, this material has higher water absorption and swelling properties.

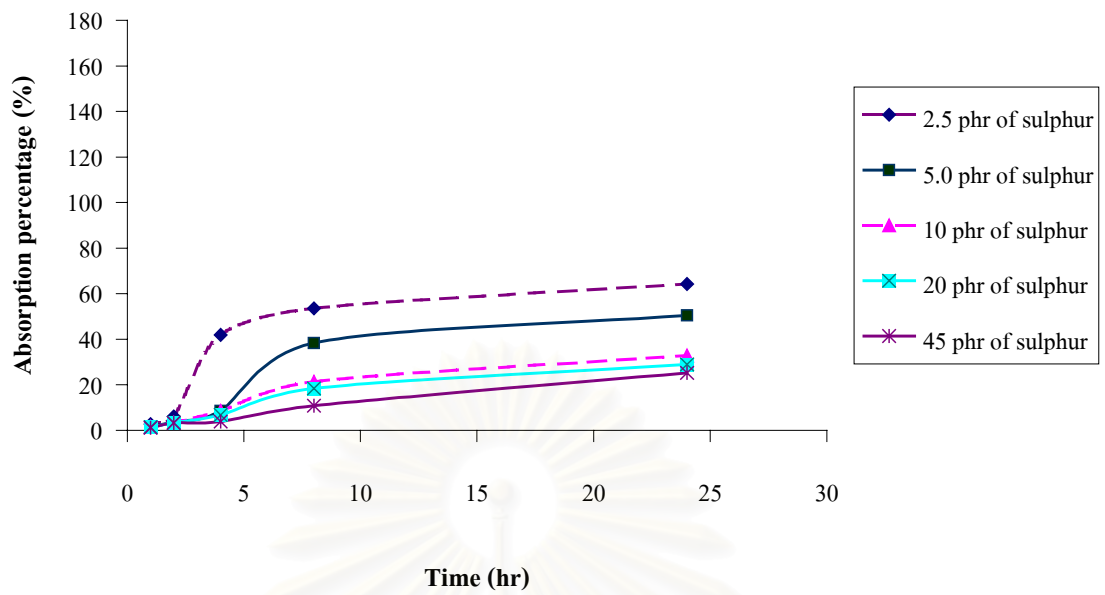


Figure 4.13 Effect of sulphur content of NR/starch mixture on water absorption.

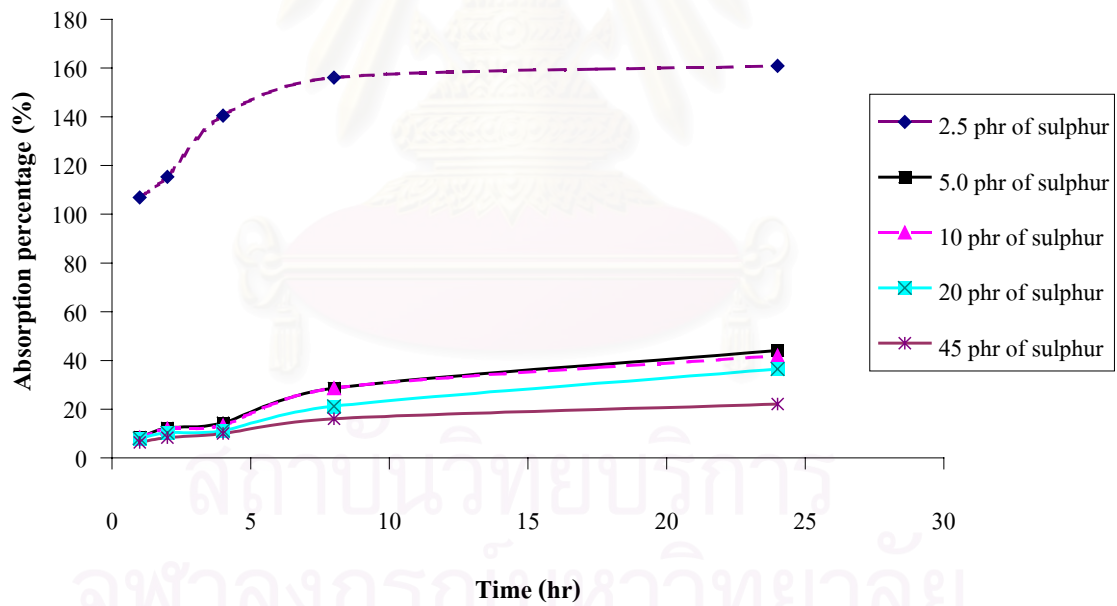


Figure 4.14 Effect of sulphur content of composite material on water absorption.

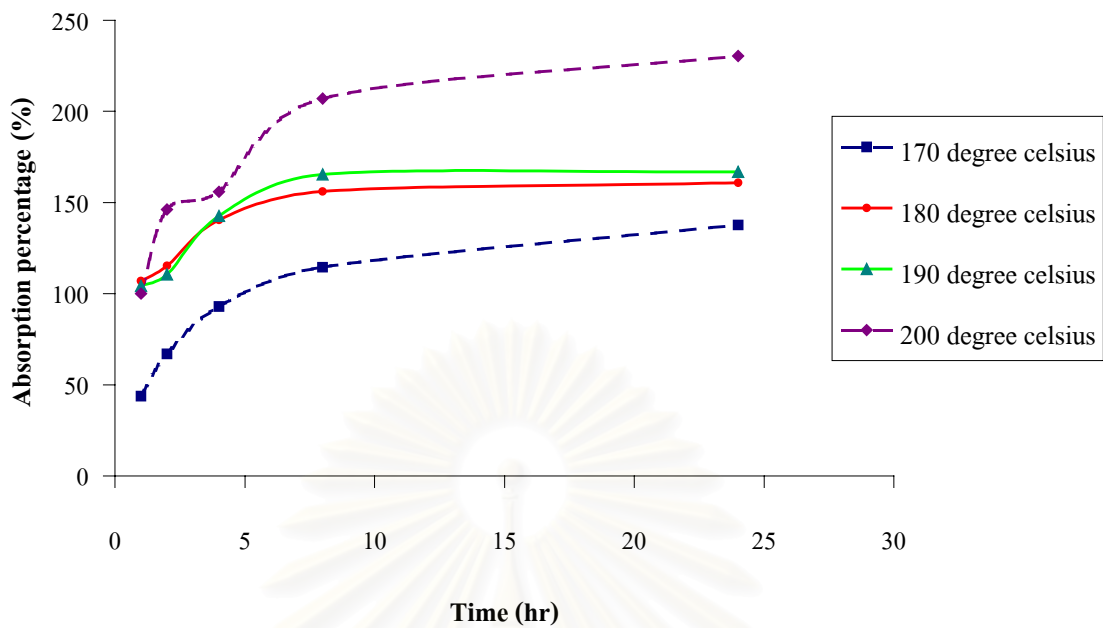


Figure 4.15 Effect of molding temperature of composite material on water absorption.

4.4.4 Effect of cross-linking agent on water absorption

The effects of cross-linking agent on water absorption for a sample containing 30% flour are presented in Figure 4.16 and 4.17, respectively. The water absorption of composite material containing benzoyl peroxide and maleic anhydride is higher than the value of material vulcanized only with sulfur. Evidences indicate that foam forming in the system of benzoyl peroxide is less than in the system of sulfur. But benzoyl peroxide is more hydrophilic and can generate greater water affinity than sulfur.

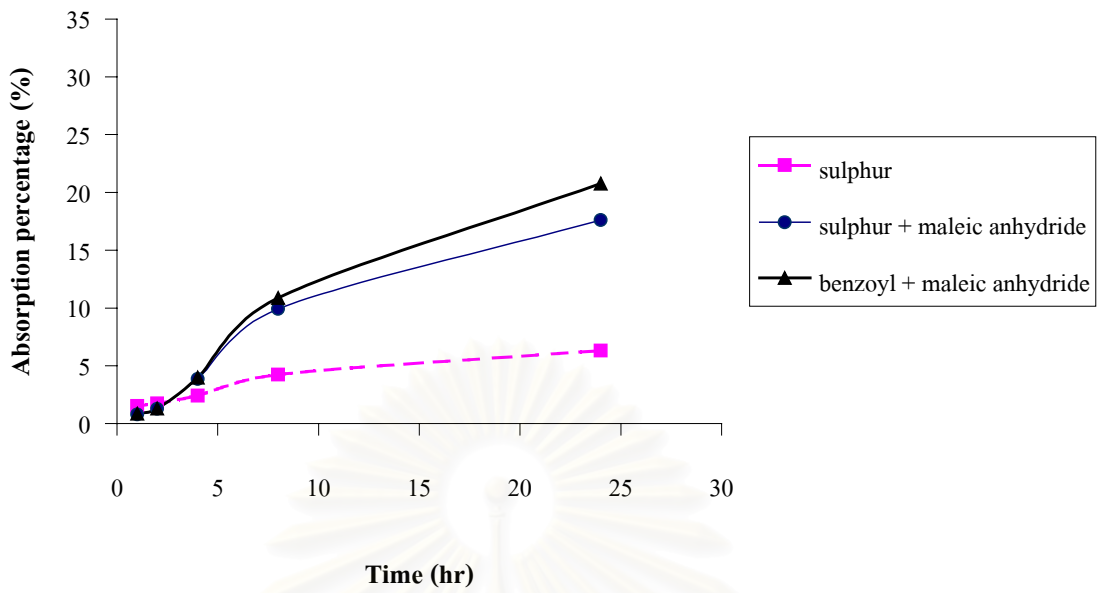


Figure 4.16 Effect of cross-linking agent of NR/starch mixture on water absorption.

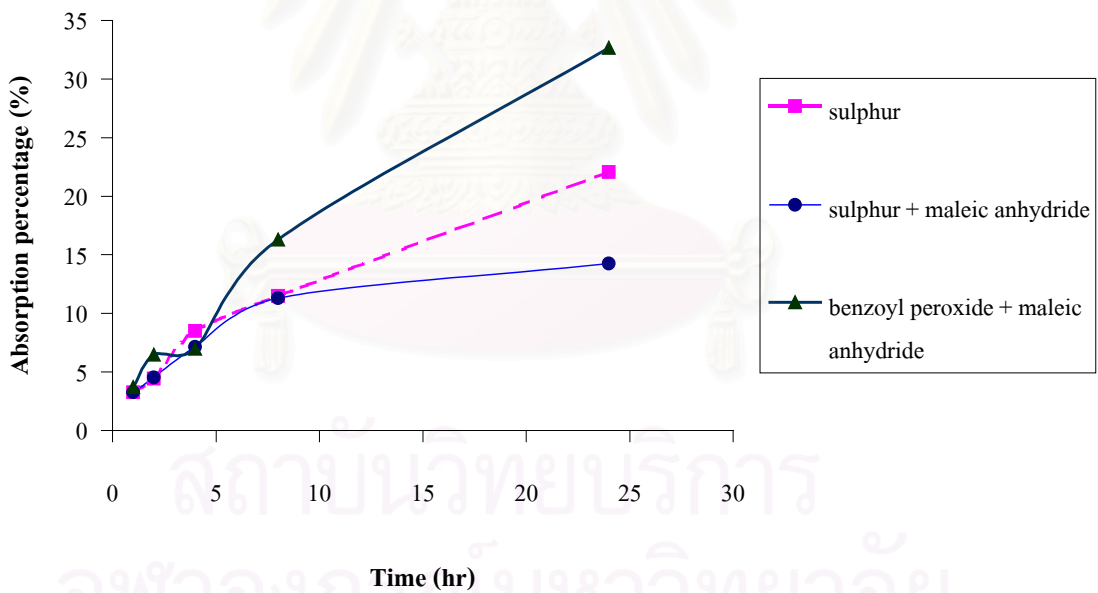


Figure 4.17 Effect of cross-linking agent of composite material on water absorption.

4.5 Oil absorption of the NR/starch mixture and composite material

Determination of swelling is carried out in tripet and the values averaged. Two sets of oil absorption values, before and after vulcanization were determined.

4.5.1 Effect of sticky rice flour content on oil absorption

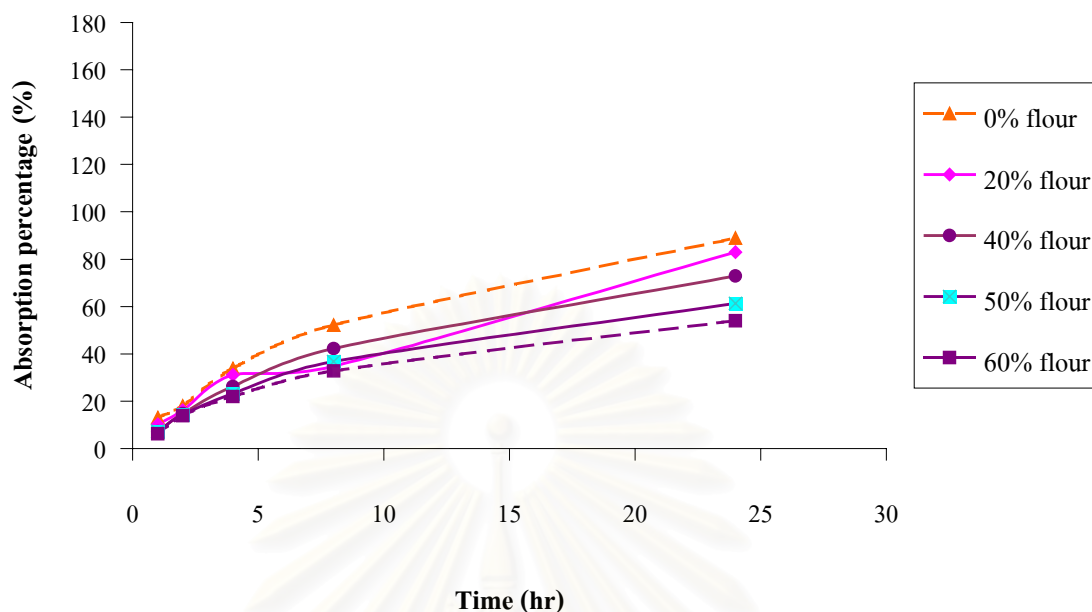


Figure 4.18 Effect of sticky rice flour content of NR/starch mixture on oil absorption.

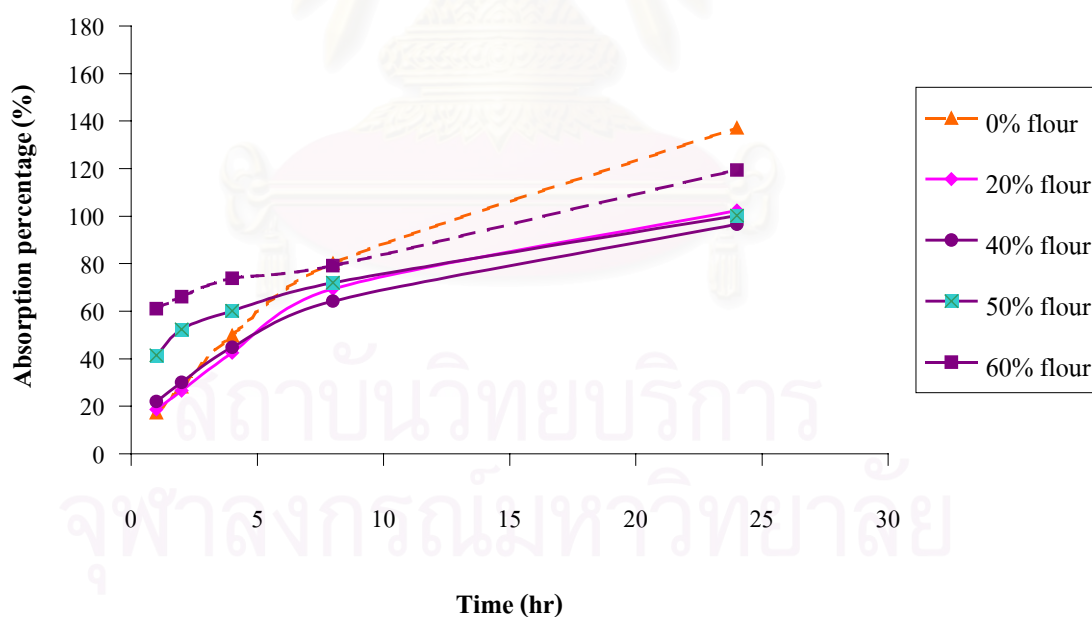


Figure 4.19 Effect of sticky rice flour content of composite material on oil absorption.

Figure 4.18 shows increasing oil absorption property with decreasing starch content. Composite material containing less starch has higher non-polar moiety and thus

allows oil to penetrate easily. But at starch content is greater than 50%, the higher foaming increase void therefore the oil uptake into the void, are shown in Figure 4.19.

4.5.2 Effect of sulphur content on oil absorption

The mixture of NR/starch with sulfur loading higher than 10 phr failed oil absorption test after 4 hours. The sample deformed and became soften and observation ended.

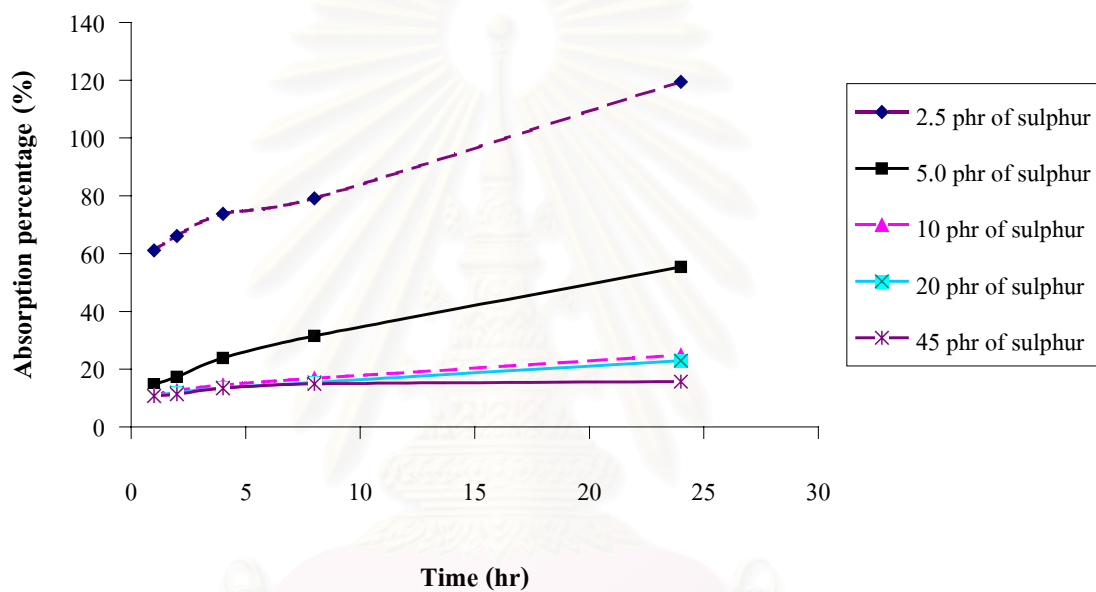


Figure 4.20 Effect of sulphur content of composite material on oil absorption.

Figure 4.20 shows increasing oil absorption property with decreasing sulfur content. At high sulfur loading, foam growth is restricted and therefore the penetration of oil becomes more difficult.

4.5.3 Effect of molding temperature on oil absorption

Oil absorption property increases with increasing molding temperature because oil penetrates freely into the cellular network of the starch granules. Porosity of composite material increases as molding temperature increases. The cellular network in composite

material fabricated at high temperature consists of mostly large void volume which enhance the adsorption and swelling as shown in Figure 4.21.

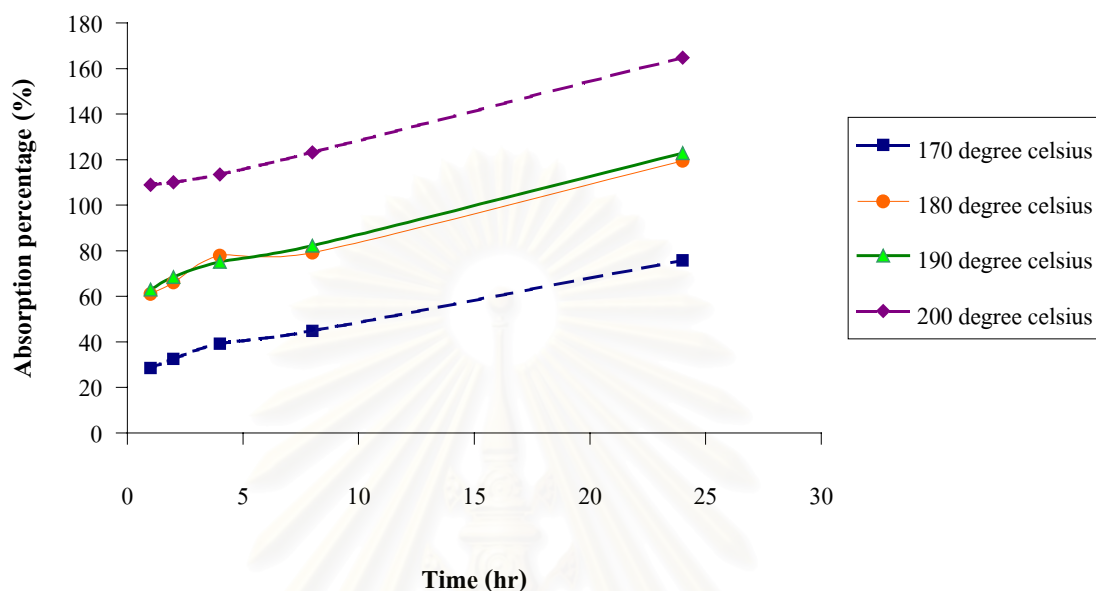


Figure 4.21 Effect of molding temperature of composite material on oil absorption.

4.5.4 Effect of cross-linking agent on oil absorption

The mixture of NR/starch failed oil absorption test after 4 hours. The sample deformed and became soften and observation ended.

Figure 4.22 compares oil absorption property of composite materials vulcanized differently. The data indicate that vulcanizing system of sulfur and maleic anhydride gives material of the highest oil absorption property due to maleic anhydride affinity to oil. The data also indicate superior oil absorption property from the system containing benzoyl peroxide than traditional vulcanizing system using containing sulfur alone.

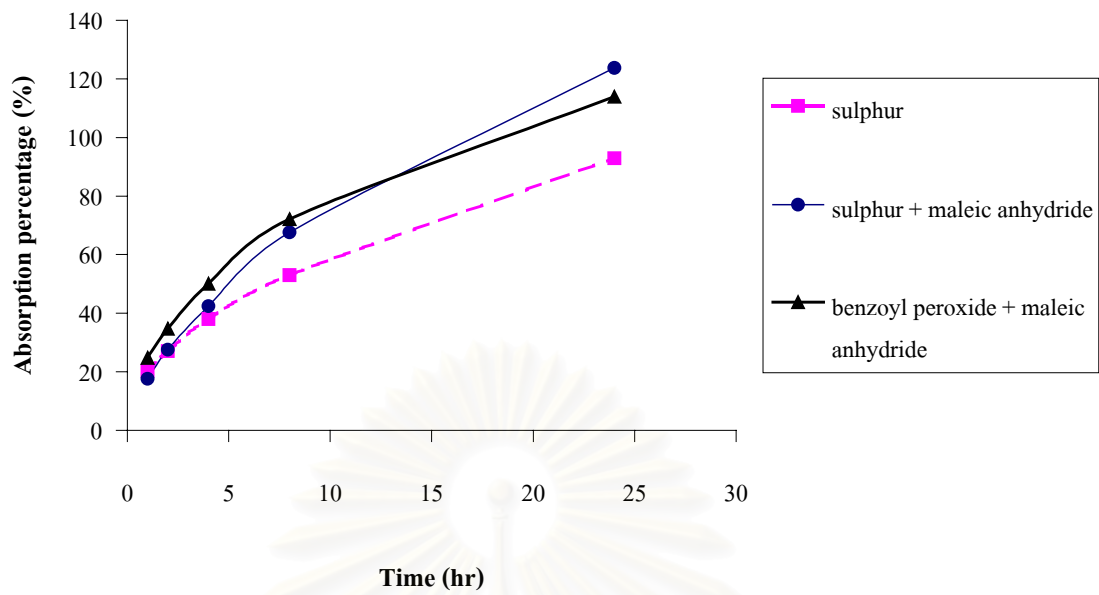


Figure 4.22 Effect of cross-linking agent of composite material on oil absorption.

4.6 Determination of $t_c(90)$

Optimum cure time is extrapolated from data of $t_c(90)$. The results suggest the best cure time to be at 180°C . Specimens containing sulfur at 2.5 and 45 phr and 60% sticky rice flour were examined.

The effects of two components, namely sulfur and starch are investigated. The cure characteristic of materials containing sulfur at 2.5 and 45 phr, are shown in Figure 4.23 respectively. It is observed that $t_c(90)$ tend to decrease appreciably with increasing molding temperature. This postulated that ratio at 180°C , $t_c(90)$ would take less time. The extrapolation of the result suggests that processing time can be reduced. Succeeding investigations indicate that the processing time of 4 to 5 minutes is quite satisfactory.

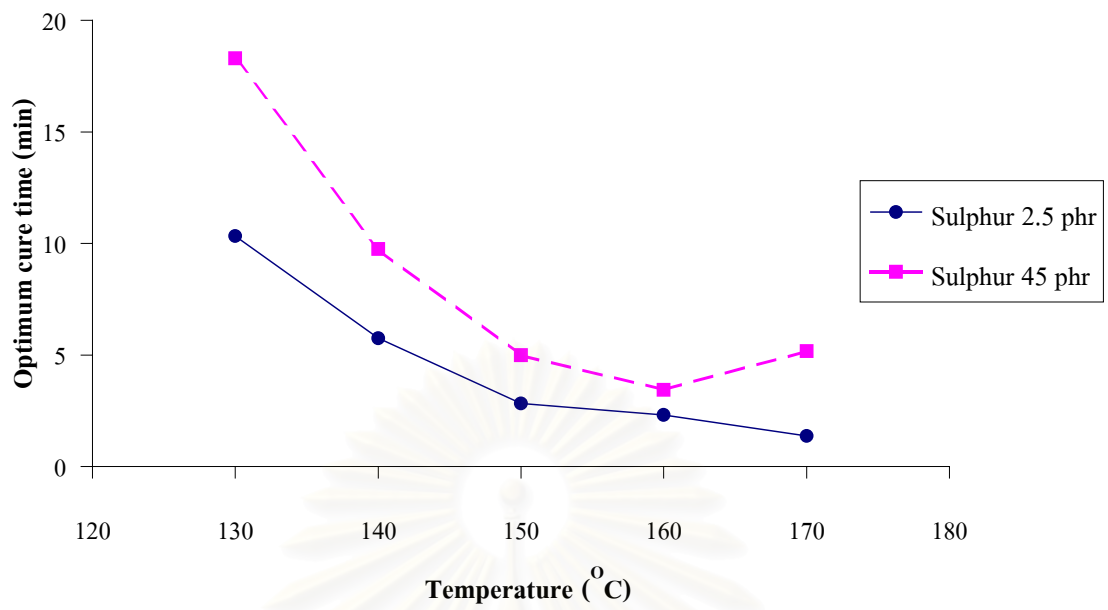


Figure 4.23 Optimum cure time of composite material.

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CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

Composite material from natural rubber and sticky rice flour can be prepared by masticating NR/starch and other chemicals using two roll mill. The mixture is then compressed at a molding temperature of 180°C for 4-5 minutes.

Density of composite material decreases with increasing starch content. At 60% starch content, the density of new material is four times less than NR. Density of new material is found to increase with increasing sulphur content resulting in strong structure. Increasing molding temperature has little effect on density.

Water and oil absorption properties of the composite material become higher at more than 50% starch content and high molding temperature. Sulphur, as cross-linking agent, has little effect on water and oil absorption properties.

Suggestions

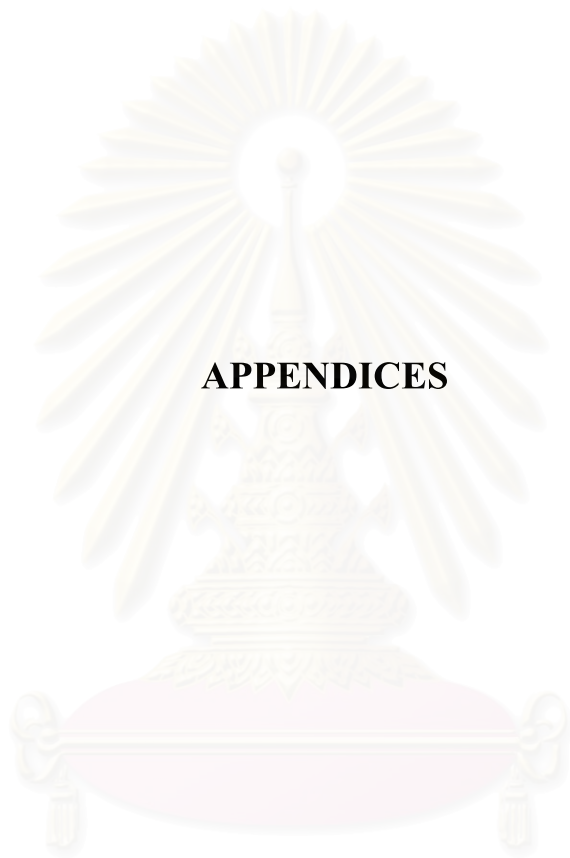
To enhance the property of composite material made from natural rubber and sticky rice flour, other inexpensive agricultural materials available locally such as straw (contains structural cellulose) can be added to adjust physical properties further. New applications such as inexpensive, light weight, biodegradable, and structural reinforcement packaging material are possible. In addition, this new composite material is perfect for the manufacturing of inexpensive biodegradable diaper due to its high water absorption. However its safety should be evaluated.

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APPENDICES

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APPENDIX A

World natural rubber production, consumption and stock during 1994-1999

Table A1 World natural rubber production, consumption and stock during 1994-1999 (x1000 tons) [2]

Year	Production	Consumption	Stock
1994	5,720	5,650	1,700
1995	6,040	5,950	1,790
1996	6,390	6,100	2,080
1997	6,390	6,460	2,010
1998	6,680	6,550	2,140
1999	6,750	6,700	2,190

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Table A2 Gelatinization characteristics of native starch [23]

Starch		Kofler gel.		At 95°	
Species	Type	Temp.range (°C)	Swelling power	Solubility (%)	Critical concentration value
Potato	Tuber	56-66	>1000	82	< 0.1
Sago	Pith	---	97	39	1.0
Tapioca	Root	58.5-70	71	48	1.4
Canna	Root	---	72	37	1.4
Arrowroot	Root	---	54	28	1.9
Sweet potato	Root	---	46	18	2.2
Corn	Cereal	62-72	24	25	4.4
Sorghum	Cereal	68.5-75	22	22	4.8
Wheat	Cereal	52-63	21	41	5.0
Rice	Cereal	61-77.5	19	18	5.6
Waxy maize	Cereal	63-72	64	23	1.6
Waxy rice	Cereal	---	56	13	1.8
Waxy sorghum	Cereal	67.5-74	49	19	2.1
Wrinkled pea	Legume	---	6	19	20.0
High-amylose corn	Cereal	---	6	12	20.0
Chick pea (Garbanzo)	Legume	---	13	15	8.3

APPENDIX B

Pictures of composite material are shown in this appendix for visual observation.



Figure B1 Composite material from natural rubber and 60% sticky rice flour heated by compression molding at 180°C / 15 min.



Figure B2 Composite material from natural rubber and 60% sticky rice flour mixed with dye (to test colouring) and then heated by compression molding at 180°C / 15 min.



Figure B3 Composite material pressed by compression molding at ambient temperature



Figure B4 Composite material from natural rubber and 60% sticky rice flour without sulphur heated by compression molding at 180 °C/ 15 min.



Figure B5 Composite material from natural rubber and 60% sticky rice flour blends with sulphur 45 phr heated by compression molding at 180°C / 15 min.

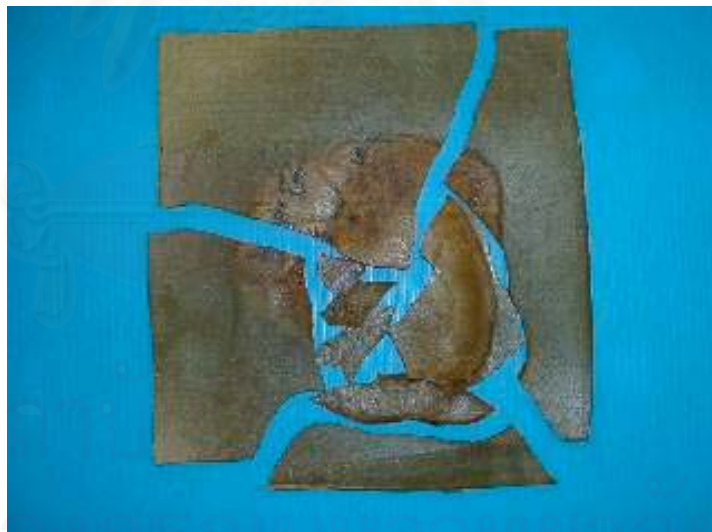


Figure B6 Composite material (from Figure B5) pressed by compression molding at ambient temperature.

The foam structure cannot be form because its high starch content, as shown below



Figure B7 Composite material from natural rubber and 60% sticky rice flour composed of maleic anhydride 10% of flour and benzoyl peroxide 2.5 phr content heated at 180°C/ 15 min.

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APPENDIX C

1. Raw testing data of water absorption

1.1 Effect of sticky rice flour content on water absorption

Table C1 Effect of sticky rice flour content on water absorption (before vulcanization)

%Sticky rice flour	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
0	0.4	1.0	1.2	2.0	2.1
10	0.5	0.9	1.5	2.0	2.8
20	1.3	1.7	2.1	3.0	4.1
30	1.5	1.8	2.4	4.2	6.3
40	1.8	2.0	2.6	5.8	8.8
50	1.9	2.1	5.2	11.1	16.7
60	2.8	6.1	41.9	53.4	64.2

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Table C2 Effect of sticky rice flour content on water absorption (after vulcanization)

%Sticky rice flour	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
0	0.5	0.9	1.1	1.8	3.7
10	0.7	1.5	2.6	4.1	7.5
20	2.8	4.3	6.5	10.5	20.3
30	3.8	4.4	8.7	11.5	22.0
40	14.9	18.9	29.7	40.3	64.7
50	48.6	79.5	93.9	120.3	131.7
60	106.9	115.3	140.5	156.1	160.9

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1.2 Effect of sulphur content on water absorption

Table C3 Effect of sulphur content on water absorption (before vulcanization)

sulphur content (phr)	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
2.5	2.8	6.1	41.9	53.5	64.3
5	1.8	3.6	8.5	38.3	50.5
10	1.6	3.4	8.5	21.3	32.9
25	1.5	3.3	6.7	18.5	29.0
45	1.1	3.3	3.9	10.9	25.2

Table C4 Effect of sulphur content on water absorption (after vulcanization)

sulphur content (phr)	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
2.5	106.9	115.3	140.5	156.1	160.9
5	8.5	12.3	14.3	28.6	43.9
10	8.4	11.9	13.3	28.6	41.9
25	7.9	10.2	11.2	21.2	36.4
45	6.4	8.3	10.0	16.0	22.2

1.3 Effect of molding temperature on water absorption

Table C5 Effect of molding temperature on water absorption

Temperature (°C)	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
170	43.8	66.9	92.9	114.5	137.7
180	106.9	115.3	140.5	156.1	160.9
190	104.2	110.6	142.6	165.3	166.8
200	100.1	146.1	155.8	207.1	230.3

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1.4 Effect of cross-linking agent on water absorption

Table C6 Effect of cross-linking agent on water absorption (before vulcanization)

Ccross-linking Agent*	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
1	1.5	1.8	2.1	3.0	4.2
2	0.8	1.3	3.9	9.9	17.6
3	0.9	1.3	4.0	10.8	20.8

Table C7 Effect of cross-linking agent on water absorption (after vulcanization)

Ccross-linking Agent*	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
1	3.2	4.4	8.4	11.4	22.0
2	3.3	4.5	7.1	11.3	14.3
3	3.7	6.5	6.9	16.3	32.7

* composition 1 is sulphur, 2 is sulphur and maleic anhydride, and 3 is bezoyl peroxide and maleic anhydride.

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2. Raw testing data on oil absorption

2.1 Effect of sticky rice flour content on oil absorption

Table C8 Effect of sticky rice flour content on oil absorption (before vulcanization)

% Sticky rice flour	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
0	13.0	18.0	33.8	52.1	88.9
10	10.5	18.2	32.2	50.2	85.1
20	10.2	16.1	31.1	34.8	82.9
30	9.3	15.1	24.2	40.4	80.4
40	7.2	14.7	26.1	42.3	72.9
50	7.3	14.3	23.2	36.7	61.3
60	6.3	14.0	22.0	32.7	54.0

Table C9 Effect of sticky rice flour content on oil absorption (after vulcanization)

% Sticky rice flour	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
0	17.4	28.9	49.9	80.2	137.2
10	18.0	28.2	46.2	75.1	126.7
20	18.7	26.6	42.6	69.4	102.3
30	20.3	27.0	38.0	53.0	92.9
40	22.1	30.0	44.9	64.2	96.6
50	41.5	52.4	60.2	72.1	100.2
60	61.1	66.1	73.8	79.1	119.5

2.2 Effect of sulphur content on oil absorption

Table C10 Effect of sulphur content on oil absorption (before vulcanization)

Sulphur Content (phr)	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
2.5	6.1	14.0	22.0	32.8	54.0
5	8.6	15.3	23.3	33.6	57.2
10	8.9	15.7	25.0	---	---
25	10.0	18.1	27.0	---	---
45	11.9	18.3	29.0	---	---

Table C11 Effect of sulphur content on oil absorption (after vulcanization)

Sulphur content (phr)	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
2.5	61.1	66.1	73.8	79.1	119.5
5	14.8	17.4	23.9	31.6	55.4
10	11.1	12.6	14.6	16.8	24.9
25	10.9	11.8	13.6	15.5	23.0
45	10.7	11.4	13.3	14.9	15.7

2.3 Effect of molding temperature on oil absorption

Table C12 Effect of molding temperature on oil absorption

Temperature(°C)	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
170	28.4	32.6	39.2	44.9	75.8
180	61.1	66.1	73.8	79.1	119.5
190	63.0	68.4	75.1	82.3	102.4
200	109.0	110.1	113.4	123.1	164.7

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2.4 Effect of cross-linking agent on oil absorption

Table C13 Effect of cross-linking agent on oil absorption (before vulcanization)

Ccross-linking Agent*	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
1	9.3	15.1	24.2	40.5	80.4
2	6.6	11.8	13.1	---	---
3	5.2	5.9	13.0	---	---

Table C14 Effect of cross-linking agent on oil absorption (after vulcanization)

Ccross-linking Agent*	Absorption percentage (%)				
	1 hr	2 hr	4 hr	8 hr	24 hr
1	20.3	27.0	38.0	52.9	92.9
2	17.6	27.5	42.5	67.7	123.8
3	24.8	34.7	50.1	72.1	114.0

* composition 1 is sulphur, 2 is sulphur and maleic anhydride, and 3 is bezoyl peroxide and maleic anhydride.

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APPENDIX D

Raw testing data of cure characteristic

Table D1 $t_c(90)$ of composite material (60% sticky rice content)

Sulphur(phr)	$t_c(90)$ (min)				
	130 °C	140 °C	150 °C	160 °C	170 °C
2.5	10.33	5.75	1.96	2.31	1.37
45	18.33	9.75	2.33	3.44	5.17

Cure characteristic curve are shown in this appendix for observation

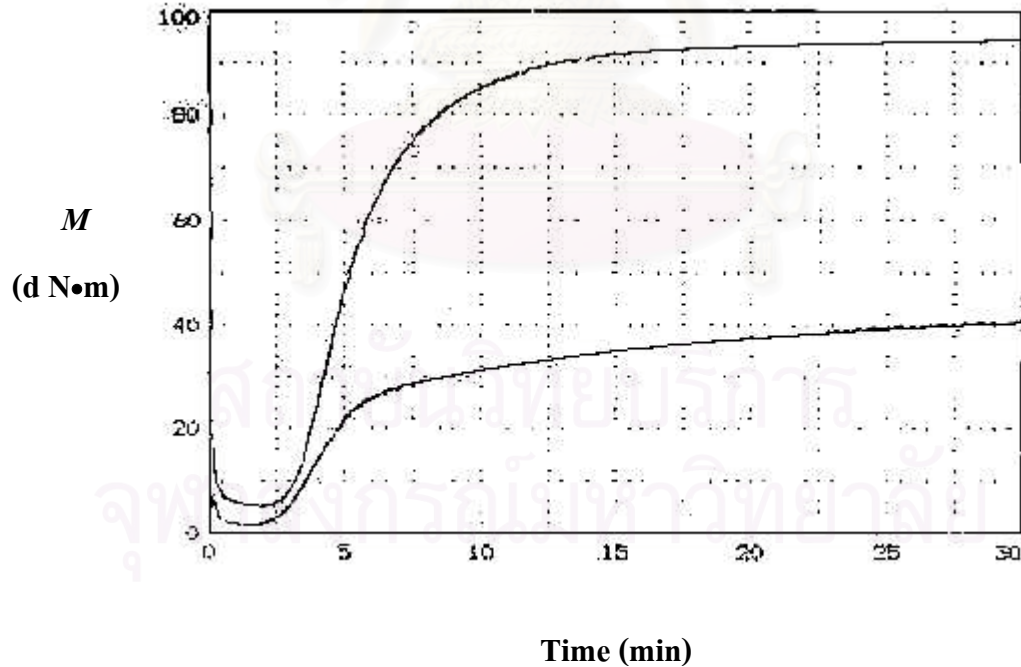


Figure D1 Cure characteristic curve from rheometer at 130°C.

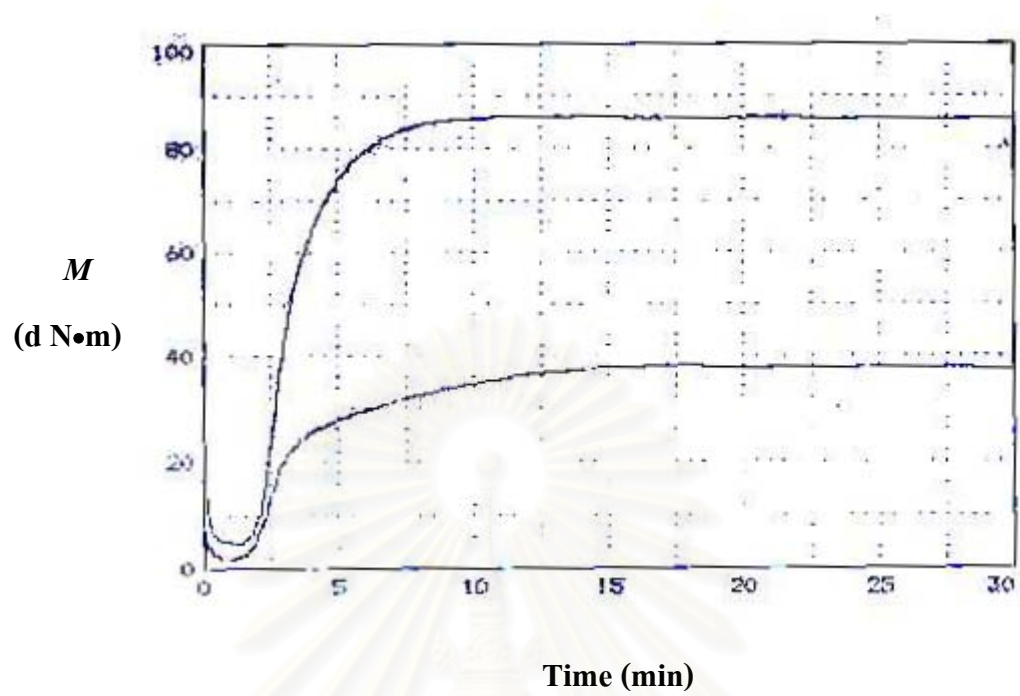


Figure D2 Cure characteristic curve from rheometer at 140°C.

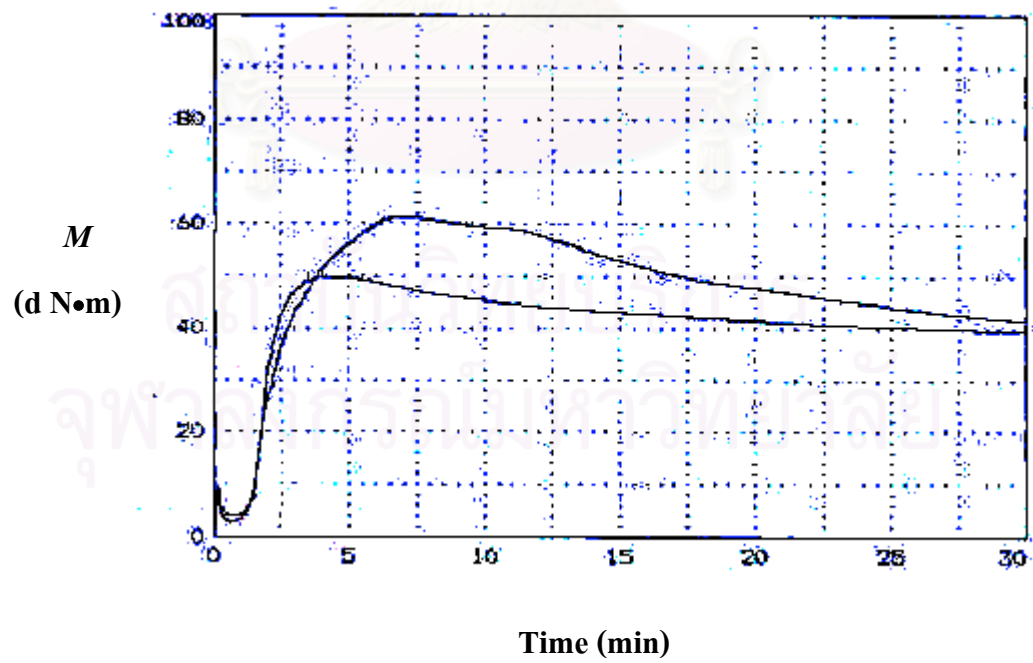


Figure D3 Cure characteristic curve from rheometer at 150°C.

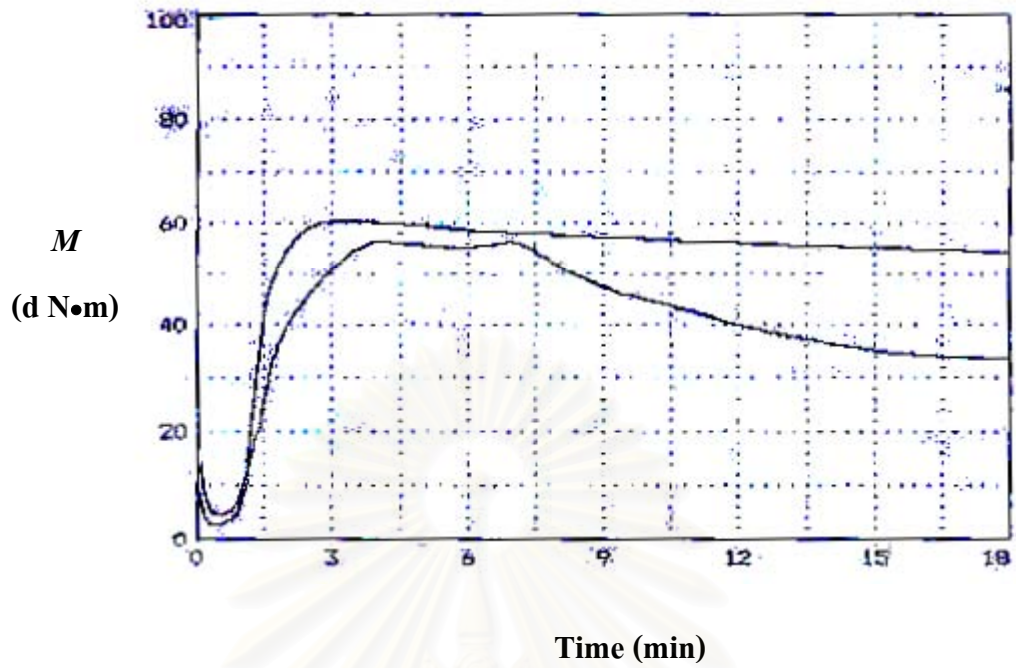


Figure D4 Cure characteristic curve from rheometer at 160°C.

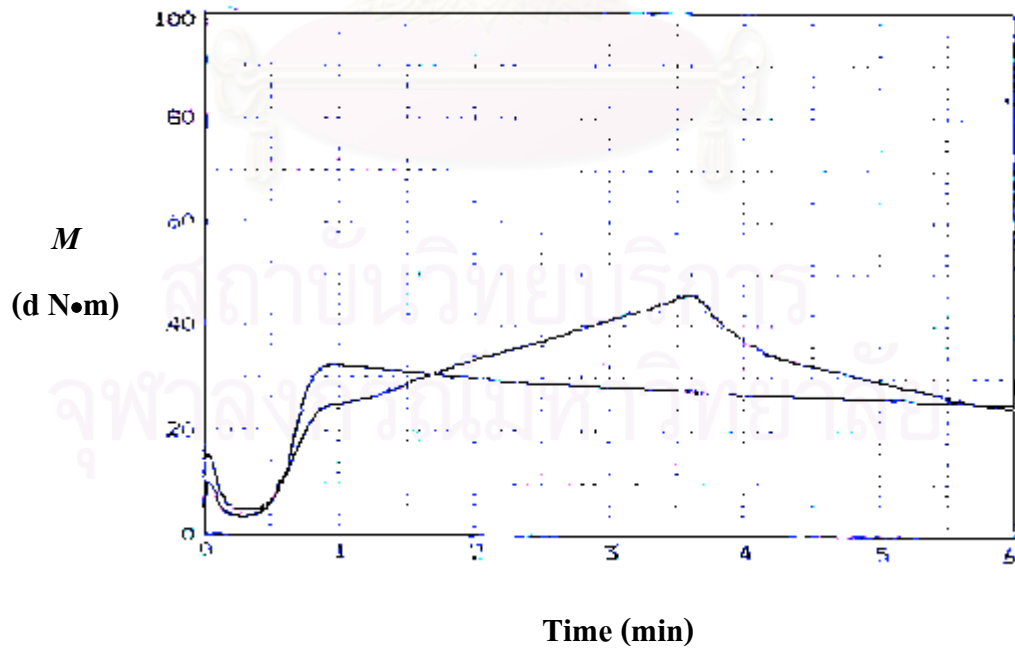


Figure D5 Cure characteristic curve from rheometer at 170°C.

VITA

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