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นางสาวกัญญ์สิรี เปาริบุตร

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PHYSICAL PROPERTIES OF EPOXIDIZED NATURAL RUBBER/CHITOSAN BLENDS

Miss Kansiree Paoribut

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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กัญญ์สิรี เปาริบุตร : สมบัติทางกายภาพของยางธรรมชาติอิพ็อกซิไดซ์ผสมกับไคโทซาน (PHYSICAL PROPERTIES OF EPOXIDIZED NATURAL RUBBER/CHITOSAN BLENDS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. กนกทิพย์ บุญเกิด, หน้า.

วัตถุประสงค์ของงานวิจัยนี้เพื่อพัฒนาฟิล์มยางธรรมชาติผสมไคโทซานจากน้ำยางและสารละลายไคโทซานที่สัดส่วน 100/0 90/10 80/20 70/30 60/40 และ 50/50 โดยวิธีเทปาดขึ้นรูปแบบใช้ตัวทำละลาย การศึกษาแบ่งออกเป็น 2 ส่วน ส่วนแรกทำการเตรียมฟิล์มยางธรรมชาติผสมไคโทซานที่มีและไม่มีสารคงรูปด้วยระบบกำมะถัน เมื่อนำฟิล์มที่ได้ไปศึกษาพบว่า ความต้านทานต่อการบวมตัวในตัวทำละลายและความทนแรงดึงของฟิล์มยางธรรมชาติผสมไคโทซานที่มีการคงรูปจะสูงกว่าที่ไม่มีการคงรูป เมื่อฟิล์มถูกนำไปบ่มเร่งด้วยความร้อน ความทนแรงดึงของฟิล์มยางธรรมชาติผสมไคโทซานที่ไม่มีการคงรูปลดลง ขณะที่ฟิล์มที่มีการคงรูปกลับเพิ่มขึ้น ซึ่งอาจมีสาเหตุมาจากการคงรูปที่เพิ่มขึ้นระหว่างการบ่มเร่ง ฟิล์มยางธรรมชาติผสมไคโทซานมีการสลายตัวทางความร้อนสองขั้น โดยที่อุณหภูมิต่ำเป็นของไคโทซานขณะที่อุณหภูมิสูงเป็นของยาง ฟิล์มยางธรรมชาติผสมไคโทซานที่มีและไม่มีการคงรูปมีการซึมผ่านของก๊าซออกซิเจนมากกว่าฟิล์มยางธรรมชาติและฟิล์มไคโทซานบริสุทธิ์ ส่วนที่สองทำการเตรียมฟิล์มยางธรรมชาติอิพ็อกซิไดซ์ผสมไคโทซานที่เติมมาเลอิกแอนไฮไดรด์ โดยน้ำยางธรรมชาติอิพ็อกซิไดซ์มีหมู่วงแหวนอิพ็อกซิไดซ์อยู่ร้อยละ 22 ฟิล์มยางธรรมชาติอิพ็อกซิไดซ์ผสมไคโทซานสามารถเตรียมได้เมื่อมีการเติมมาเลอิกแอนไฮไดรด์เท่านั้น โดยคาดว่ามาเลอิกแอนไฮไดรด์นอกจากจะทำให้ยางธรรมชาติอิพ็อกซิไดซ์เกิดการเชื่อมขวางแล้วยังทำให้ยางธรรมชาติอิพ็อกซิไดซ์และไคโทซานเกิดพันธะเคมีระหว่างกันทำให้ไม่พบการแยกเฟส ยางธรรมชาติอิพ็อกซิไดซ์ผสมไคโทซานที่อัตราส่วน 90/10 ที่เติมมาเลอิกแอนไฮไดรด์ 2 phr จะให้ค่าความทนแรงดึงสูงที่สุด ฟิล์มยางธรรมชาติอิพ็อกซิไดซ์ผสมไคโทซานที่อัตราส่วน 70/30 60/40 และ 50/50 ที่เติมมาเลอิกแอนไฮไดรด์ 3 phr เมื่อผ่านการบ่มด้วยความร้อนจะมีค่าความทนแรงดึงสูงขึ้น ซึ่งอาจมีสาเหตุมาจากการเชื่อมขวางของยางธรรมชาติอิพ็อกซิไดซ์ที่เพิ่มขึ้น จากการทดสอบคุณสมบัติทางความร้อนพบว่าฟิล์มยางธรรมชาติอิพ็อกซิไดซ์ผสมไคโทซานที่ไม่มีการแยกเฟสจะมีการสลายตัวเพียงขั้นเดียวเท่านั้น นอกจากนี้ยังพบว่าฟิล์มยางธรรมชาติอิพ็อกซิไดซ์ผสมไคโทซานที่เติมมาเลอิกแอนไฮไดรด์มีการซึมผ่านของก๊าซออกซิเจนต่ำกว่าฟิล์มยางธรรมชาติอิพ็อกซิไดซ์และฟิล์มไคโตซานบริสุทธิ์

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5571916423 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: NATURAL RUBBER / EPOXIDIZED NATURAL RUBBER / CHITOSAN / MALEIC ANHYDRIDE / SOLUTION CASTING METHOD

KANSIREE PAORIBUT: PHYSICAL PROPERTIES OF EPOXIDIZED NATURAL RUBBER/CHITOSAN BLENDS. ADVISOR: ASST. PROF. KANOKTIP BOONKERD, Ph.D., pp.

The objective of this study was to develop natural rubber/chitosan (NR/CS) films from rubber latex and CS solution at different rubber to CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50 using a solution plating method. The study was divided into two parts. In the first part, the NR/CS films were prepared from pristine NR latex with and without sulfur curing agents. The study showed the cured NR/CS films showed higher swelling resistance and tensile strength (TS) than the uncured films. After thermal aging, the TS of the uncured NR/CS films decreased while that of the cured ones increased. This might be due to the further thermal curing during aging. Both uncured and cured NR/CS films showed two decomposition peaks. One at low temperature was attributed to the decomposition of CS whereas the one at higher temperature was due to the decomposition of NR. The NR/CS film had higher oxygen permeability (OP) than the pure NR and CS film. For the second part, the films were prepared from epoxidized NR latex (ENR) with 22% epoxidation in the presence of maleic anhydride (MA). The result showed that the ENR/CS film can be obtained only when adding MA. It was believed that MA did not only crosslink ENR chains but also chemically bonded ENR and CS chains, thus dismissing phase separation. The ENR/CS film at the ratio of 90/10 with MA of 2 phr showed highest TS. After thermal aging, the films at the ENR/CS ratios of 70/30, 60/40 and 50/50 with MA of 3 phr had higher TS. This might be due to the further thermal curing during aging. Thermal decomposition testing showed that the ENR/CS film without phase separation showed only one decomposition peak. Moreover, it was found that the ENR/CS film had lower OP than the pure ENR and CS film.

Field of Study:	Petrochemistry and	Student's Signature	....
	Polymer Science	Advisor's Signature	....
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CHAPTER I
INTRODUCTION

1.1 Statement of Problems

Recently, many researches have been studied about natural polymers such as natural rubber, cellulose, chitosan, poly(lactic acid) to replace the use of synthetic polymer. The reason is not only due to the shortage of petrochemical product, making the price rise but also environmental problems found. So, there are efforts to create or develop materials that can replace the plastic. Material from renewable biomass sources and not harmful to life called as bioplastic is one of the most outstanding candidates.

Natural rubber (NR) is an industrial crop and export commodity of Thailand that has received the support from government to grow and promote. In 2554 [1], Thailand is the world's number one NR products exporter. NR is biomaterial from renewable resource derived from rubber tree. It has excellent physical properties such as high mechanical strength, excellent flexibility, resistance to impact and tear, easy for gas to transport through and low cost which makes it a suitable alternative to improve the brittleness of materials [2]. However, it has unsaturated hydrocarbon chain structure and non-polar character. Therefore, NR has sensitivity to chemicals and solvent (ozone and weathering) which causes limitations in variety of applications. In the past several years, the most popular chemical modification of NR in order to suppress above drawbacks is epoxidation. Epoxidized natural rubber (ENR) is derived from the partial epoxidation of the NR molecule. ENR is non-toxic and biocompatible polymer which has lower swelling in hydrocarbon oils, lower gas permeability and higher hardness [3].

Chitosan (CS) is a type of bioplastics derived by deacetylation of chitin which is isolated from crabs shrimp and lobsters. Currently, shrimp shell which is waste from consumption has been used as a substrate in the preparation of chitin - chitosan. The process is not complicated. CS has been used more than chitin because chitin is insoluble in most solvents compared to CS soluble in dilute acidic solvent [4]. CS can be used as a film for edible products. This is because CS can control the moisture transferring between the external environment and food, thus slowing the spoilage of food more than polyethylene [5]. However, the brittleness of CS is a major disadvantage. So, CS is not appropriate for some applications such as the packaging materials. However, the brittleness can be reduced when carefully mixing CS with flexible polymer [6, 7]. From literature survey, it has been found that the mechanical and thermal properties of the NR film can be improved once CS was introduced into the NR. However, the improvement was limited due to the low compatibility between NR and CS phase [8]. Moreover, in literature NR was cured by peroxide which generally gave lower strength than sulfur cure. There was also another study trying to improve the compatibility between NR and CS by grafting CS onto the ENR chains [9]. The reaction occurred through a ring-opening of ENR with functional groups of CS. Even it was expected that the grafting could enhance the compatibility between two polymers, the results showed that there was the formation of agglomerate CS particle. Moreover, there was only 5% of CS grafting onto the NR chains, thus just causing resistance to solvent and mechanical properties of the NR slightly increase.

In this research, we proposed alternative approaches to improve the mechanical properties and compatibility of the NR/CS film. The NR/CS films were prepared from NR latex and CS solution using a solution casting method. There were two type of NR latex including pristine NR latex and ENR latex. For the pristine NR, sulfur curing system was used to crosslink NR, while for ENR latex, difunctional molecule, maleic anhydride (MA), was used to crosslink ENR. The effect of rubber to CS weight ratio and the presence of crosslinking network on the characteristic, solvent resistance, tensile properties, thermal aging resistance, thermal decomposition and gas barrier behavior of films are evaluated here.

1.2 Objectives

The objectives of this research are as follows:

1.2.1 To prepare the rubber/CS films from pristine and ENR latex with CS solution using a solution casting method.

1.2.2 To study the effect of the rubber/CS weight ratio and the presence of crosslinking networks on the physical, mechanical and thermal properties, swelling resistance, and gas permeation of the obtained rubber/CS film.

1.3 Scopes of the research

1.3.1 To review related research.

1.3.2 To design experimental procedure.

1.3.3 To prepare rubber/CS films by blending the following rubber latex with CS solution at different rubber to CS weight ratios:

- a) Natural rubber (NR).
- b) Pre-vulcanized natural rubber (PNR).
- c) Epoxidized natural rubber (ENR).

1.3.4 To determine mechanical properties of the rubber/CS films as follows:

- a) Tensile strength by using a universal testing machine.
- b) Tensile strength after aging by using a universal testing machine.

1.3.5 To determine thermal decomposition behavior using a thermal gravimetric analysis.

1.3.6 To determine solvent resistance by evaluating swelling index and oxygen permeability of rubber/CS blends.

1.3.7 To determine gas permeation by evaluating oxygen diffusion coefficients.

1.3.8 To evaluate the optimal composition to obtain the rubber/CS film with the improved properties.

1.3.9 To analyze data, summarize the results and write thesis.

CHAPTER II

THEORETICAL AND LITERATURE REVIEWS

2.1 Natural rubber (NR) [10]

Natural rubber (NR) is extracted from rubber tree (Hevea Brasiliensis). The pioneer who brought rubber tree to Thailand is Praya Rasadanupradit Mahirasornpakdee (Corzimby Na Ranong) since A.D. 1900 in Trang. Afterwards, rubber became a top economic plant that generates revenue to our country. In 2002, Thailand was the number one rubber producer in the world with quantity of 2.61 million tons. NR was used in many industries i.e. wheel, motorcycle, condom, glove, elastic band. Consequently, there are supports to grow more rubber trees and expand all over the country.

The information about rubber plantation from 2007 to 2013 and the export values of rubber products are given in **Tables 2.1** and **2.2**.

Table 2.1 Rubber plantation in Thailand during 2007 – 2013 [11]

Year	Area of crops (Farm)	Area of slit (Farm)	Product (Ton)	Yield per acre (Kg)
2007	13,608,757	10,569,366	2,979,722	282
2008	14,355,378	10,893,098	3,070,520	282
2009	15,362,346	11,042,811	3,022,324	274
2010	16,716,945	11,371,889	3,166,910	278
2011	17,254,317	11,600,447	3,090,280	266
2012	18,095,028	12,058,237	3,051,781	253
2013	18,461,231	12,765,636	3,348,897	262

Table 2.2 The export values of rubber during 2010 - 2013 (Unit : million baht) [12]

List	Value of the Years			
	2010	2011	2012	2013
Vehicle tire	82,285.75	111,659.04	104,650.20	103,926.30
Elastic band	9,746.07	11,056.31	10,733.20	9,776.60
Gloves	30,445.53	34,382.14	36,456.70	32,494.30
Other	33,833.71	38,315.83	107,979.66	16,582.00
Total	156,311.06	195,413.32	259,819.76	162,779.20

Fresh latex from rubber trees is a white liquid in colloid state having a density of 0.980 – 0.975 g/ml. The particles of rubber look like pear shape at size 0.05-5 micron. The rubber particles can suspend in the liquid due to negative charges at the surface pushing each other all the time, thus making these particles to be suspendible, and preserving the colloidal state of rubber.

2.1.1 Components of the latex

Latex has two main components including rubber texture and non-rubber texture [13].

2.1.1.1 Rubber texture

Rubber texture is the hydrocarbon compound, with 25-45% dry rubber texture. It is elastic due to its big molecule is a line composed of continuous isoprene suborder. A rubber piece consists of messy molecular coil. These molecules are bendable and stretchable. Traction or elongation loosens rubber molecule. When let the rubber free from tension, rubber molecular line will try to shrink back to the same coil condition.2. Non-rubber texture is about 65% comprised of two parts including water part (serum), and lutoid part with other substances called Frey Wyssling.

All components of the latex are listed in **Table 2.3**.

Table 2.3 Components of the latex [14]

Components	Ratio (%)	The average ratio (%)
All solid	48-27	36
Dry rubber content	45-25	33
Proteins and fatty acids	1.5-1	1.2-1
Resins	1.25-1	1
Ashes	>1	<1
Carbohydrate (sugar)	1	1
Water	The rest	64

2.1.2 Chemical structure of NR

Chemical structure of NR is cis-1,4-polyisoprene as shown in **Figure 2.1**. For each molecule, NR is composed of units of isoprene (C_5H_8) splice together in a long line (linear). In general, NR has an average molecular weight in the range 200,000-400,000 g/mole with a very broad molecular weight distribution. Glass transition temperature (T_g) of NR is about $-72^{\circ}C$, meaning that if the NR is stored in a temperature below -72°C, properties of NR will change from the usual flexibility to solid brittle as well.

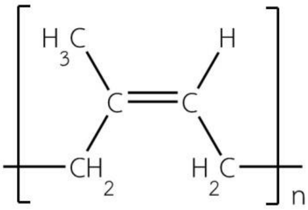


Figure 2.1 Cis-1,4-polyisoprene

2.1.3 General qualification of NR [15]

2.1.3.1 Elasticity

It is the outstanding performance of NR because of its spiral molecular structure, and Van der Waals forces attracting between polymer chains which are weak forces.

2.1.3.2 Elongation at break

Pure NR without any filler can be elongated up to 1,000%, and will be reduced when filler is added. According to level of vulcanization, this performance makes NR popular among productions of elastic rubber band and balloon.

2.1.3.3 Tensile strength

Due to the high order of rubber molecules, therefore, NR can easily crystallize when has been stretched. The occurred crystal will strengthen rubber. Therefore, NR is considered to have a very high tensile strength without any help of filler, 20 MPa or higher. Adding filler will increase level of tensile strength which is different from ability of artificial rubber that normally has so low tensile strength until it cannot be used in the engineer usage unless filler has been added.

2.1.3.4 Tear strength

Because NR can crystallize when it is elongated, therefore, NR has very high tear strength even in the room and high temperature condition. Adding filler will help to increase tear strength of the rubber.

2.1.3.5 Dynamic properties

It means there is elasticity while it has the heat build-up from lower usage, leading to low energy lost in form of low heat (hysteresis). Thus, NR has low accumulated heat when it is used in dynamic condition. This rubber is suitable to huge wheel production e.g. truck wheel, plain wheel, because wheel that has high accumulated heat can make an explosion.

2.1.3.6 Abrasion resistance

NR has high abrasion resistance and higher than artificial rubber e.g. EPDM rubber, chloroprene rubber (CR), butyl rubber, and silicone rubber, but less lower than SBR rubber.

2.1.3.7 Insulation

NR has a high specific resistivity up to 1015 or 1016 ohm.cm which considered to be very high.

2.1.3.8 Liquid and chemical resistance

Because its chemical structure comprises of hydrogen and carbon only, NR is a non-polar hydrocarbon substance. NR without chemical filler or raw rubber will be molten well in non-polar solvent e.g. toluene and benzene. But when there is crosslinking, it will make rubber swollen in the solvent due to chemical linkage of molecular network. In addition, NR is also good resistant to diluted acid and base.

2.1.3.9 Service temperature

NR can be used very well in the temperature range of 55-°C to°70 C. If NR is kept at the low temperature for a long time, NR will crystallize, then become hard and less elasticity. But if the temperature is too high, NR will be deteriorated. So there are inventions of rubber with chemical formula added to prevent deterioration (antioxidant).

2.1.4 Modification of NR [16]

Although NR has so many good attributes, but due to its chemical structure that comprises only of carbon and hydrogen, and many double bonds of carbon (C=C), it makes NR dissolve in non-polar solvent and be difficult to mix with polar polymer. It will be deteriorated easily when exposed to the sun or heat. NR will become harder and brittle, and cannot be used any further. There are many approaches to improve the properties of NR (as seen in **Figure 2.2**) e.g. mixing NR with synthetic rubber, chlorination, hydrogenation, cyclization, epoxidation, or graft copolymerization. Attribute of each type depends on function group inside its structure as mentioned above.

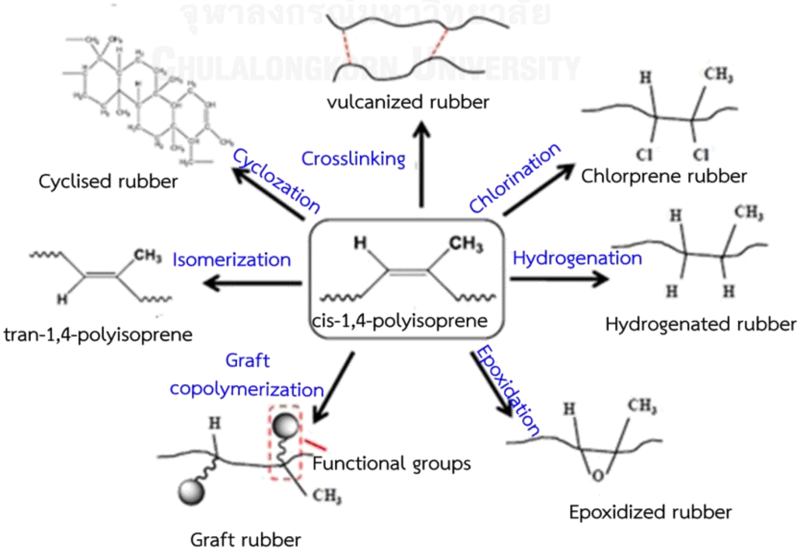


Figure 2.2 Various modification methods for NR [16]

2.1.4.1 Crosslinking of NR

It is an adjustment of NR by a process of creating the network junctures by the insertion of crosslinks between polymer chains. The chains stick tighter and chemically link to other chains, making NR resistant to weather, and get better dynamic and mechanical properties such as modulus of elasticity at breaking point, tensile strength, pressure, or impact. The crosslinking can be technically called as vulcanization. The most practical crosslinking agent for diene rubber is sulfur. It was discovered by Charles Goodyear in 1839 [17]. The process is usually carried out by heating the rubber. When rubber is highly crosslinked, rubber will has high hardness, less elasticity, high modulus. Rubber is no longer elastic material any more. It is called as an ebonite.

2.1.4.2 Mixing NR with other polymers

To obtain certain properties such as high solvent resistance, NR is usually mixed with other polymers. Normally the properties of the obtained product attribute of both rubber and polymer. The properties depend on type of polymer, preparation, proportion of rubber and polymer, chemicals, and compatibility of the polymer. Sometimes, compatibilizer is added to strengthen material. Generally, there are two methods as follows:

1. *Mixing NR with synthetic rubber*

NR can be blended with many kinds of rubber. Mostly for vehicle wheel, NR is blended with styrene-butadiene rubber (SBR) due to its low accumulated heat, good stickiness, well cohesive with surface, and resistant to weather [18].

2. Mixing NR with thermoplastic

The mixture of NR with thermoplastic is called as a thermoplastic elastomer or TPE. TPE has combined attributes of rubber and thermoplastic which are hardness at room temperature, elasticity like rubber, while can be molten by the heat which is an attribute of thermoplastic. Consequently, TPE can be reprocessed again. The examples of thermoplastic that can be mixed with NR is polyurethane (PU) [19], polystyrene (PS) [20]. Besides simple blending [19], **Figure 2.3** shows the formation of an interpenetration network (IPN) between NR and PS. The styrene monomers were added into the NR networks and then polymerized, forming a NR/PS IPN.

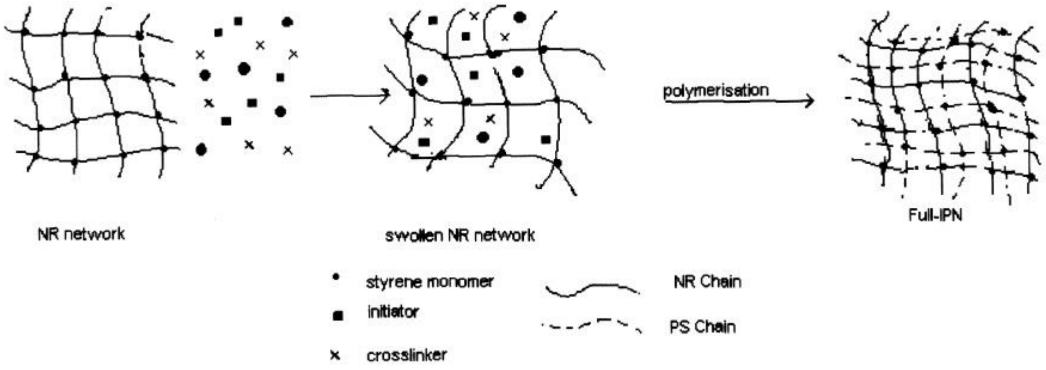


Figure 2.3 Formation of NR/PS IPN [21]

2.1.4.3 Ring creation of NR

It is a crosslinking method within NR molecule, creating a ring within structure of NR by cyclization in the acid condition, with catalyst and heating. The obtained product is called as a cyclized rubber. The rubber is stronger and has higher interaction between different molecules, therefore, it is generally used as a surface coatings, lacquer, and printing ink.

2.1.4.4 Isomer creation of NR

As mentioned earlier, the chemical structure of NR is cis-1,4-polyisoprene. Therefore, NR has high elasticity at low temperature due to its spiral chain and soft attraction. Changing chemical structure of NR to trans-1,4-polyisoprene as shown in **Figure 2.4** via isomerization reaction, causing rubber chains come closer to another chain. Consequently, the obtained product becomes stronger.

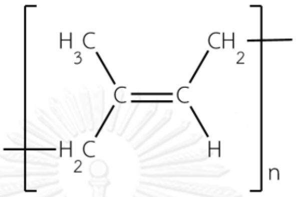


Figure 2.4 Trans-1,4-polyisoprene

2.1.4.5 Reaction with double bond of NR

Since the NR has C=C in the structure, it results NR in having a fast reaction with other chemicals e.g. oxygen and ozone, making NR deteriorate more easily by the environment. Thus, there are many inventors trying to solve this problem by reacting double bond of NR with specific chemical. Some reactions are shown here as follows:

1. *Chlorination*

The reaction can be carried out by sodium hypochlorite (NaOCl) and hydrochloric acid (HCl). The presence of chlorine group makes rubber more resistant to oil and non-polar solvent.

2. Hydrogenation

The reaction can be carried out either by hydrogen gas with the presence of catalyst (as shown in **Figure 2.5**) or diimide generated in situ by heating p-toluenesulphonyl hydrazide [22]. The reduction of double bond by hydrogenation process makes the rubber more resistant to heat, oxygen and ozone according to level of hydrogenation.

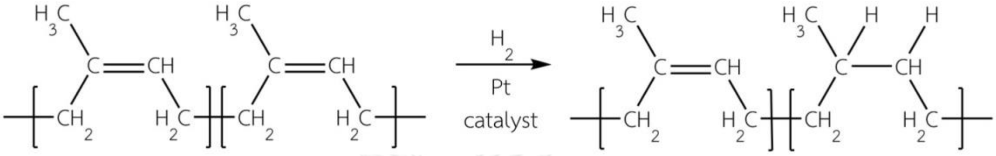


Figure 2.5 Hydrogenation reaction of NR [22]

3. Epoxidation

The reaction can be carried out by peroxy acid, creating cyclic ether with a three-atom ring. The presence of epoxide ring (as shown in **Figure 2.6**) gives rubber with better resistance to weather, heat, oil, and organic solvent. In addition, this rubber can be a good compatibilizer for rubber with polymer that has low compatibility such as PE and Nylon 6 [23].

Figure 2.6 Epoxy group

2.1.4.6 Grafting polymer on NR chain [13]

Graft copolymers of NR and polymers can be prepared by polymerization of monomer initiated by free radicals in the presence of NR or by attachment of a polymer to NR backbone by chemical reaction. The outcome rubber will be harder due to part of thermoplastic inside molecular structure. **Table 2.4** shows the list of monomers reported that can be grafted onto the NR chains and theirs products and applications.

Table 2.4 The list of monomers that can be grafted onto the NR and their products and applications [16]

Monomer	Initiator	Products/Applications
Styrene	Butyl hydroperoxide/ Tetraethylene pentamine (BHP/TEPA)	Thermoplastic elastomer with good mechanical properties
2-hydroxyethyl methacrylate	Cumene hydroperoxide (CHPO) and TEPA	Additive for enhancing adhesion plywood surface
Butyl acrylate	Gamma ray (Co-6)	Film with good tensile strength
2-(methylamino) methacrylate	CHPO/TEPA	High polarity NR
Methyl methacrylate	Gamma ray (Co60-), hydrogen peroxide and sodium thiosulfate	Thermoplastic elastomer with good mechanical properties
Maleic anhydride	Benzoyl peroxide	Compatibilizer

Nakason [24] studied on the grafting of maleic anhydride (MA) onto NR using a solution method as shown in **Figure 2.7**. It was found MA can be successfully grafted onto the NR chain. This can be confirmed by the presence of C=O stretching vibration of succinic anhydride ring on IR spectra. The degree of grafting increased with increasing in MA monomer concentration.

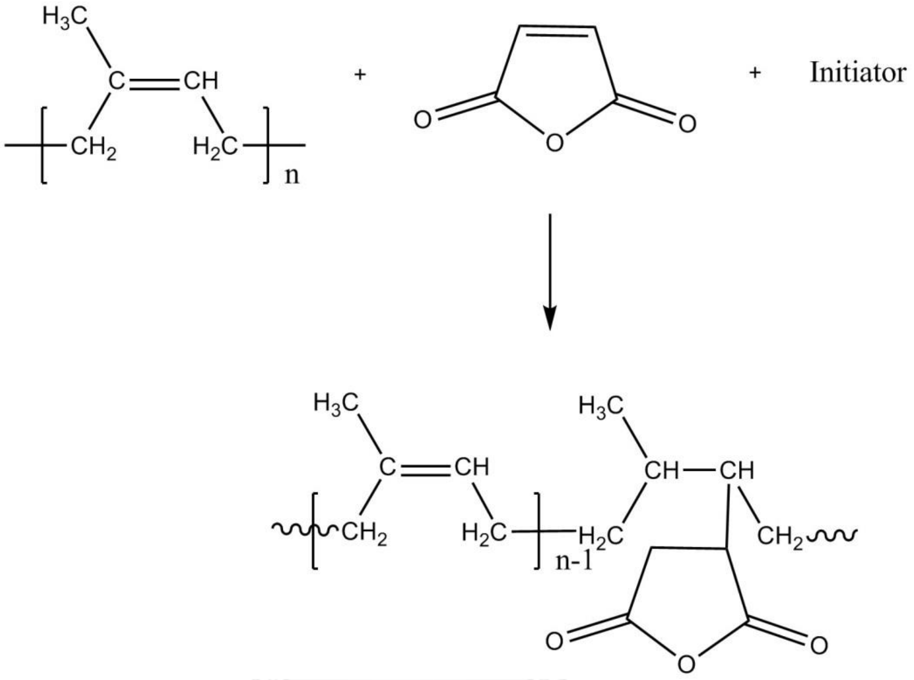


Figure 2.7 Formation of NR-g-MA [24]

2.1.4.7 Liquid natural rubber [25]

Liquid natural rubber (LNR) is a weight reduction of NR molecule by cutting molecular chain, or making the rubber molecule decompose at double bond. This rubber can easily flow, be stable at room temperature, durable, resistant to humidity, ozone, weather. It is normally used as a roller for cotton industry, printing press, shoe glue, and electric insulator.

2.2 Epoxidized natural rubber (ENR) [16, 26]

Epoxidized natural rubber, known as ENR, is derivative of natural NR molecules with epoxide ring. The reaction is called epoxidation. ENR is resistant to oil, air permeability and climate than NR. There are two types of commercial ENR based on the degree of epoxidation. The ENR is commonly used in ENR-25 refers to the ENR, reactive 25% epoxidation. And 50% ENR is reactive 50% epoxidation, has high polar. In addition, ENR also has the ability to crystallize when being stretched as well as NR. As a result, the tensile strength of ENR is high.

A typical formation of ENR from NR was carried out by employing peroxycarboxylic acid as shown in **Figure 2.8.**

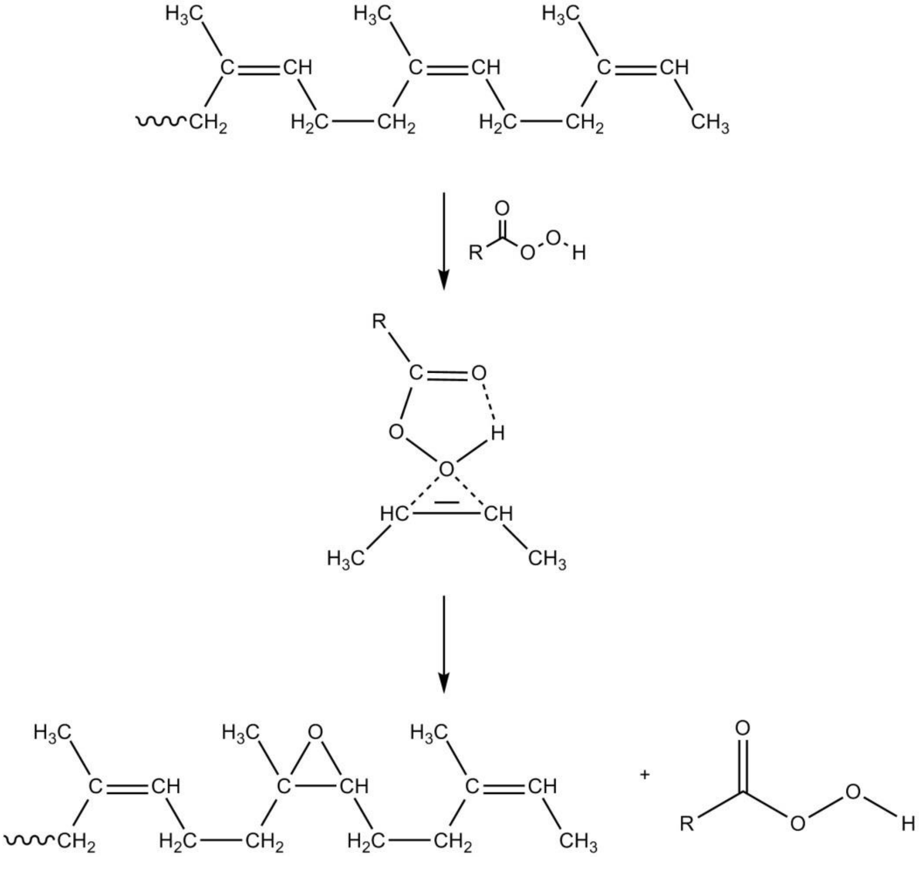


Figure 2.8 Epoxidation of ENR/peracid [27]

2.2.1 Ring-opening reaction

The ring opening reaction (as shown in **Figure 2.9**) is a side reaction which occurs in the epoxidation reaction. Due to it has water and acids in the reaction, make epoxide ring in molecule is opened. The ring-opened reaction of ENR is based on mole percent of epoxide. At high acid concentrations and elevated temperatures secondary ring-opened products predominated and less occurs furan formation.

In addition, the three membered rings of epoxide group are very sensitive to the reaction and easy occurs ring-opened reaction when using acid or base as catalyzed.

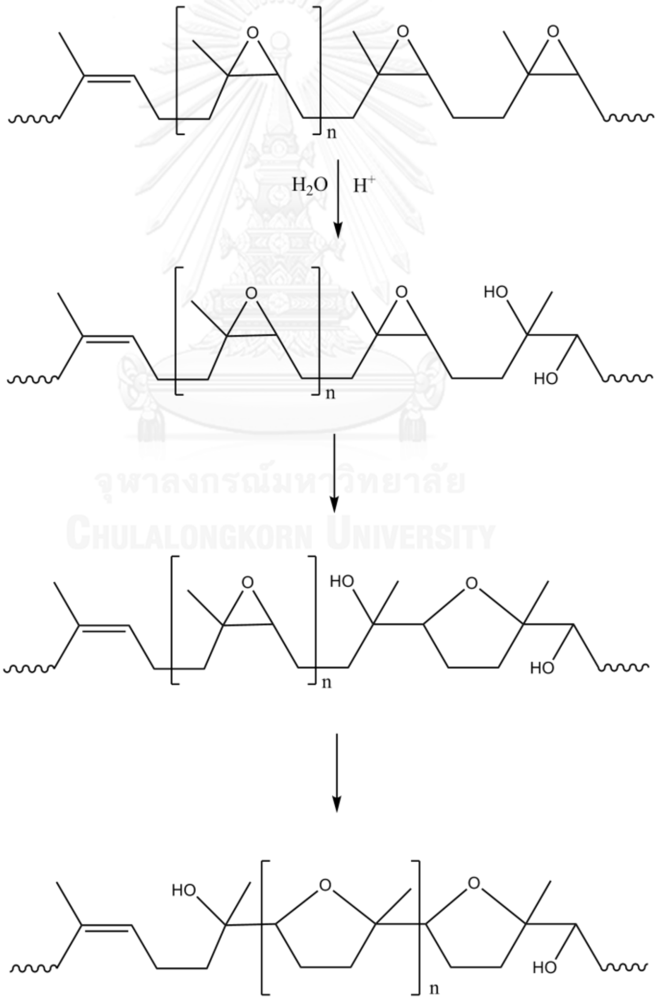


Figure 2.9 Ring opening of ENR and furan formation [26]

From **Figure 2.9**, it was reported that at high acid concentrations there is a side reaction, while at low acid concentrations epoxidation takes place at the low reaction rate. In theory, furan formation occurs until the reaction was stopped. The occurrence of side reaction can be characterized by ^{1}H-NMR and IR spectroscopy as shown in **Table 2.5**.

Table 2.5 The ^{1}H-NMR chemical shift and IR absorbance of by product from side reaction during epoxidation

Functional groups	**^{1}H-NMR chemical shift (ppm)**	**IR Wavenumber (cm^{-1})**
Hydroxyl (-OH)	-	3600-3200
Carbonyl (C=O)	-	1710-1740
Formate	9.75	1725
Epoxy (cis-1,4polyisoprene)	2.70	1250,870
Tetrahydrofuran	3.65	1065
-C-H	3.85	-

2.2.2 Basic of ENR preparation [28, 29]

The ENR can be prepared by two technique as following:

2.2.2.1 Latex

The latex method is an easy and fast technique and more popular in commercial production. First, NR latex is treated with nonionic stabilizer to make the latex particles stabilized for prevented agglomeration of rubber when added acidic. Then,

- if peracetic acid is used, it is added slowly over 2 hours and is kept at 20°C of less for 24 hours.
- if hydrogen peroxide and formic acid are used, the conditions are at 50°C at for 24 hours.

Finally, the product is neutralized by immersing in alkaline solution such as ammonia to raise the pH above 8 and washing with water until the residue acid is completely removed.

2.2.2.2 Solution technique

The solution technique starts from dissolving block rubber in the solvent, then adding peracid into the rubber solution. Okwn prepared ENR at 33% of epoxide level. The TSR5 (NR) was dissolved in carbon tetrachloride, then solution of NR was epoxidized using formic acid (0.34 mol phr) and 30% hydrogen peroxide (0.75 mol phr) at 0°C for 5 hours.

2.2.3 Analysis of %epoxidation

2.2.3.1 Titration

This method is uncomplicated and appropriate with the analysis of ENR with degree of epoxidation less than 15%. This method uses hydrogen bromide in aqueous acetic and reacts with the hydrogen peroxide. The carboxylic acid, ethyl, ester, aldehyde and peroxide will not interfere with the titration reaction.

2.2.3.2 Fourier Transform infrared (FT-IR) spectrometer

Generally, organic molecular absorb energy in the infrared region, resulting in vibration of the bonds in the molecule. This causes a change of the dipole moment at which infrared absorption of various functional groups have a different identity for absorption. Generally, the position of the absorption spectrum is identified by wave number of units (cm^{-1}). The concentration of the absorption signal is related to the concentration of the functional groups of the samples. **Figure 2.10** shows the FT-IR spectrum of ENR.

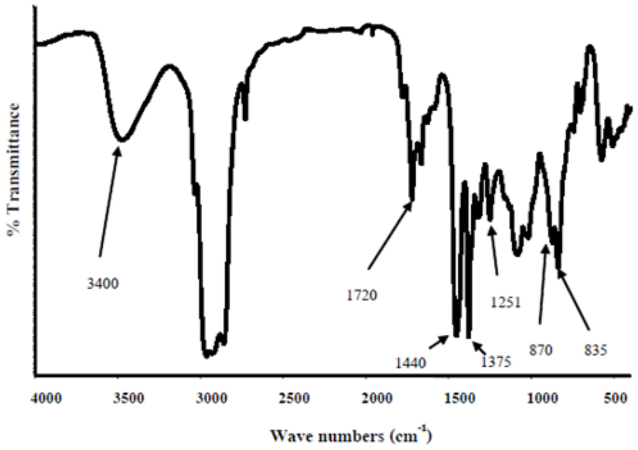


Figure 2.10 FT-IR spectrum of ENR [30]

The absorption of oxirane ring appeared at wave number of 800-950 cm^{-1}, depending on the structure of the main chain of diene polymer. Chain of cis-1,4-polyisoprene changed to the structure of cis-epoxy showed the absorption at the wave number of 870 cm^{-1}. Calculation the amount of epoxy can be done by creating a standard curve (calibration internal standard as shown in **Figure 2.11**) [31] that can be obtained by determining the ratio of intensity of the absorption spectrum at 870 cm^{-1} to the spectrum at 1375 cm^{-1} due to the vibration of the C-H bond of the methyl group of isoprene in the following equation:

$$A_r \quad = \quad a_{870} / (a_{870} + a_{835}) \qquad \text{... (2.1)}$$

Where, A_r = The ratio of the absorption spectra

a_{870} = The intensity of peak at 870 cm^{-1}

a_{835} = The intensity of peak at 835 cm^{-1}

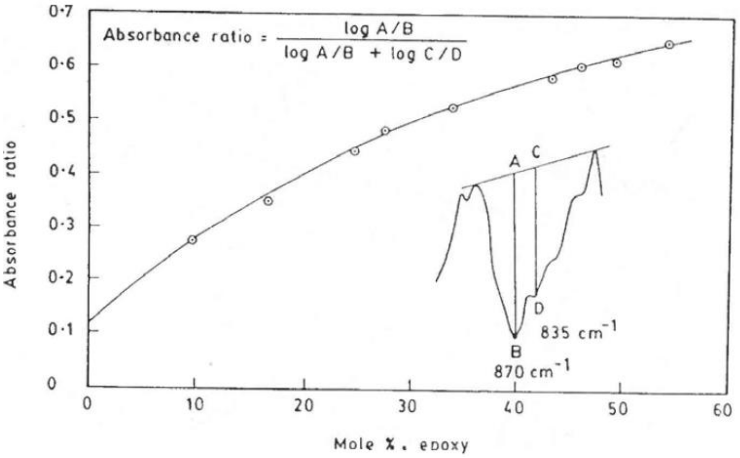


Figure 2.11 Calibration of internal standard for determining the % epoxidation [31]

2.2.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

1. ^{1}H NMR analysis

The percentage of epoxidation of ENR can be determined using ^{1}H-NMR signal of olefins proton at 5.14 ppm and proton adjacent with epoxide groups at 2.70 ppm (as shown in **Figure 2.12**). The amount of epoxy can be obtained from the integration of the resonance of those two protons and then by using the following equation [32]:

$$\%\ \text{Epoxide content} = 100 \times (A_{2.70} / (A_{5.14} + A_{2.70})) \qquad \ldots (2.2)$$

where, $A_{2.70}$ = The area under the peak at 2.70 ppm (proton adjacent epoxide unit)

$A_{5.14}$ = The area under the peak at 5.14 ppm (olefins proton)

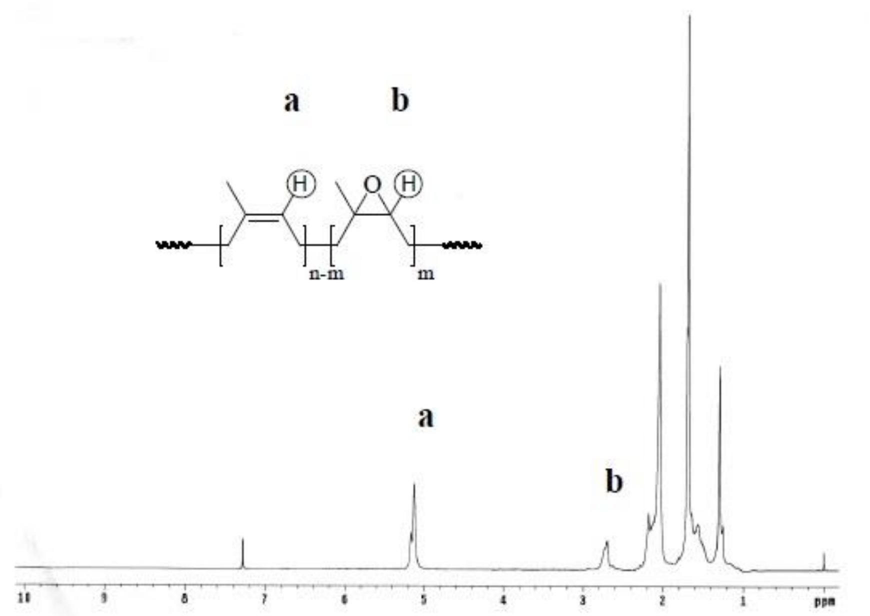


Figure 2.12 ^{1}H-NMR signal of ENR [30]

2. ^{13}C-NMR analysis

Chemical structure of 1,4-polyisoprene can be also analyzed by ^{13}C-NMR spectroscopy. A resonance of olefins carbon appears at 125 ppm while that of epoxy carbon appears at 64 ppm. Therefore, the amount of epoxidation can be possibly determined from the area under signal at 64 ppm and 125 ppm using the following equation [32]:

$$\% \text{ Epoxide content} = 100 \times (A_{64.5} / (A_{64.5} + A_{124.4,\ 125,\ 125.7})) \quad \ldots (2.3)$$

Where, $A_{124.4}$, $A_{125.7}$ = The area under the peaks of olefins carbon.

$A_{64.5}$ = The area under the peak of epoxide groups.

2.2.4 Properties of ENR [25, 28]

Properties of ENR depends strongly on the degree of epoxidation. When %epoxidation increases,

1. Glass transition temperature resulting in good significant in physical properties increases.
2. Hardness and tear strength increases.
3. Flexibility at low temperature reduces.
4. Solubility in non-polar solvent decreases.
5. Air permeability decreases.
6. Wet traction at ambient temperatures increases

2.2.5 Applications of ENR [28]

The presence of epoxide ring can widen the application of rubber as follow:

1. Wear, wet grip and low rolling resistance for fuel economy.
2. Tyre inner liners and inner tubes.
3. Non-slip flooring materials and sports shoe.

2.3 Chitosan (CS) [33-35]

Chitosan (CS) is a natural polysaccharide consisting copolymer of ß-(1-4)-D-gulcosamine and acetyl-ß-(1-4)-D-glucosamine. CS can be obtained by alkaline N-deacetylation of chitin, the second most abundant natural polymer in the world after cellulose. It can be found in the cell walls of certain algae, fungi and in the shells of crustaceans. **Figure 2.13** shows the structure of chitin and chitosan.

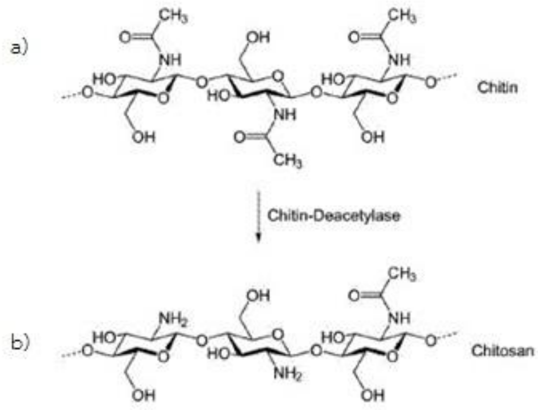


Figure 2.13 Structure of a) chitin b) chitosan [36]

The CS has nontoxic, biodegradable, biocompatible and antimicrobial. It dissolves in aqueous solutions of organic acid and mineral acids at specific conditions. However, CS does not dissolve in organic solvents and pure water. The degree of deacetylation dominates the solution of chitosan. CS has been widely studied in the field such as food, cosmetics, agriculture, biomedicine and biotechnology.

2.3.1 Production of CS

There are several ways to prepare CS from chitin. **Figure 2.14** shows a process of chitosan production [35]. The procedure can be summarized as follows:

Step 1: Washing with water

Frozen prawn shells are washed with hot water at 60°C, then dried in an oven at 60°C and crushed to small pieces.

Step 2: Deproteination

The small prawn shells are treated with 5% sodium hydroxide (NaOH) to remove protein and other organic materials, then washed with water until the solution is near neutral. Then, the washed shells are dried in a vacuum oven at 60°C.

Step 3: Decoloration

The dried shells are washed with acetone at room temperature for 24 hours. Then, they are dried in an oven at 60°C.

Step 4: Demineralization

The dried shells are treated with 0.5% HCl for 24 hours at 20°C to remove inorganic which is calcium carbonate. Then, they are washed with a lot of water to remove $CaCl_2$ and other impurities. This product is called as chitin.

Step 5: Deacetylation of chitin

The chitin obtained after step 4 was deacetylated using NaOH. Degree of deacetylation depends on the concentration of NaOH and reaction time and temperature. After the reaction, chitosan is washed with distilled water until it is neutral, then dried in an oven at 60°C.

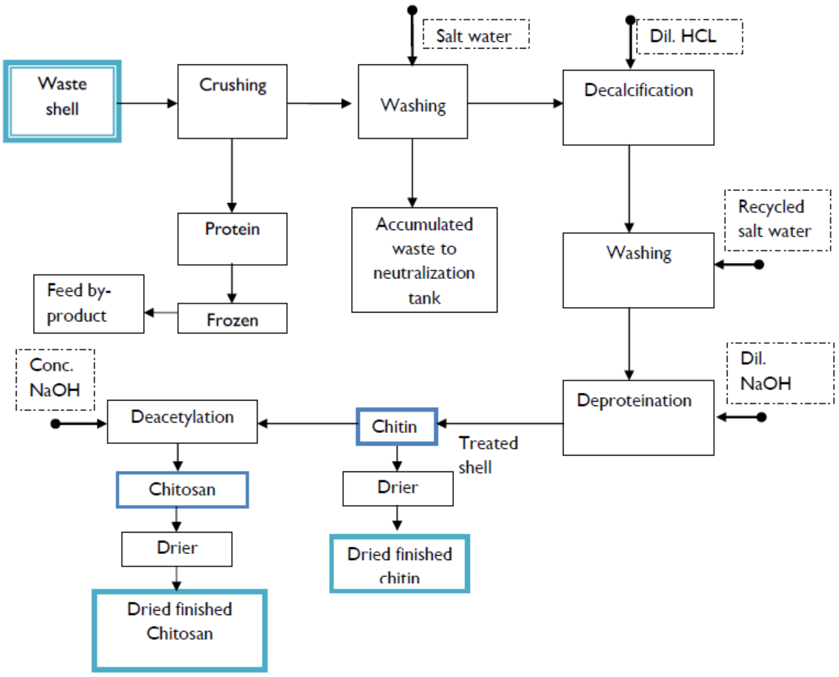


Figure 2.14 Manufacturing process of chitin-chitosan [37]

2.3.2 Chitosan modification

Many researches have made structural modifications to improve the properties of CS for the specific application. CS is widely used to improve the chemical structure of the group that can react with the polymer others. Sridhari [38] prepared CS mixed with maleic anhydride (MA) in dimethyl acetamide. The probability of mechanism between MA and CS is shown in **Figure 2.15**. The CS/MA leads to the formation of a trisubstituted derivative of CS (on one amine and two hydroxyl groups of the saccharide unit), which is well confirmed by titration of carboxylic group.

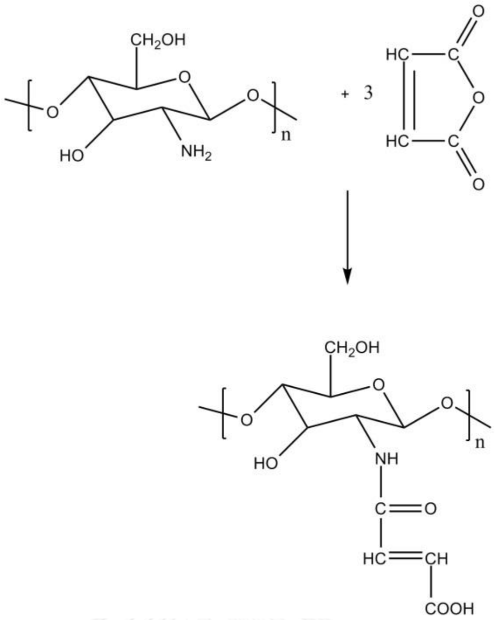


Figure 2.15 Proposed mechanism of reaction between CS and MA [38]

2.3.3 Applications of chitosan [4, 39, 40]

Typically, chitin and CS have similar properties. But chitin has restrictions because chitin cannot dissolve in the various solvents due to its crystalline structure. Therefore, CS is more interested because it can dissolve in the dilute acid solvents. This makes CS suitable for several applications.

2.3.3.1 Agriculture

In the past to the present, Thailand is an agricultural country and the main income is from agriculture. Science and technology has contributed to the current value of agriculture. However, the increase in agriculture product also leads to the high use of chemical pesticides. Therefore, the research on natural substances earns more attention. And CS is another popular option in this field recently.

1. CS is used as a binder in seed coating to resistant fungal.

2. CS is used as a seed incrusting agents to increase productivity and insect protection.

3. CS is used as a tree-protecting agent to protect the surface erosion from plants, fungi, and also rain.

2.3.3.2 Supplementary food

CS is used as a weight loss supplements because the chitosan can absorb fat and reduce the accumulation of fat and cholesterol.

2.3.3.3 Food industry

The antibacterial and antifungal properties found in CS can be used during the storage and preservation of food.

2.3.3.4 Wastewater treatment applications

1. CS is used in water treatment processes to extract heavy metals and toxic metals such as mercury, lead, copper, silver, magnesium by forming complexes with metal ions.

2. CS is a good coagulation and sedimentation agent. Because CS contains amino groups (positively charged), CS can bind to the negatively charged substances, causing the precipitation which is a treatment to clear up.

2.3.3.5 Textile and Paper

1. CS blended with synthetic fibers can control humidity, wipe sweat, comfortable wearing, be resistant to wash, long lasting color and also prevent bacteria and fungus.

2. CS blended with cotton to reduce the wrinkle.

3. CS is a binder in inks and dyes for color adhesion, fast drying, resistant to oils and solvents.

2.3.3.6 Fertilizers

CS is the fertilizers in legumes which are nitrogen higher plants. Nitrogen in the CS is released in suitable quantities for plants.

2.3.3.7 Medical

Because CS can degrade within the body of the animal and prevent some infections, this leads to the use of CS in the medical such as wound healing or wound dressing, contact lenses, blood dialysis membrane and homeostatic materials.

2.4 Literature reviews

In 2000, Carone and coworkers [41] grafted NR with polyamide 6 (PA6) using maleic anhydride (MA) as a compatibilizer. It was found that MA molecules reacted with both rubber and PA6 matrix during processing (as shown in **Figure 2.16**). The NR-g-PA6 with MA showed degradation temperature above 800°C.

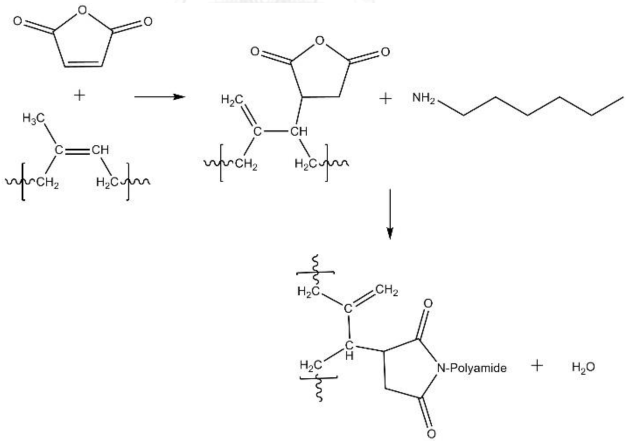


Figure 2.16 The proposed mechanism of NR-g-PA6 formation when using MA as a compatibilzer [41]

In 2004, Nakason and coworkers [24] grafted NR with MA using benzoyl peroxide (BPO) as an initiator agent for free radical graft copolymerization. FT-IR spectrum showed peaks of MA onto the NR structure. Glass transition of NR grafted MA was higher than that of the pure NR.

In 2007, Rao and coworkers [8] prepared thermoplastic elastomer from blending NR with CS, then formed the NR/CS films by a solution casting method. The results showed that when increasing CS content, the NR/CS films had higher tensile strength and hardness but lower elongation at break. It was also found that the presence of CS enhanced thermal aging resistance. However, this research found that the amount of CS that could be added into NR latex was limited to 35% due to the poor compatibility between two polymers. The NR/CS film dissolved in solvent such as benzene. In 2009, researchers have further developed the NR/CS film by adding dicumyl peroxide acting as a crosslinking agent [42]. The results showed that the peroxide cured NR/CS films had higher tensile strength and good resistance in benzene than the uncured NR/CS films.

In 2008, Siwaroj [43] has prepared the NR film with the presence of CS in the form of discrete particles. First, the CS in the form of suspensions was prepared using a ball mill, then mixed with pre-vulcanized latex. The film was produced by a dipping process using a glass tube as a mold. The results showed that the tensile strength, elongation at break and tensile thermal aging of the NR films with the presence of discrete CS were lower than the pure NR films. Although it was expected that the presence of CS will inhibit the growth of bacteria, the NR film with the presence of CS and the pure NR film showed the same resistance to the growth of bacteria.

In 2009, Kittagran [44] have prepared thermoplastic elastomer by grafting CS onto the ENR chain using zinc (II) perchlorate hexahydrate as a ring-opening agent. The level of epoxidation was varied at approximately 21, 50 and 53 mole%. The FT-IR and ^{1}H-NMR spectra confirmed that the CS was successfully grafted onto the ENR chain (as shown in **Figure 2.17**). Thermal gravimetric analysis (TGA) showed two-step thermal decomposition around 170-300°C and 360-500°C, which were referred to the decomposition of CS and NR, respectively. Although the CS chain was chemically bound to the NR chain, SEM images showed that CS formed agglomerate and heterogeneously dispersed in a continuous NR matrix.

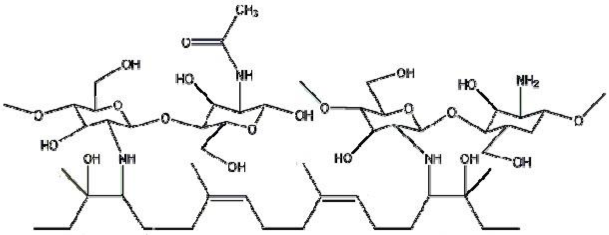


Figure 2.17 The proposed mechanism of ENR-g-CS formation [44]

In 2010, Su-il and coworkers [6] prepared chitosan-incorporated low density polyethylene (LDPE) film for keeping fresh meat. The oxygen permeability was not affected by the incorporation of CS, while the water vapor permeability increased due to the hydrophilic nature of CS. The tensile strength and elongation at break decreased when increasing concentration of CS. This can be explained by a decrease in the intergrity of LDPE film matrix by CS molecules. Films with 8% of CS maintained fresh red color at the surface of meat for 5 days, while the pure PE films maintained the redness at the surface of meat for only 3 days.

In 2012, Mia and coworkers [45] studied thermal properties and gas permeability of CS coated PE films when using glycerol (GLY) as a plasticizer. The coated films showed a good visual and thermal stability, as well as a good adhesion between the PE surface and CS/GLY as revealed by SEM images. The gas permeability of the coated films was lower than that of the PE film due to the interaction of CS and GLY restricting the flow of gases. The interaction of CS and GLY was confirmed by the shift of N-H and O-H vibration peaks of the CS in the FT-IR spectrum.

In 2013, Guna and coworkers [46] prepared biocomposites from the blend of with ENR50 and LENR50 (low molecular weight of ENR) using sulfur curing system. The results showed that for CS-ENR50, the increase in CS loading increased torque value, tensile strength, modulus at 100% strain. However, However, the increase in CS loading did not effect on the cure time and elongation at break. On the other hand, for CS-LENR50, when increasing CS loading no significant change in cure time and tensile strength were observed. The water uptake of CS-LENR50 increased when increasing CS loading. For each CS loading, the water uptake of CS-LENR50 was higher at that of CS-ENR50. For both CS-ENR50 and CS-LENR50, increasing CS loading, decreased the toluene absorbency. For both biocomposites, two decomposition temperatures were found.

In 2014, Daosheng and coworkers [2] studies the effect of DCP, sulfur and phenolic resin curing system on the structure and properties of the poly(lactic acid)/natural rubber (PLA/NR) blend. The sulfur and DCP showed a small influence on the degradation of PLA. The phenolic resin reduced mechanical properties and thermal stability of the blends. Compared with the three curing systems, the PLA/NR blend (60/40 w/w) cured with DCP showed the optimum of mechanical properties and thermal stability.

In 2015, Marie and coworkers [47] prepared PE films consisting of CS ethylene vinyl acetate (EVA) as a plasticizer using a twin-screw extruder. The results showed that the elastic modulus and tensile stress at yields of PE/CS films were lower than those of the pure PE. However, when adding EVA, the PE/CS films now had higher elastic modulus and tensile stress at yield than the PE films. The oxygen permeability of the PE films did not change when adding CS. However, the addition of EVA resulted the PE/CS films in having higher oxygen permeability. This might be because the large vinyl acetate groups of EVA formed large space between the polymer chains, thus allowing the oxygen molecule travel through the films easier.

As seen from above literatures, there are many attempts to prepare the NR/CS film with better properties and also compatibility. However, the recent results still are far from the goal. In this study, the aim was to develop new approaches to prepare the NR/CS film. The characteristic, physical and thermal properties of the obtained films were investigated to evaluate the proper preparation condition.

CHAPTER III

EXPERIMENTAL

3.1 Conceptual Framework

This research has been prepared various natural rubber/chitosan (NR/CS) films and investigated their mechanical, thermal aging, decomposition, swelling, and oxygen permeability properties. The NR/CS films were mainly prepared from the NR latex and CS solution using a solution casting method. There were two types of rubber including pristine NR and epoxidized NR used. The study was focused to determine the effects of type of rubber, rubber to chitosan ratio, and vulcanization on the properties of the obtained films. The overview of research plan is described in **Figures 3.1-3.2**, respectively.

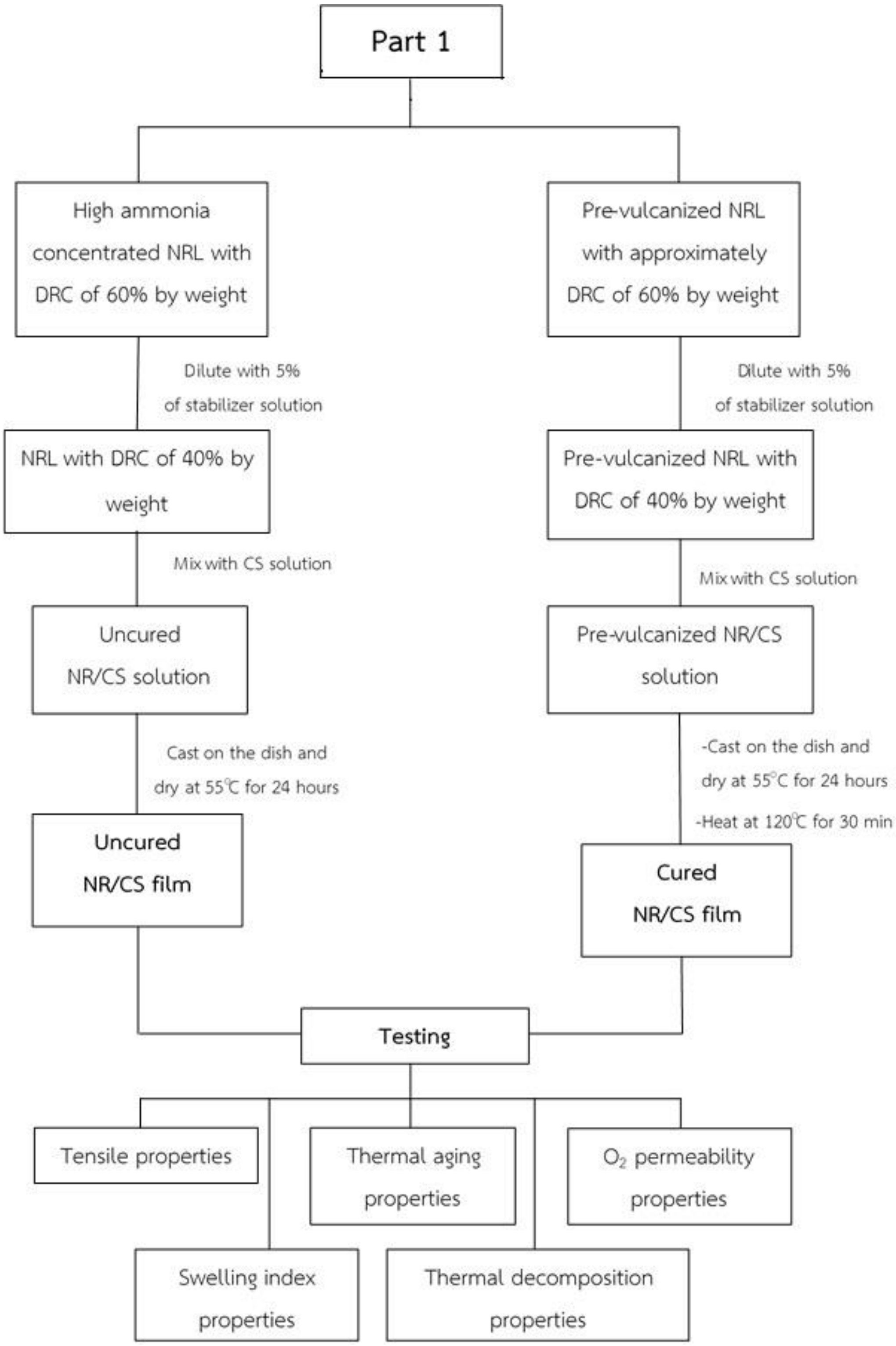


Figure 3.1 The overview procedure of preparation and characterization of NR/CS films

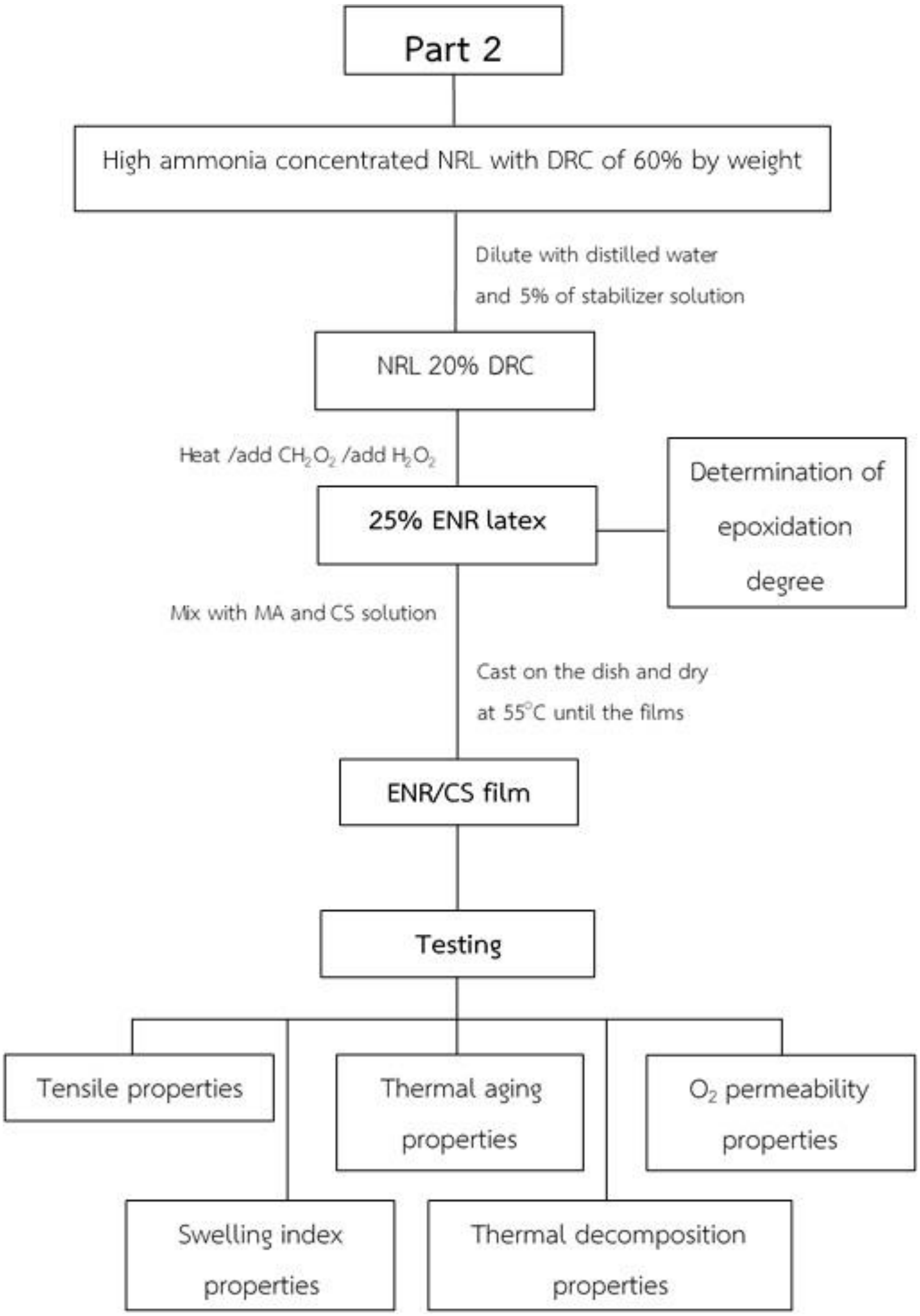


Figure 3.2 The overview procedure of preparation and characterization of ENR/CS film

3.2 Materials and Chemical Agents

Materials and chemical agents used in this research are shown in **Table 3.1**.

Table 3.1 Materials and chemical agents

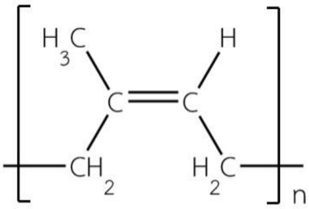
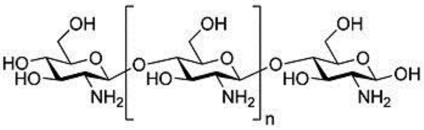
Material/Chemical Agent (Function)	Grade	Manufacture/ Resource
Natural rubber  (matrix)	High ammonia concentrated natural rubber latex	Rubber Research Institute of Thailand
Pre-vulcanized natural rubber latex (matrix)	Medical gloves formula	Rubber Research Institute of Thailand
Chitosan  (matrix)	Deacetylation degree of 85% M_w 500,000 g/mol	Seafresh Industry Public Co., Ltd., Thailand
Sodium hydroxide (NaOH) (pH modifier)	Commercial grade	RCI Labscan Ltd., Thailand

Table 3.1 (cont.)

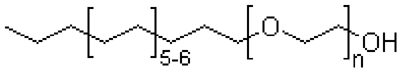
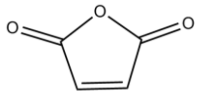
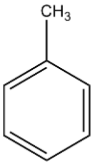
Material/Chemical Agent (Function)	**Grade**	**Manufacture/ Resource**
Alcohols C_{16-18} ethoxylated  (stabilizer)	Imbentin^{TM}AG/168S/180G M_w 1,050 g/mol	Behn Meyer Chemical (T) Co., Ltd., Thailand
Maleic anhydride (MA, $C_4H_2O_3$)  (crosslinking agents)	Commercial grade	QReC Chemical Co.,Ltd., New Zealand
Acetic acid (CH_3COOH) (solvent)	Commercial grade	J.T. Baker-A Division of Mallinckrodt Baker, Inc., USA
Formic acid (HCOOH) (epoxidizing agent)	Commercial grade	Farmitalia Carlo Erba Ltd., Italy
Hydrogen peroxide (H_2O_2) (epoxidizing agent)	Commercial grade	RCL Labscan Ltd., Thailand
Methyl alcohol (CH_3OH) (coagulating agent)	AR grade	QReC Chemical Co.,Ltd., New Zealand
Sodium carbonate (Na_2CO_3) (pH neutralizing agent)	Commercial grade	Merck KGaA, Darmstadt., Germany

Table 3.1 (cont.)

Material/Chemical Agent (Function)	**Grade**	**Manufacture/ Resource**
Deuterated chloroform ($CDCl_3$) (solvent)	Commercial grade	RCL Labscan Ltd., Thailand
Acetone (C_3H_6O) (solvent)	AR grade	QReC Chemical Co.,Ltd., New Zealand
Toluene (C_7H_8)  (solvent)	AR grade	RCL Labscan Ltd., Thailand

3.3 Characterization and Testing

The physical and mechanical properties of the NR/CS film and ENR/CS film were characterized and tested by the following instruments shown in **Table 3.2**.

Table 3.2 List of instruments

Instrument	Model	Manufacture/Location
Hand-held digimatic micrometer	-	Department of Materials Science, Faculty of Science, Chulalongkorn university
Nuclear magnetic resonance spectroscopy (NMR)	BRUKER YX 400	Department of Chemistry, Faculty of Science, Chulalongkorn university
Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR)	NICOLET 6700	Department of Materials Science, Faculty of Science, Chulalongkorn university
Thermogravimetric analyzer (TGA)	TGA/SDTA851^{e}	Department of Materials Science, Faculty of Science, Chulalongkorn university
Universal testing machine	INSTRON-5843	Department of Materials Science, Faculty of Science, Chulalongkorn university
Universal oven	HPC-100	Department of Materials Science, Faculty of Science, Chulalongkorn university
Oxygen permeability tester (OPT)	MOCON OX-TRAN 2/21	Faculty of Engineering, Chulalongkorn University

3.4 Experimental Procedures

3.4.1 Preparation of matrix

3.4.1.1 Preparation of natural rubber latex (NRL) with dry rubber content (DRC) of 40%

High ammonia concentrated NRL with DRC of 60% by weight was diluted with 5% (w/v) of stabilizer in distilled water to get a stabilized homogeneous NRL with DRC of 40%.

3.4.1.2 Preparation of pre-vulcanized natural rubber latex (NRL) with dry rubber content (DRC) of 40%

The formulation of pre-vulcanized NRL used in this study is tabulated in **Table 3.3**. Pre-vulcanized NRL with approximately DRC of 60% by weight was diluted to DRC of 40% with 5% (w/v) of stabilizer in distilled water.

Table 3.3 Formulation of pre-vulcanized NRL

Ingredients	(phr)
60% Natural rubber	100
5% Stabilizer	5
10% Potassium hydroxide	2
10% Teric	0.29
50% Sulfur	1.6
50% ZDEC	0.8
50% ZMBT	0.8
50% Wingstay L	2
50% Zinc oxide	2

3.4.1.3 Preparation of 1% (w/v) chitosan (CS) solution

A CS solution with 1% (w/v) was prepared by dissolving CS flake in a 2% (v/v) acetic acid aqueous solution with vigorously stirring for 24 hours at room temperature and then filtered with a filter paper to remove the undissolved CS.

3.4.1.4 Preparation of 25% epoxidized natural rubber (ENR) latex

High ammonia concentrated NRL with DRC of 60% was first diluted with distilled water to have DRC of 20%. Then the diluted NRL was stabilized by adding 5 parts per hundred dry rubbers (phr) of a non-ionic surfactant (alcohols C_{16-18} ethoxylated). The stabilized NRL was stirred for 1 hour at room temperature to eliminate ammonia and then heated to 40°C. To prepare the NRL with 25% epoxidation (ENR25 latex), 0.3M of 85% (w/w) formic acid was then slowly dropped into the stabilized NRL. The temperature was increased to 50°C prior to the addition of 0.3M of 30% w/w hydrogen peroxide. The reaction was carried out for 20 hours to obtain the desired epoxidation level. To confirm the level of epoxidation, the small amount of ENR latex was precipitated with methanol. The obtained product was washed with water, and with 5% (w/v) sodium carbonate solution, and then with water again. The cleaned product was dried in oven at 60°C and analyzed by ^{1}H-NMR and FT-IR spectroscopy.

3.4.2 Preparation of films

3.4.2.1 Preparation of uncured NR/CS film

The stabilized NRL with DRC of 40% (from *3.4.1.1*) was mixed with 1% (w/v) CS solution (from *3.4.1.3*) at different NR/CS weight ratios of 100/0 to 90/10, 80/20, 70/30, 60/40 and 50/50. The mixtures were stirred for 24 hours to get a homogeneous NR/CS solution. The mixed NR/CS solution was immediately plated on a clean petri dish and allowed to dry in an oven at 55°C for 24 hours. The films with the thickness of 0.5-1.0 mm were obtained.

3.4.2.2 Preparation of cured NR/CS film

The stabilized pre-vulcanized NRL with DRC of 40% (from *3.4.1.2)* was mixed with 1% (w/v) CS solution (from *3.4.1.3*) at different NR/CS ratios of 100/0 to 90/10, 80/20, 70/30, 60/40 and 50/50. The mixtures were stirred for 24 hours to get a homogeneous NR/CS solution. The pre-vulcanized NR/CS solution was then immediately plated on a clean petri dish and allowed to dry in an oven at 55°C for 24 hours. Finally, to obtain the cured NR/CS film, the dried films were further heated at 120°C for 30 min. The cured NR/CS films with the thickness of 0.5-1.0 mm were obtained.

3.4.2.3 Preparation of ENR/CS film

The ENR latex (from *3.4.1.4*) was mixed with the CS solution (from *3.4.1.3*) at different ENR/CS ratios of 100/0 to 90/10, 80/20, 70/30, 60/40 and 50/50. Then 0, 1, 2 and 3 phr of maleic anhydride (MA) used as crosslinking agent was added into the ENR/CS solution. The mixtures were stirred at 60°C for 5 hours to obtain a homogeneous mixed solution and to crosslink matrix. The mixed ENR/CS/MA solution was immediately casted on the clean petri dish and allowed to dry in an oven at 55°C until the films with constant weight were obtained. The ENR/CS films with the thickness of 0.5 - 1.0 mm were obtained.

3.5 Characterization and Testing

3.5.1 Evaluation of dry rubber content (DRC)

The NR latex was weighed and subsequently dried in an oven at 60°C for 48 hours. Film was then reweighed, to determine their volume fraction of the rubber in the latex. The %DRC of concentrated NR latex used in this study was determined by the method described in ASTM D1076-97.

$$\% \text{ DRC} = (W_r \div W_t) \times 100 \qquad \text{... (3.1)}$$

where, W_r = Weight of dried sample (g)

W_t = Weight of NR latex sample (g)

3.5.2 Characterization of chemical structure of ENR

Chemical structure and chain compositions of ENR were characterized by ^{1}H-NMR spectroscopy on a BRUKER YH400 (as shown in **Figure 3.3**) using $CDCl_3$ as a solvent. ATR-FTIR spectra of ENR was recorded on a NICOLET 6700 model spectrometer (as shown in **Figure 3.4**). The spectra were obtained in the wavenumber of 500 to 4000 cm^{-1} by 64 scanning at a spectral resolution of 4 cm^{-1}.

Degree of epoxidation can be determined from ^{1}H-NMR spectra using the following equation [32]:

$$\% \text{ Epoxide content} = 100 \times (A_{2.70} / (A_{5.14} + A_{2.70})) \qquad \text{... (3.2)}$$

where, $A_{2.70}$ = The area under the curve at 2.70 ppm (proton adjacent epoxide unit)

$A_{5.14}$ = The area under the curve at 5.14 ppm (olefins proton)

Figure 3.3 Nuclear magnetic resonance spectrometer (BRUKER YX400)

Figure 3.4 ATR-FTIR spectrometer (NICOLET 6700)

3.5.3 Evaluation of degree of swelling

The degree of swelling or swelling index of the obtained film was studied by immersing sample into toluene (a good solvent for natural rubber). Small pieces of films with rectangular shape were weighed with digital scale, then immersed into toluene for 3 days at the ambient temperature. The weight of swollen samples (W_s) was measured after removing the surface toluene with a filter paper. Then, the swollen samples were dried at the room temperature. The dried samples were weighed again (W_d). The swelling index (SI) was calculated using the following equation:

$$\text{Swelling index (SI)} = ((W_s - W_d) \div W_s) \times 100 \qquad \text{...(3.3)}$$

where, W_s = Weight of swollen samples (g)

W_d = Weight of dried samples (g)

3.5.4 Evaluation of tensile properties

The tensile test was carried out according to ISO 37 method using a universal testing machine (INSTON-5843) as shown in **Figure 3.5**. The film was cut into the dumb-bell shaped sample using a type IV Die as shown in **Figure 3.6**. The modulus at 100% and 300% strain, tensile strength and elongation at break of the sample were determined at a crosshead speed of 500 mm/min. At least five samples were tested and the average value was reported.

Figure 3.5 Universal testing machine (INSTON-5843)

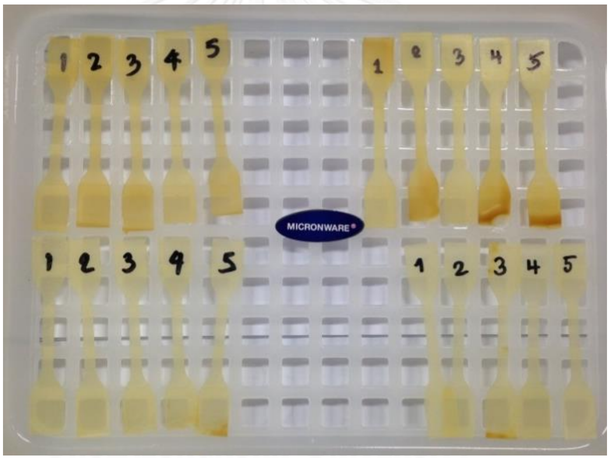


Figure 3.6 Dumb-bell shaped sample according to ISO 37

3.5.5 Evaluation of thermal aging properties

The thermal aging property of sample was studied by determining tensile properties of the sample heated in an oven at 50°C for 7 days and comparing with those of the unaged sample. Then, the aged samples were cooled at ambient temperature for at least 16 hours before tensile testing. The tensile properties of the aged sample were determined using the same condition as the unaged one. At least five samples were tested.

Relative tensile properties were calculated and used as an indicator for thermal aging resistance. Relative tensile properties including relative 100% modulus (relative M100), relative tensile strength (relative TS) and relative percent elongation at break (relative EB) were determined using the following equation:

$$\text{Relative M100} = \text{M100}_a \div \text{M100}_u \quad \text{...(3.4)}$$

where, M100_a = 100% modulus of aged sample (MPa)

M100_u = 100% modulus of unaged sample (MPa)

$$\text{Relative TS} = \text{TS}_a \div \text{TS}_u \quad \text{...(3.5)}$$

where, TS_a = Tensile strength of aged sample (MPa)

TS_u = Tensile strength of unaged sample (MPa)

$$\text{Relative EB} = \text{EB}_a \div \text{EB}_u \quad \text{...(3.6)}$$

where, EB_a = Elongation at break of aged sample (%)

EB_u = Elongation at break of unaged sample (%)

3.5.6 Evaluation of decomposition temperature

The thermal decomposition temperature of the obtained film was evaluated under nitrogen atmosphere using a thermogravimetric analyzer (TGA/SDTA 851e, Mettler Toledo) as shown in **Figure 3.7**. A 10-12 milligram of sample was heated from 50°C to 700°C at a rate of 20°C/min. The onset, endset and differential decomposition temperature were reported.

Figure 3.7 Thermogravimetric analyzer (TGA/SDTA 851e)

3.5.7 Evaluation of oxygen permeability

Oxygen permeability (OP) was measured according to ASTM D 3985 at 23°C, 0% relative humidity using MOCON instrument (OX-TRAN MODEL 2/21) as shown in **Figure 3.8**. Testing was performed at room temperature in a dust free chamber. Oxygen transmission rate (OTR) was obtained in units of ccO_2/m^2.day.atm. Multiplying these values by film thickness provided oxygen diffusion coefficients. For each OP value, two samples were tested.

Figure 3.8 Oxygen permeability tester (MOCON OX-TRAN)

CHAPTER IV

RESULTS AND DISCUSSION

The films of uncured and cured natural rubber (NR) and epoxidized natural rubber (ENR) blended with chitosan (CS) were prepared here using a solution casting method. The characteristic, physical and thermal properties and oxygen permeability of the obtained uncured and cured NR/CS and ENR/CS were examined. The results and discussion were divided into two parts based on the type of NR. The first part was focused on the properties of the uncured and sulfur cured NR/CS films, while the second part paid attention to the properties of the ENR/CS films when adding maleic anhydride (MA). In both parts, how the presence of CS and the CS content effected on the characteristic and properties of the films was discussed.

4.1 Physical and thermal characterisitcs of NR/CS films

4.1.1 Characteristic of NR/CS film

The images of the uncured and cured NR/CS films are shown in **Figures 4.1** and **4.2**, respectively. The films were yellowish.

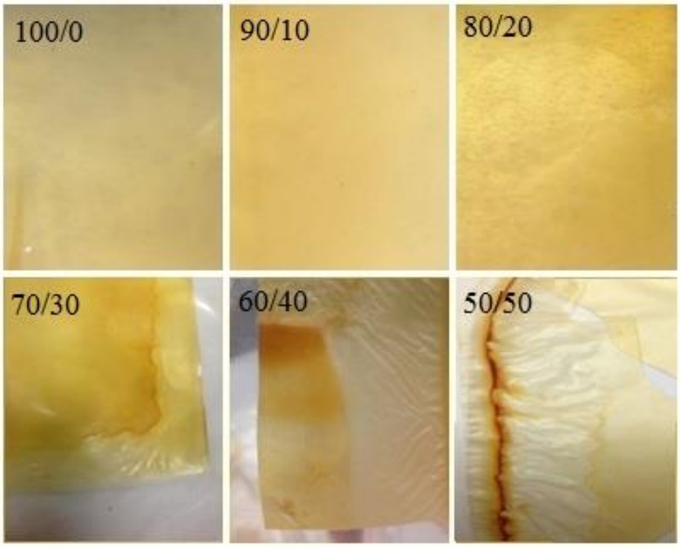


Figure 4.1 The images of the uncured NR/CS films at different NR/CS ratios

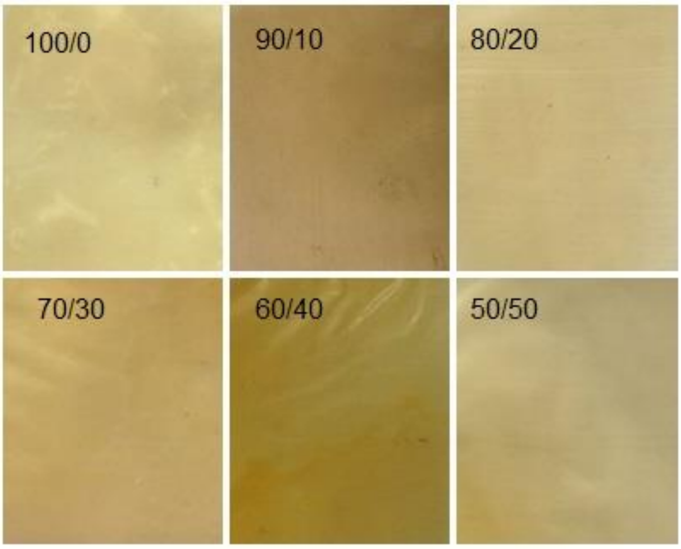


Figure 4.2 The images of the cured NR/CS films at different NR/CS ratios

For uncured NR/CS films, the pure NR film was highly flexible and tacky. Once CS which is rigid and brittle was introduced into the NR films, the obtained uncured NR/CS films became less flexible and more rigid. The phase separation was initially observed at the NR/CS ratio of 70/30 (as seen in **Figure 4.1**) and became more severe at the higher CS content. The darker area was contributed to the rubber phase. The films at the NR/CS ratio of 50/50 could break inside the CS region during peeling off from the mold.

To prepare the cured NR/CS films, the pre-vulcanized NR latex comprising of sulfur as a crosslinking agent was used. The cured NR/CS films were tougher and less tackier than the uncured ones due to the presence of the crosslinking network. Unlike the uncured NR/CS films, no macroscopic phase separation was observed. This might be attributed to the formation of semi-interpenetrating polymer networks (semi-IPNs). The NR latex was mixed with the CS solution, then crosslinked. The CS chains may be trapped in the NR network, thus inhibiting macroscopic phase separation.

4.1.2 Swelling resistance

NR is non-polar material. Therefore, NR has very poor swelling resistance in all non-polar solvents. Various methods can be carried out to enhance the solvent resistance of NR. Besides the formation of the NR crosslinking network, one of the most promising methods is the blending NR with another polymer which has higher solvent resistance. As known, CS is a natural polymer which has high solvent resistant toward both non polar and polar solvent. It was expected that the addition of CS into NR will lead to the increased solvent resistance of the NR.

The solvent resistance of uncured and sulfur cured NR/CS film comprising of CS at different contents are shown in **Figure 4.3**. The uncured pure NR film completely dissolved in toluene. However, once the CS was introduced into the uncured NR film, the complete dissolving of film was no longer observed. Moreover, the swelling index inversely proportional to the swelling resistance gradually decreased with the increase in CS content. The reduction of solvent uptake was not only due to the reduction of NR content but also the polar nature of CS and the additional interaction between NR and CS which inhibited the transmission of solvent molecules [9]. The significant decrease in swelling index was observed when increasing CS content from 10 to 20% by weight. However, at higher CS contents the swelling index gradually decreased. The formation of the infinite NR crosslinking networks significantly increased swelling resistance. For the cured NR/CS, the swelling index gradually decreased with increasing in CS loading.

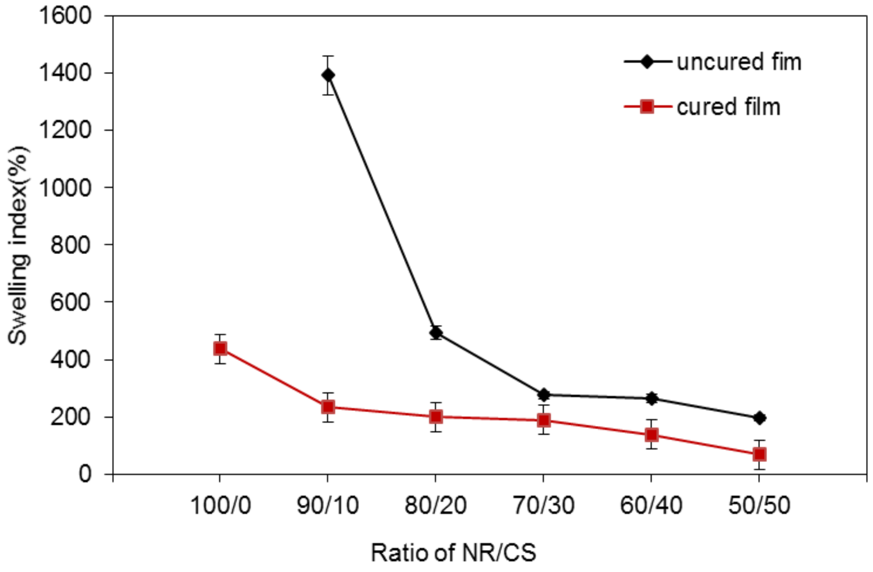


Figure 4.3 Swelling indices of the uncured and cured NR/CS films at different NR/CS ratios

4.1.3 Tensile properties of NR/CS film

Figures 4.4 and **4.5** show the effect of CS content on modulus at 100% and 300% strain (M100, M300) of the uncured and cured NR/CS film.

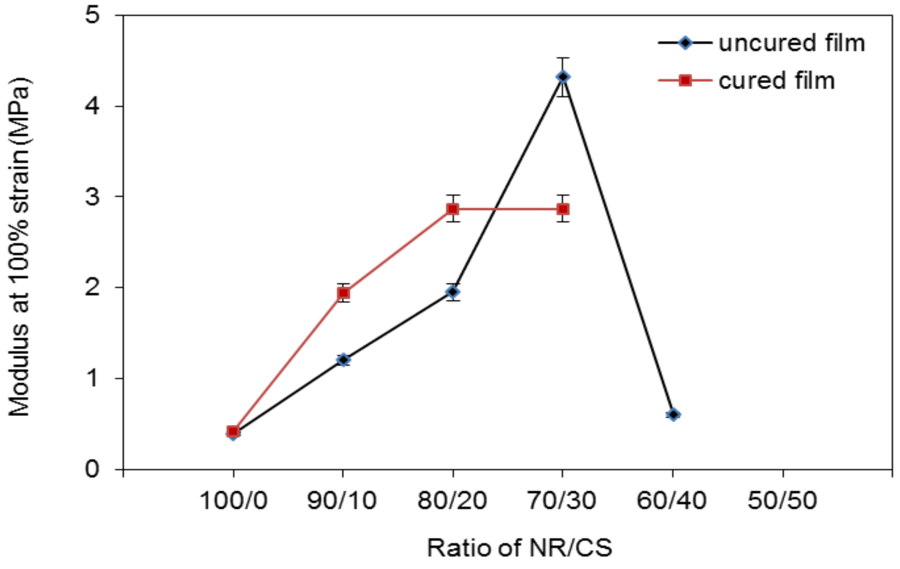


Figure 4.4 Modulus at 100% strain of the uncured and cured NR/CS films at different NR/CS ratios

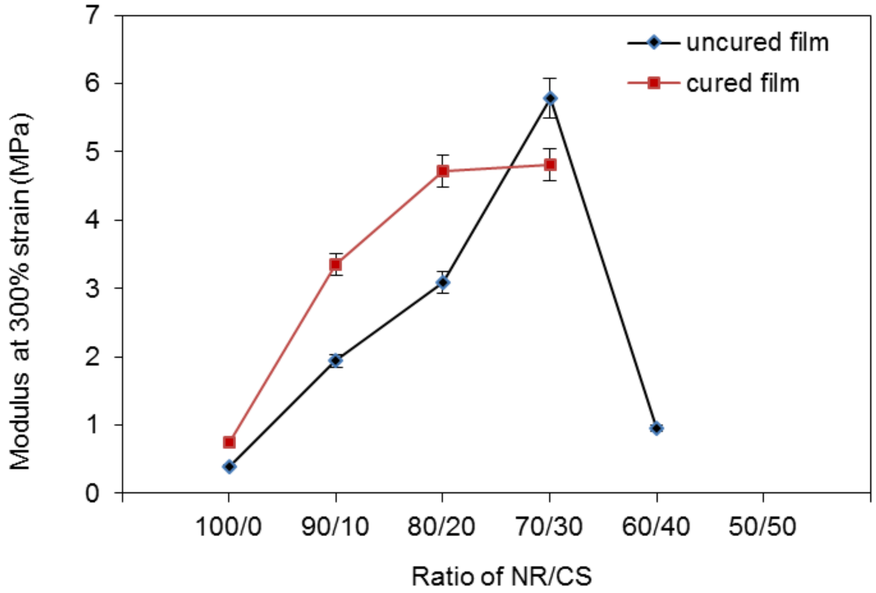


Figure 4.5 Modulus at 300% strain of the uncured and cured NR/CS films at different NR/CS ratios

The result showed that for both uncured and cured films the M100 and M300 passed through maximum with increasing in CS contents. The maximum M100 and M300 of the uncured and cured NR/CS films were observed at the NR/CS ratio of 70/30. The initial increase in modulus was due to the incorporation of rigid CS into the soft and flexible NR matrix and interaction between NR and CS chain. However, at higher CS loading, the brittleness of CS played a more important role, thus reducing the stiffness of the film. At 100% strain, both uncured and cured pure NR showed comparable modulus. This was because at 100% strain the degree of chain extension was quite low. The NR chain between two linkages of the cured NR film still was not fully stretched out. Therefore, no influence of vulcanization on modulus at 100% strain was observed. At 300% strain, the cured pure NR film had higher modulus. This was because the extension to 300% strain of the cured pure NR film was constrained by the presence of the crosslinking points, thus resulting the cured sample in having higher M300 than the uncured one.

The tensile strength and elongation at break of the uncured and cured NR/CS films with different NR/CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 are shown in **Figures 4.6** and **4.7**.

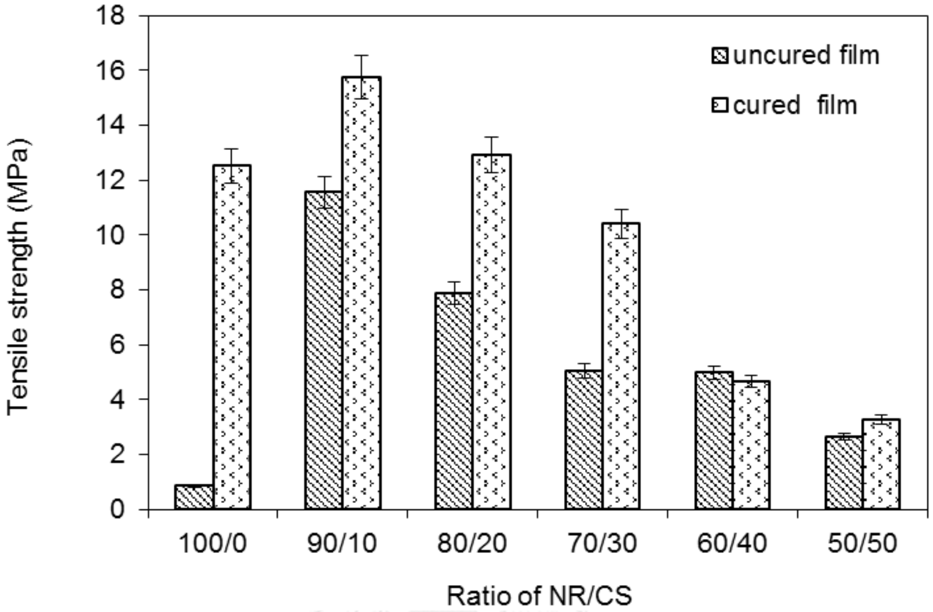


Figure 4.6 Tensile strength of the uncured and cured NR/CS films at different NR/CS ratios

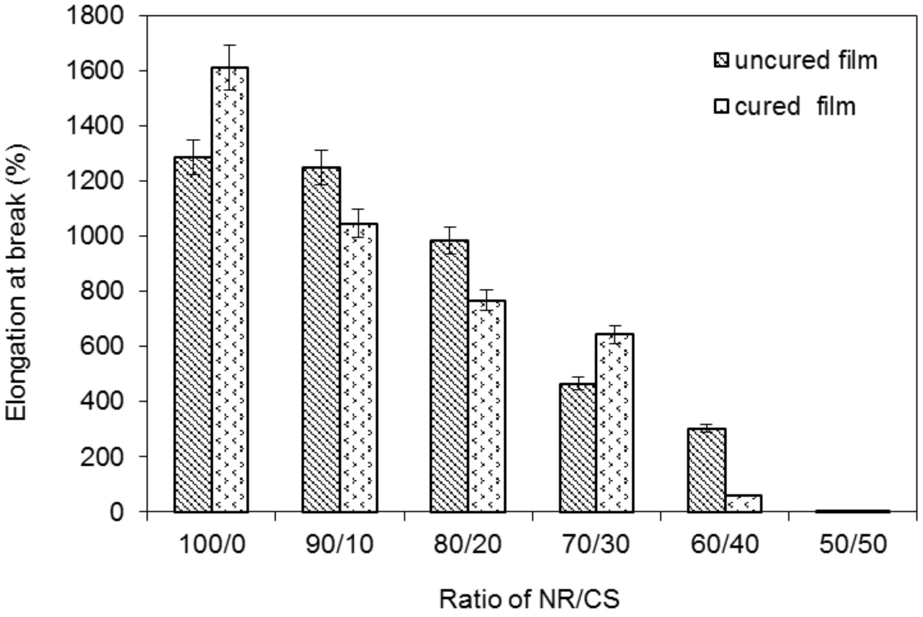


Figure 4.7 Elongation at break of the uncured and cured NR/CS films at different NR/CS ratios

For the uncured film, the pure NR film showed lowest tensile strength but highest elongation at break. The tremendously low tensile strength might be due to the flow of rubber chain under the tension load. By replacing 10 parts of the uncured NR with CS, the tensile strength of the film was significantly enhanced, while the slight decrease of elongation at break was observed. The increment of tensile strength was about 1258%. At higher CS content, it was found that the tensile strength of the uncured films gradually dropped with the increase in the CS content. However, the uncured NR/CS films at the NR/CS ratios of 80/20, 70/30, 60/40 and 50/50 still had tensile strength higher than the uncured pure NR film. The presence of CS caused all films broke at lower elongation. The significant drop in elongation at break was observed when the CS content was 20 parts or higher. The film at the NR/CS ratio of 50/50 behaved like the brittle film, thus giving very low elongation at break.

The cured pure NR film had a much higher tensile strength than the uncured one. In contrast to the uncured film, replacing 10 parts of the cured NR with CS now only slightly increased in the tensile strength of the film. The increment of tensile strength was 26%. Further increasing in CS loading reduced the tensile strength of the film. The cured NR/CS films at the NR/CS ratio of 80/20 had tensile strength comparable to that of the cured pure NR film. However, the tensile strength of the cured NR/CS films at the NR/CS ratios of 70/30, 60/40 and 50/50 was lower than that of the cured pure NR film. By comparing the result here with the literature, it was found the NR/CS films cured with sulfur in this study gave higher tensile strength than the ones cured with peroxide from the literature [42]. Both the relative weakness of the sulfidic linkages, which can break more readily under strain, and the ability to reform the sulfide bond, render the sulfur cured rubber with a higher mechanical strength [48].

When comparing tensile strength of the uncured and cured films, it was found that the cured films at the NR/CS ratios of 90/10, 80/20 and 70/30 gave higher tensile strength than the uncured ones. However, at the NR/CS ratios of 60/40 and 50/50, both uncured and cured films showed comparable tensile strength.

In general, CS is more brittle and rigid than NR. When film contained NR at higher level than CS, NR played a major role on the strength. As seen earlier, the cured pure NR film gave much higher tensile strength than the uncured one. Therefore, for film consisted of NR at ratio much higher than CS, the cured film showed higher tensile strength than the uncured one. Once NR content decreased, the influence of cured NR on strength became invisible. Thus, no matter NR was cured or not, the tensile strength of both uncured and cured film became comparable.

4.1.4 Thermal aging resistance of NR/CS film

Tensile properties of aged samples at different NR/CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 heated at 55^{o}C for 7 days were compared with those of unaged samples here. Due to the presence of double bond in the main chain, natural rubber is prone to degrade under thermal oxidative aging, causing chain scission. Consequently, the aged rubber shows lower mechanical properties than the unaged ones. The decrease in modulus, tensile strength and elongation at break of the uncured NR/CS film due to thermal aging are seen in **Figures 4.8, 4.9, 4.12, 4.14**, respectively. The uncured films at the NR/CS ratios of 70/30, 60/40 and 50/50 broke at strain lower than 100%. For the cured NR/CS films, however, the different behavior was observed. **Figures 4.10** and **4.11** showed that the modulus at 100% and 300% strain of the cured NR/CS films after aging were nearly comparable with those before aging. Although the rubber chain scission still took place during thermal aging, the post thermal curing may also coincidently occur. In the case of sulfur vulcanization, the post thermal curing occurs via desulfurization of polysulfidic linkages, causing the formation of shorter linkages and the formation of new linkages also. Hence, this leads to the rubber networks with higher crosslinking density. The rubber chain scission results in the pronounced decrease in modulus (as seen from the uncured NR/CS film in **Figures 4.8** and **4.9**) whereas the desulfurization causes the increase in modulus. By combining both effects, this may be a reason why the modulus which is the resistance to change the shape due to the external force of the cured NR/CS films did not change much as seen from the relative modulus which was close to 1 in **Figures 4.10** and **4.11**.

Although the difference in modulus of the cured NR/CS films before and after aging was not observed, **Figures 4.13** and **4.15** showed that both tensile strength and elongation at break of the cured NR/CS films increased after aging.

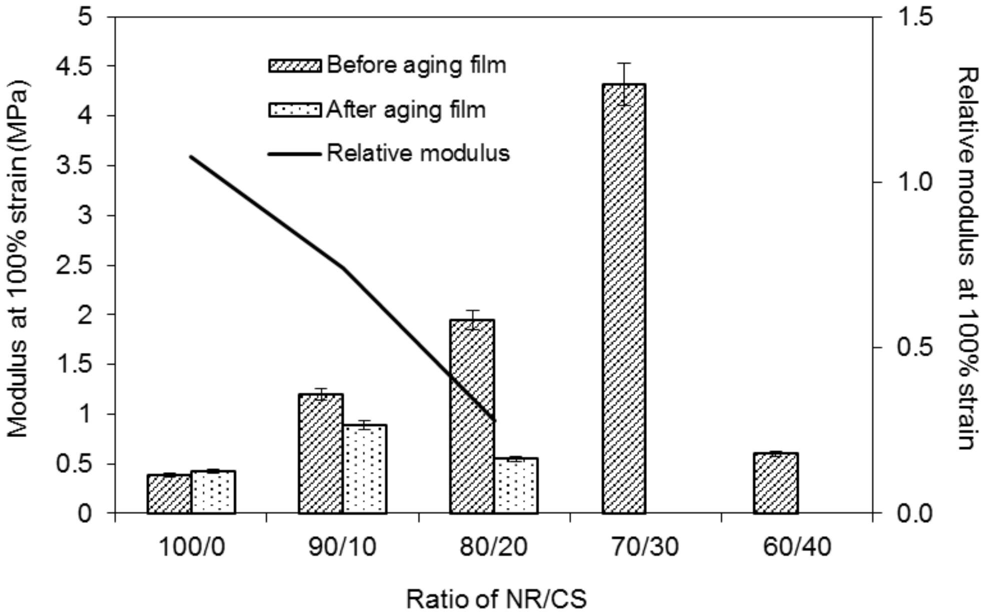


Figure 4.8 Modulus and relative modulus at 100% strain of the uncured NR/CS films at different NR/CS ratios before and after thermal aging

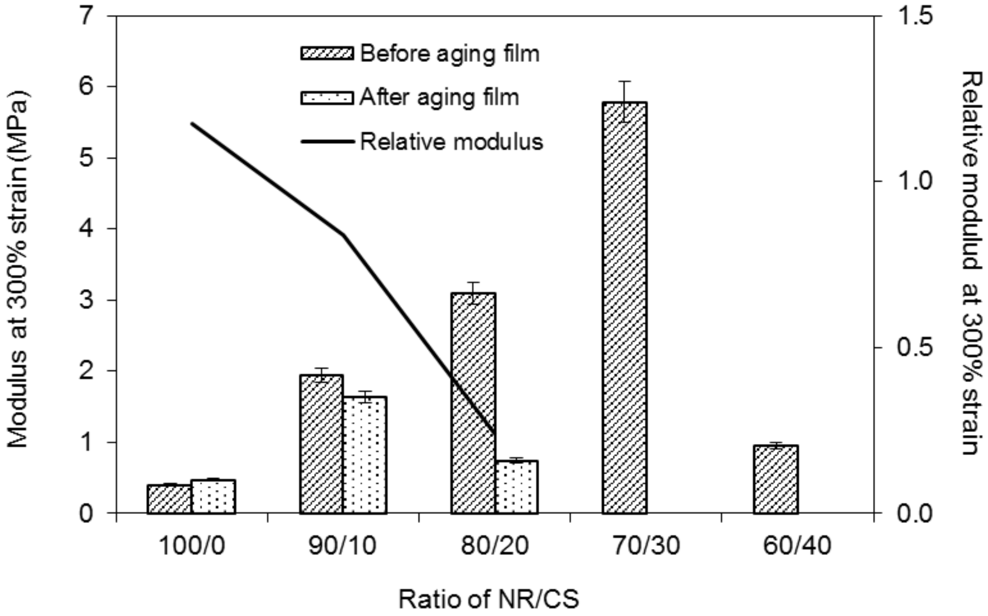


Figure 4.9 Modulus and relative modulus at 300% strain of the uncured NR/CS films at different NR/CS ratios before and after thermal aging

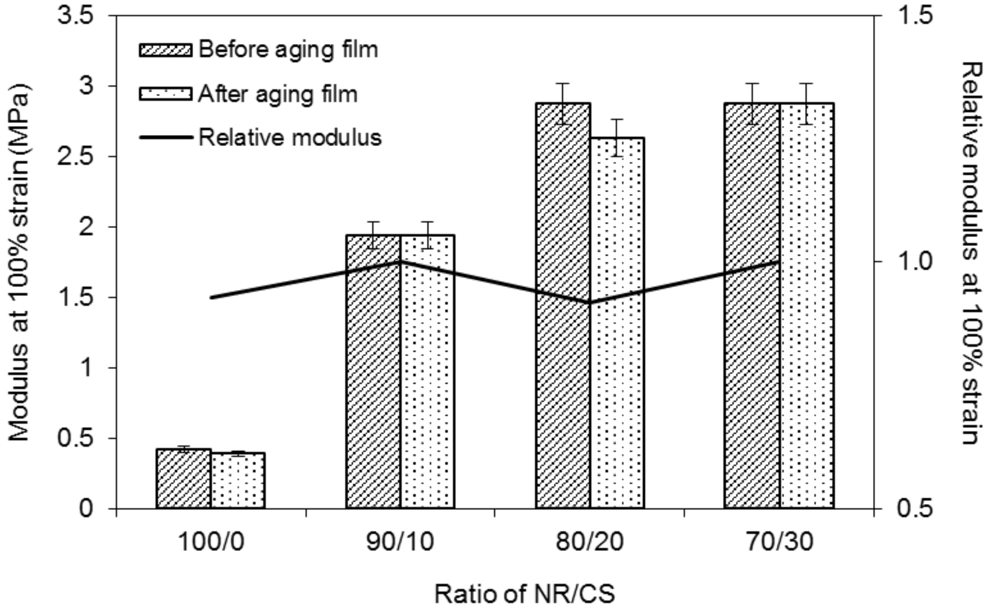


Figure 4.10 Modulus and relative modulus at 100% strain of the cured NR/CS films at different NR/CS ratios before and after thermal aging

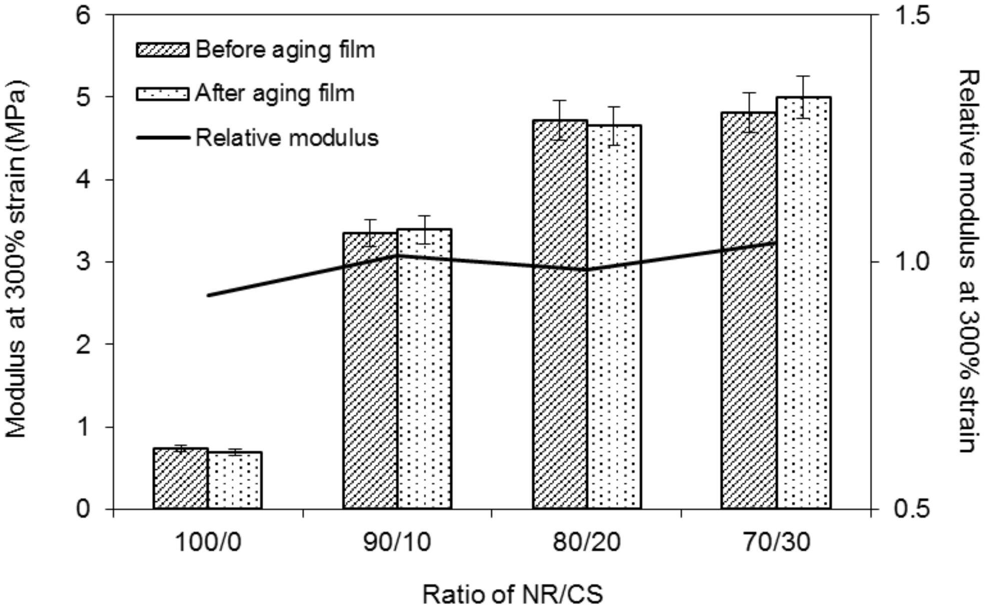


Figure 4.11 Modulus and relative modulus at 300% strain of the cured NR/CS films at different NR/CS ratios before and after thermal aging

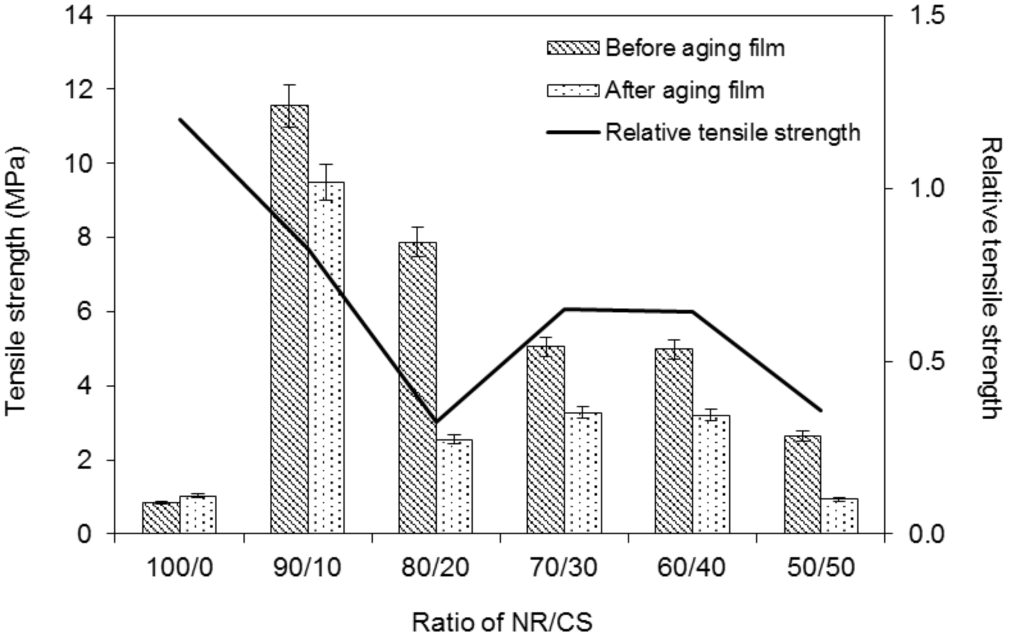


Figure 4.12 Tensile strength and relative tensile strength of the uncured NR/CS films at different NR/CS ratios before and after thermal aging

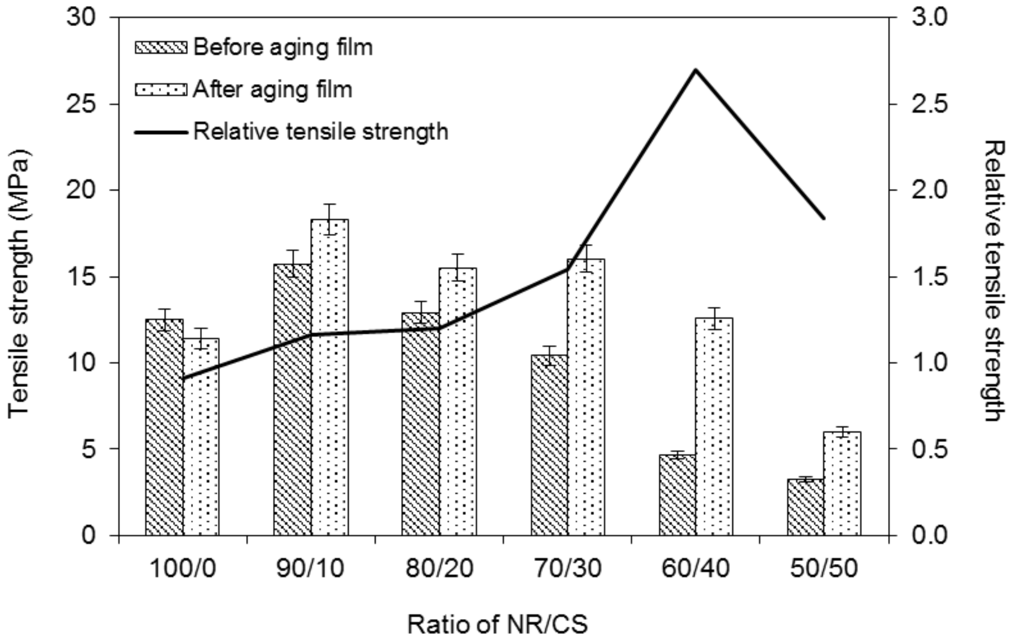


Figure 4.13 Tensile strength and relative tensile strength of the cured NR/CS films at different NR/CS ratios before and after thermal aging

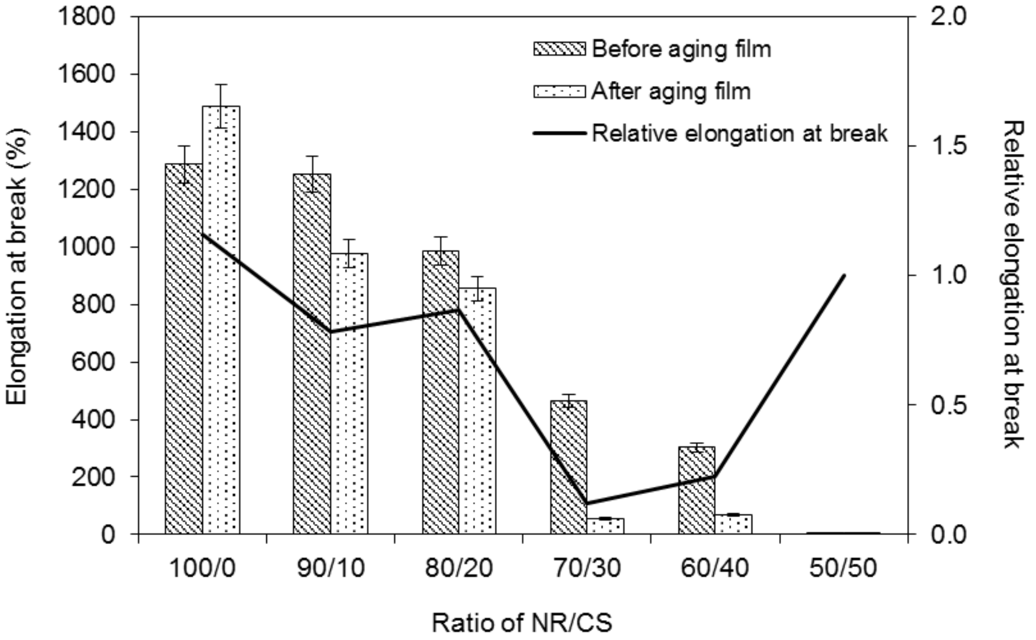


Figure 4.14 Elongation at break and relative elongation at break of the uncured NR/CS films at different NR/CS ratios before and after thermal aging

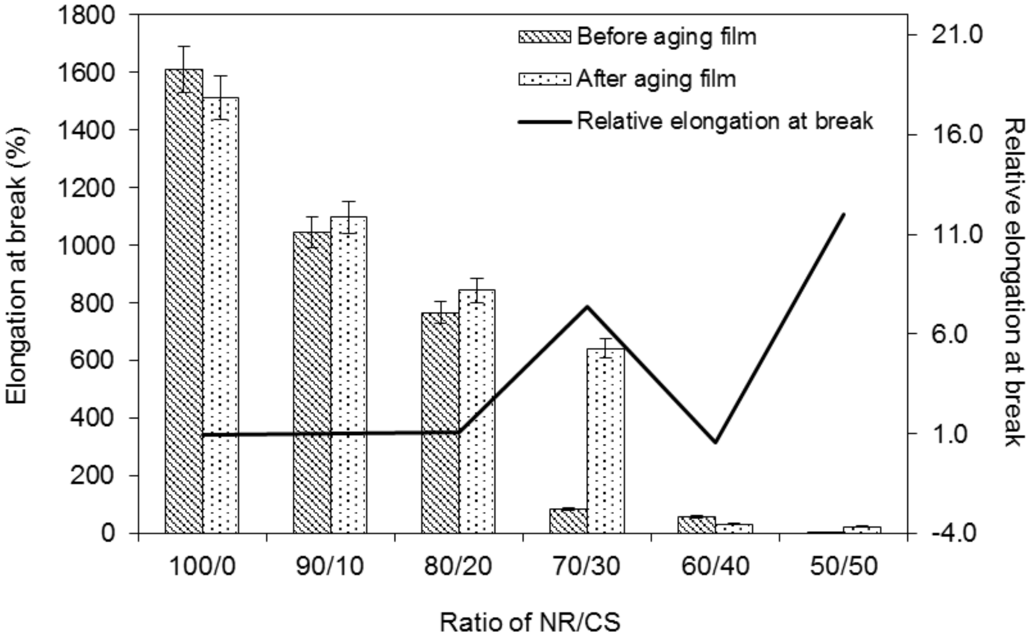


Figure 4.15 Elongation at break and relative elongation at break of the cured NR/CS films at different NR/CS ratios before and after thermal aging

4.1.5 Thermal decomposition properties of NR/CS film

Figures 4.16 and **4.17** show the TGA and DTA thermograms of the uncured and cured NR/CS films at different NR/CS ratios.

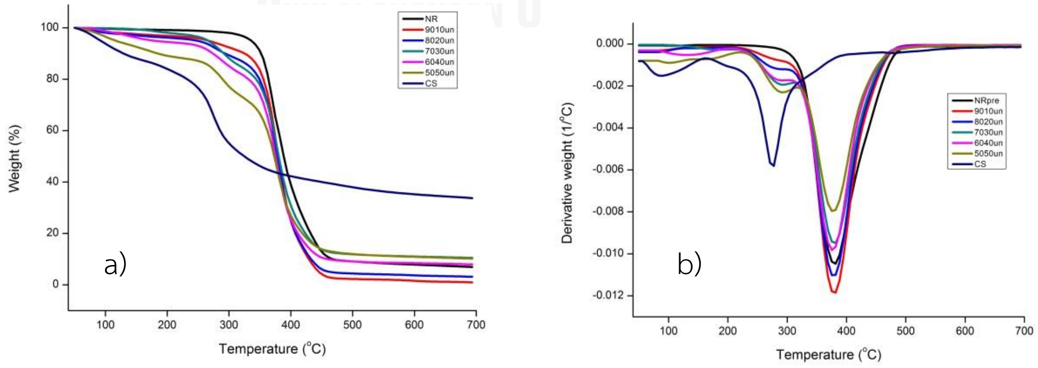


Figure 4.16 a) TGA and b) DTA thermograms of the uncured NR/CS films at different NR/CS ratios

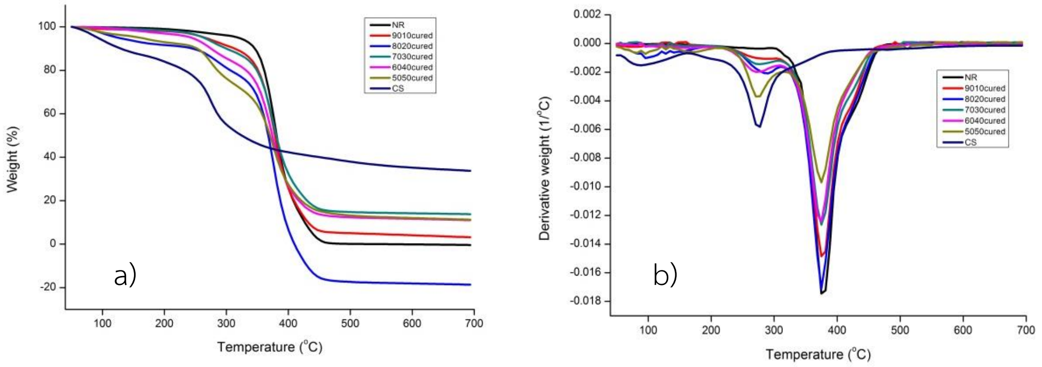


Figure 4.17 a) TGA and b) DTA thermograms of the cured NR/CS films at different NR/CS ratios

From above figures, the onset, endset and differential decomposition temperature of the uncured and cured NR/CS films at different NR/CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 0/100 are given in **Tables 4.1** and **4.2**, respectively. The result showed that the pure CS and both uncured and cured pure NR showed a single decomposition peak at 275.44, 377.56 and 380.15°C, respectively. The decomposition temperature (**Figures 4.16** and **4.17**) of the pure CS, the uncured and cured pure NR was a range of 250.73-324.54°C, 351.99-406.74°C and 328.07-411.03°C, respectively. Although the cured pure NR began to decompose at lower temperature than the uncured pure NR, its differential and endset decomposition temperatures was only slightly different from those of the uncured pure NR. For cured pure NR, the shift of onset decomposition temperature to lower temperature may be due to the decomposition of chemical agents in the prevulcanized NRL.

For both uncured and cured NR/CS films, two decomposition steps were observed. The onset decomposition temperatures at lower and higher temperature were corresponding to the initial degradation of CS and NR, respectively. Although the onset decomposition temperatures of the CS in both uncured and cured NR/CS films seemed to appear at slightly higher temperature than that of the pure CS, their corresponding differential decomposition temperature were almost similar to that of the pure CS. The presence of another phase which is NR here may delay the initial thermal decomposition of the CS phase, thus shifting the onset of decomposition to higher temperature. For both uncured and cured NR/CS films, the onset decomposition temperature of NR in the NR/CS films also shifted to higher temperature than that of the pure NR, while no significant difference in differential decomposition temperature of NR in the NR/CS film and in the pure NR film was observed. The shift of onset decomposition temperature of NR in the NR/CS film to higher temperature than that of the pure NR may be also due to the presence of second phase.

Although for both uncured and cured NR/CS films, the presence of CS shifted the onset decomposition of NR phase to higher temperature, the increase in CS loading from 10% by weight to higher loading did not change the thermal decomposition behavior of the NR phase much.

Table 4.1 Thermal decomposition temperatures of the uncured and cured NR/CS films

NR/CS ratio	Onset temperature of mass loss (°C)		Endset temperature of mass loss (°C)	Peak temperature from DTA curve (°C)	
	1st peak	2nd peak		1st peak	2nd peak
100/0	351.99		406.74	377.56	
90/10	264.26	354.31	407.32	271.79	379.59
80/20	269.80	356.15	406.81	277.56	377.56
70/30	267.95	356.15	409.59	279.49	379.59
60/40	252.92	354.31	405.20	281.38	373.78
50/50	264.26	356.15	407.40	289.08	377.56
0/100	250.73		324.54	275.44	

Table 4.2 Thermal decomposition temperatures of the cured NR/CS films at different NR/CS ratios

NR/CS ratio	Onset temperature of mass loss (°C)		Endset temperature of mass loss (°C)	Peak temperature from DTA curve (°C)	
	1st peak	2nd peak		1st peak	2nd peak
100/0	328.07		411.03	380.15	
90/10	226.68	326.09	406.82	275.44	377.23
80/20	262.28	333.61	407.65	285.08	375.83
70/30	262.28	346.79	409.30	278.61	375.83
60/40	254.77	331.76	405.02	275.44	374.44
50/50	258.59	339.28	410.72	273.79	373.75
0/100	250.73		324.54	275.44	

4.1.6 Oxygen permeability (OP) of NR/CS films

The OP values of the uncured and cured films at the NR/CS ratios of 100/0, 80/20 and 0/100 are shown in **Figure 4.18**. It was found that the uncured pure NR film had an OP of 4018 cc / (m^2 - day) which was higher than the pure CS film having an OP of 2615 cc / (m^2 - day). Due to NR has the glass transition temperature much lower than CS [49], thus allowing the oxygen pass through the film much easier. However, once introducing 20% by weight of CS into the NR film, the uncured NR/CS film had an OP higher than both pure NR and CS. The tremendously increased OP in the uncured NR/CS film may be due to the increase in free volume between boundary of two heterogeneous phase. The cured pure NR had an OP of 28 cc / (m^2 - day) which is much lower than the uncured pure NR. The formation of crosslinking between rubber chains decreased the chain flexibility [50], thus being more difficult for O_2 to transport through. Consequently, the cured pure NR and cured NR/CS film had lower OP than the uncured pure NR and uncured NR/CS film, respectively. Similar to the uncured NR/CS film, the cured NR/CS film had much higher OP than the cure pure NR and pure CS.

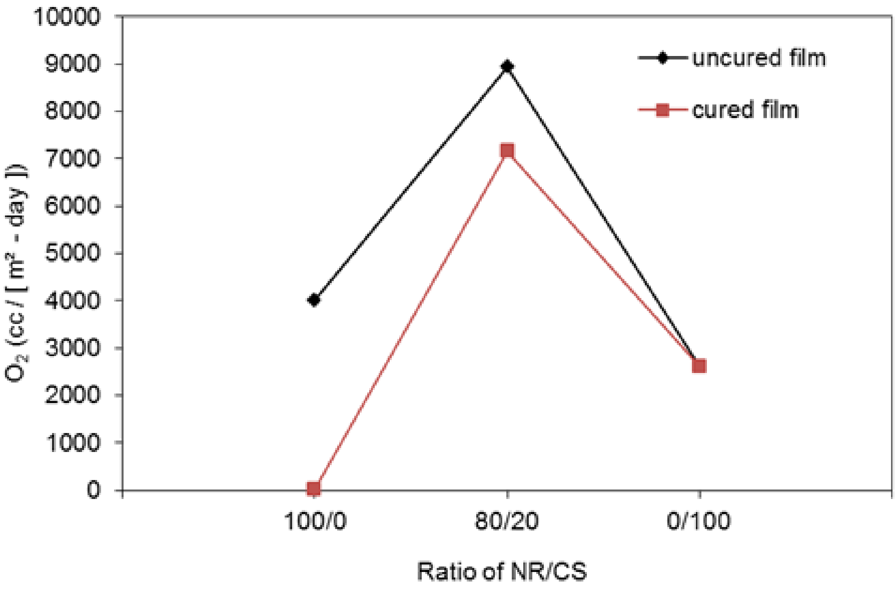


Figure 4.18 Oxygen transmission rate of the uncured and cured NR/CS films

4.2 Physical and thermal characterisitics of ENR/CS films

4.2.1 Characterization of chemical structures and degree of epoxidation of ENR

Natural rubber latex was modified by an in-situ epoxidation reaction using a formic acid and hydrogen peroxide. Comparison between the FT-IR spectrum of the obtained ENR and that of the virgin NR is shown in **Figure 4.19**. The characteristic peaks referring to the NR structure and epoxy groups are tabulated in **Table 4.3**.

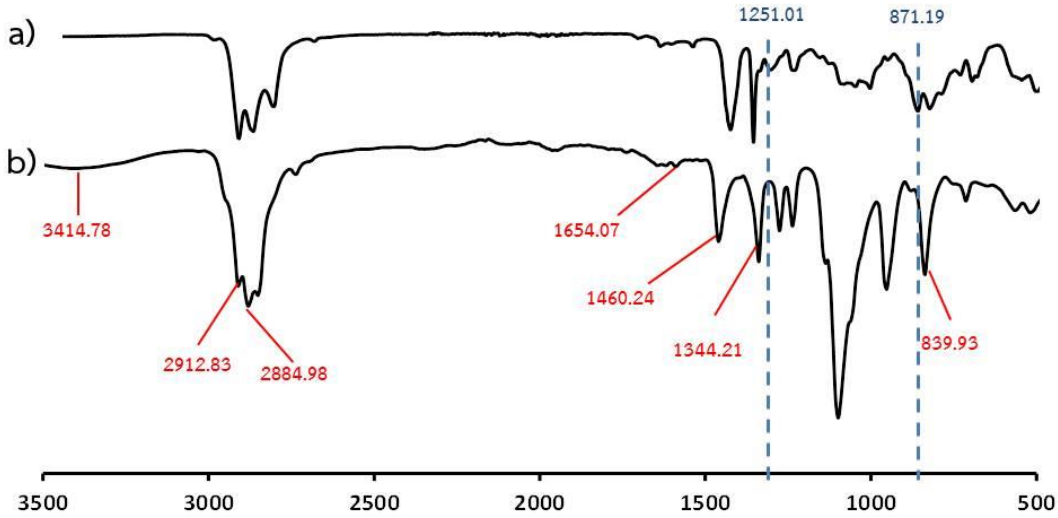
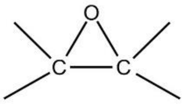
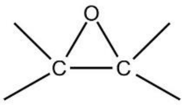


Figure 4.19 FT-IR spectra of a) the obtained ENR b) virgin NR

Table 4.3 The assignments of FT-IR spectrum of NR structure and epoxy groups

FT-IR spectrum of NR		
Wavenumber (cm^{-1})		Approximate description of vibrational mode
Reference*	Observed	
836	839	δ (=C-H)$_{op}$ of 1,4-PI
1385-1370	1344	δ_s(CH$_3$) of 1,4-PI
1470-1435	1460	δ of CH$_3$, CH$_2$
1660	1654	ν(C=C) of cis-1,4
1740	1737	ν (C=O)
2853	2856	νs(CH$_3$) of cis-1,4
2929	2912	νas(CH$_3$) of cis-1,4
2969	-	νas(CH$_3$) of trans-1,4

FT-IR spectrum of ENR		
Wavenumber (cm^{-1})		Approximate description of vibrational mode
Reference*	Observed	
870	871	ν of (C=O) 
1255	1251	ν (C-C) of 

*Reference [30]

The presence of absorbances at 1251 cm^{-1} and 871 cm^{-1} associated with the epoxide groups confirmed the formation of ENR. The appearance of the peak at 1251 cm^{-1} is due to the stretching and contracting in phase of the epoxy ring bonds. The peak at 871 cm^{-1} is due to the C-C stretching during contraction of the C-O bond.

Figure 4.20 shows the ^{1}H-NMR spectra of the obtained ENR. **Table 4.4** shows the assignments of the resonance peaks.

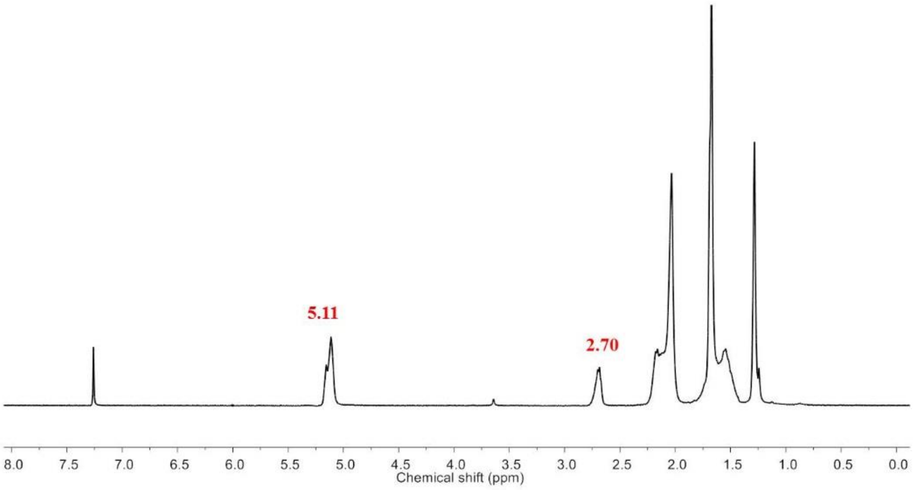
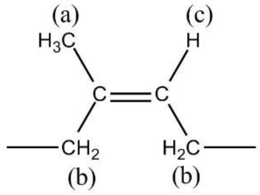
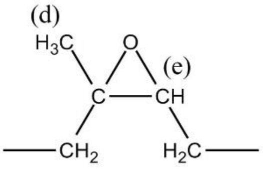


Figure 4.20 ^{1}H-NMR spectra of the obtained ENR

Table 4.4 The assignment of ^{1}H-NMR resonance of the obtained ENR

Structure	^{1}H-NMR (ppm)	
	Reference*	Observed
	c = 5.11	c = 5.11
	e = 2.68	e = 2.70

*Reference [32]

The peak at 5.11 ppm is attributed to olefinic protons of the 1,4-isoprene units. This peak was observed from both the obtained ENR and virgin NR sample. After epoxidation, the obtained ENR shows a new peak at 2.70 ppm attributed to the methine protons attached to oxirane ring. The formation of a new peak at 2.70 ppm confirmed that the NR was epoxidized.

Degree of epoxidation of the obtained ENR was quantitatively calculated from the ^{1}H-NMR spectra using equation 3.2 [32]. The result shows that the 22 mol% of isoprene unit of virgin NR was epoxidized.

4.2.2 Characteristics of the ENR/CS films

4.2.2.1 The formation of film without maleic anhydride

The epoxide ring was introduced to the NR chain in order to increase the polarity of NR. It was expected that the compatibility between ENR and CS will increase, thus enhancing the mechanical properties of the ENR/CS film.

Figure 4.21 shows the images of the ENR/CS film at the ratio of 100/0, 90/10 and 80/20. It was observed that the films at above ratios had dark brown color and were very sticky. It was impossible to remove the film from a casting mold without tearing.

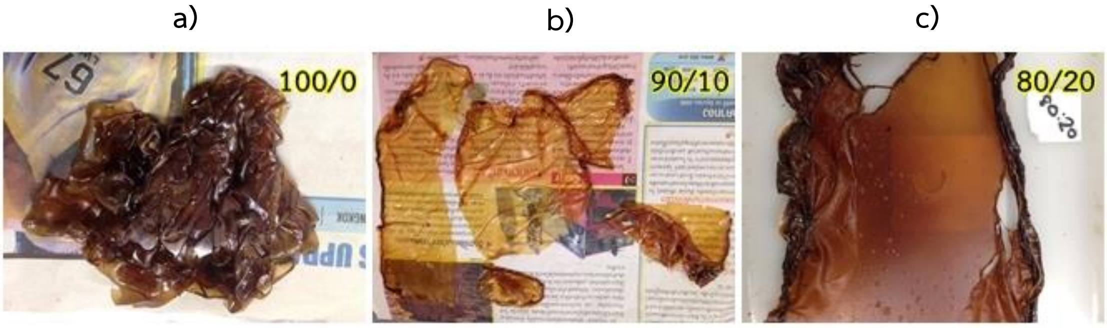


Figure 4.21 The images of the film at the ENR/CS ratio of a) 100/0 b) 90/10 c) 80/20

4.2.2.2 The formation of film with maleic anhydride

Even it was expected that the ENR will be blended very well with the CS due to the smaller difference in the polarity, the ENR/CS film cannot be formed. Moreover, the pure ENR also cannot form film here. Both pure ENR and ENR/CS compounds were very sticky. One reason might be due to the severe degradation of polymer during drying. However, it was found that once maleic anhydride (MA) was introduced into the ENR latex and ENR/CS mixture, the pure ENR and ENR/CS films can be obtained, respectively. Besides sulfur and peroxide, due to the existing of reactive oxirane, ENR may alternatively be crosslinked via ring opening using difunctional molecules such as amine compounds [*], or dicarboxylic acid [*]. From our previous study, it was found that blending ENR with MA led to the formation of compound that can no longer dissolve in the solvent. The rheology study also showed that the torque needed to oscilliate the die fully filled up with the heated ENR/MA compound gradually increased as a function of time. The increase of torque can be implied that the crosslinking reaction took place. Therefore, the reason that the pure ENR and ENR/CS film can be formed when adding MA was because of the formation of crosslinking network enhancing the thermal stability and reducing thermal chain scission. Furthermore, it was reported [38] that CS can react with MA as shown in **Figure 4.22.**

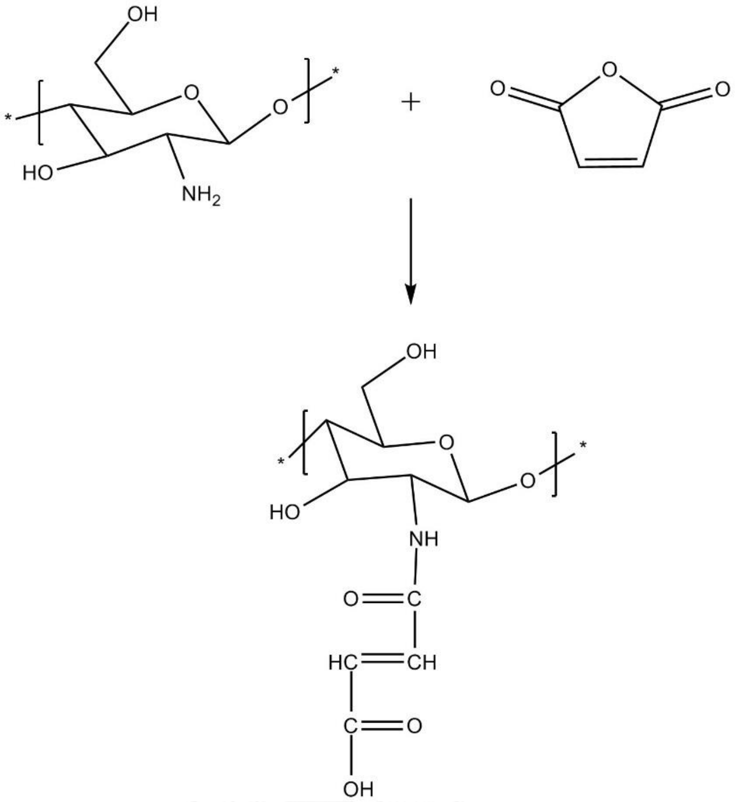


Figure 4.22 The proposed reaction between CS and MA [38]

By adding suitable amount of MA into the ENR/CS blend, it was found that the ENR/CS film without phase separation can be formed. The films had lighter color and were very smooth. Besides crosslinking ENR and reacting with CS, it was also proposed here that MA may couple ENR and CS chain together as shown in **Figure 4.23**.

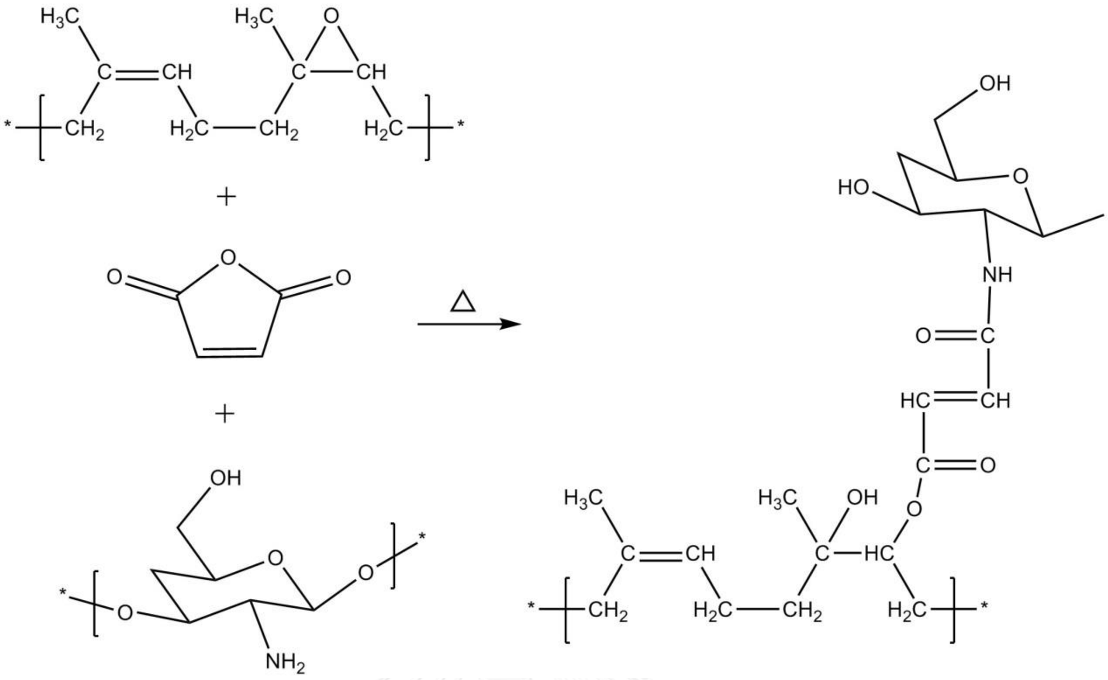


Figure 4.23 Proposed coupling mechanism between ENR and CS chain by MA

4.2.2.3 The effect of the MA content and ENR/CS ratio on the formation of the ENR/CS films

From experiment, it was found that the formation of ENR/CS films depended strongly on both MA content and ENR/CS ratio. The suitable amount of MA varied with the ENR/CS ratio as tabulated in **Table 4.5**. A check mark indicates that the film can be formed, while the cross mark means that the film cannot be formed.

Table 4.5 The suitable amount of MA for the formation of the ENR/CS film at different ENR/CS ratios

ENR/CS	MA 1 phr	MA 2 phr	MA 3 phr
100/0	✓	✗	✗
90/10	✓	✓	✓
80/20	✓	✓	✓
70/30	✗	✓	✓
60/40	✗	✗	✓
50/50	✗	✗	✓

For the pure ENR film, it was found the suitable MA content was 1 phr. At higher MA level, the pure ENR film became brittle and easy to break. For the film at the ENR/CS ratio of 90/10 and 80/20, by increasing in MA level from 1 to 3 phr the film still can be formed. For the film at the ENR/CS ratio of 70/30, 1 phr of MA was not enough. The film could only be formed when MA level was 2 or 3 phr. Finally, the suitable MA content for forming the film at the ENR/CS ratio of 60/40 and 50/50 was 3 phr.

Figure 4.24 shows the feature of the films at the ENR/CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 when adding MA at 1 phr.

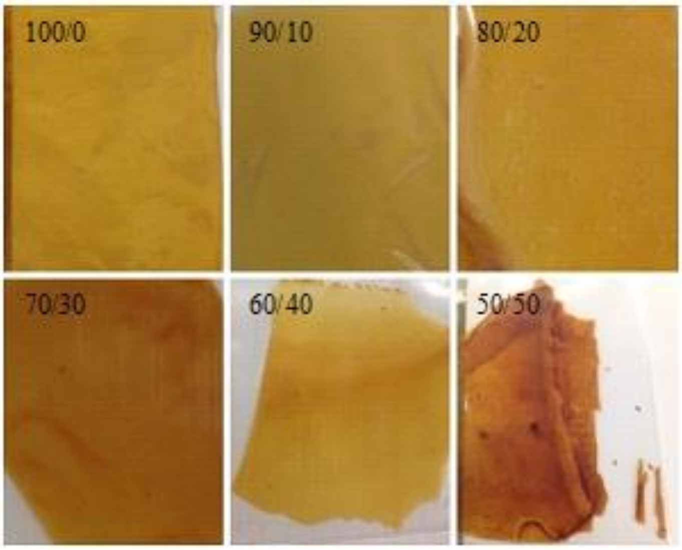


Figure 4.24 The images of the ENR/CS films at different ENR/CS ratios with MA of 1 phr

The pure ENR film with 1 phr of MA was medium yellow, sticky and elastic. At 1 phr of MA, only films at the ENR/CS ratio of 90/10 and 80/20 can be formed. The films became tougher and less flexible than the pure ENR film. At higher CS level, the ENR/CS films were very brittle.

Figure 4.25 shows the images of the films at the ENR/CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 when adding MA at 2 phr.

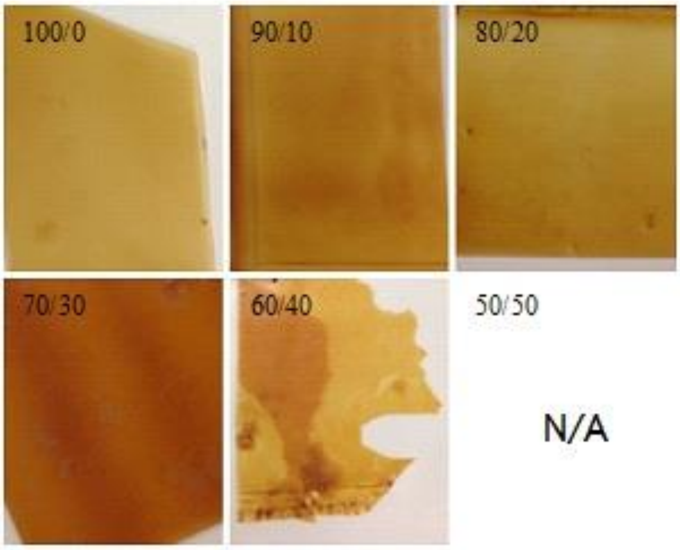


Figure 4.25 The images of the ENR/CS films at different ENR/CS ratios with MA of 2 phr

Figure 4.26 shows the images of the films at the ENR/CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 when adding MA at 3 phr.

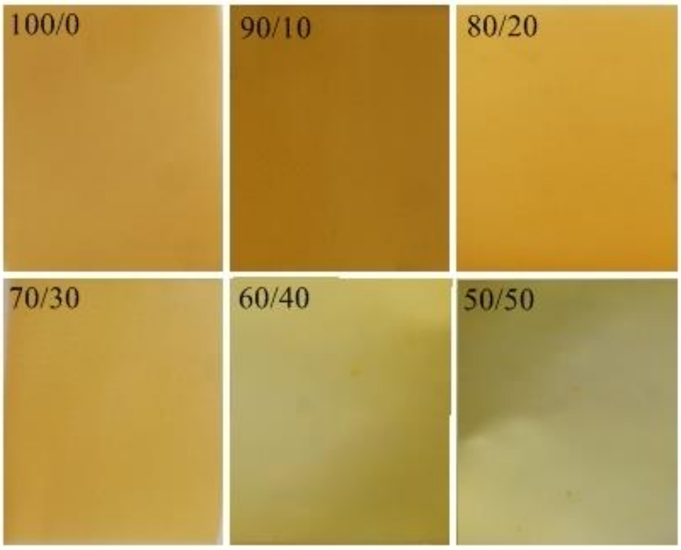


Figure 4.26 The images of the ENR/CS films at different ENR/CS ratios with MA of 3 phr

From Figures **4.24-4.26**, it was observed that when the suitable amount of MA was added into the ENR/CS mixture, the homogenous ENR/CS film without macroscopic phase separation can be formed. This is not only due to the formation of semi-interpenetrating polymer networks (IPNs) but also the interaction of ENR and CS chain. Some CS chains were trapped inside the ENR network and some chemically bonded to the ENR chain as shown earlier in **4.23**.

4.2.3 Swelling resistance

The swelling index of the ENR/CS films at different ENR/CS ratios with maleic anhydride (MA) of 1, 2 and 3 phr are shown in **Figure 4.27**. It can be clearly seen that the increase in MA acting as a crosslinking agent led to the significantly decreased swelling index. From Part I, it was found that the swelling index of the cured and uncured NR/CS films decreased with increasing the CS content. The decreased swelling index was due to the substitution of NR which has high swelling index with the high solvent resistant CS. However, it was found in this part that for the ENR/CS film with MA of 1 and 2 phr, the swelling index increased with increasing the CS content. As mentioned in the previous topic, MA can react with ENR chain forming the crosslinking rubber network and also interact with CS forming the MA grafted CS. Although the presence of CS can decrease the swelling of film, it also consumed MA, thus reducing the formation of the rubber networks. The reason why at the MA of 1 and 2 phr the swelling index of the ENR/CS films increased with increasing the CS content might be due the shortage of MA acting a crosslink agent for ENR. On the other hand, for the ENR/CS film with MA of 3 phr, initially the swelling index only slightly increased then later decreased with increasing in the CS content. The increase in MA loading reduced the shortage of MA for crosslinking ENR. So now the influence of CS on the decrease in the swelling index of the film became pronounced.

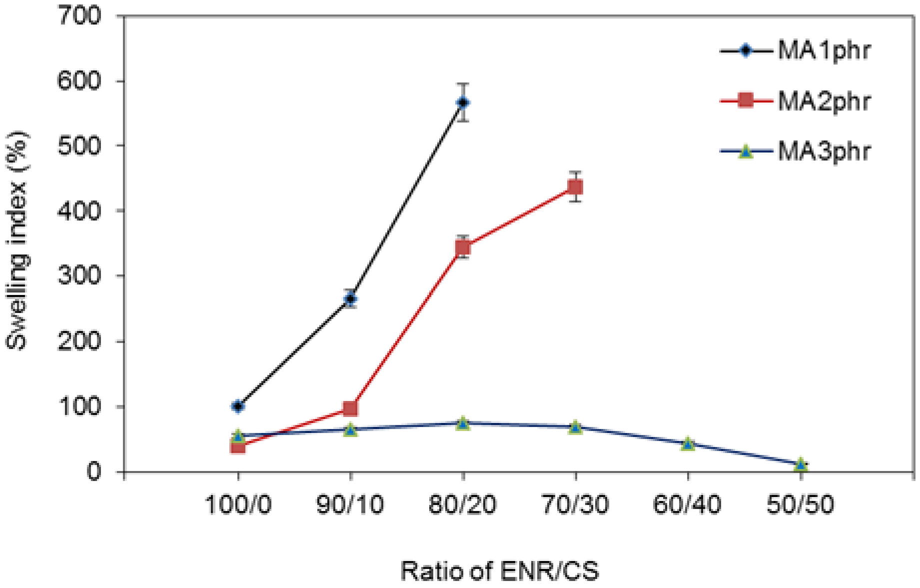


Figure 4.27 Swelling indices of the ENR/CS films at different ENR/CS ratios and with MA of 1, 2, and 3 phr

4.2.4 Tensile properties

Tensile properties of the ENR/CS film at different ENR/CS ratios and with MA of 1, 2, and 3 phr were discussed here. All samples broke at strain lower than 100% strain. Therefore, no modulus of the ENR/CS films was reported here. Tensile strength and elongation at break of the ENR/CS film are shown in **Figures 4.28** and **4.29**, respectively.

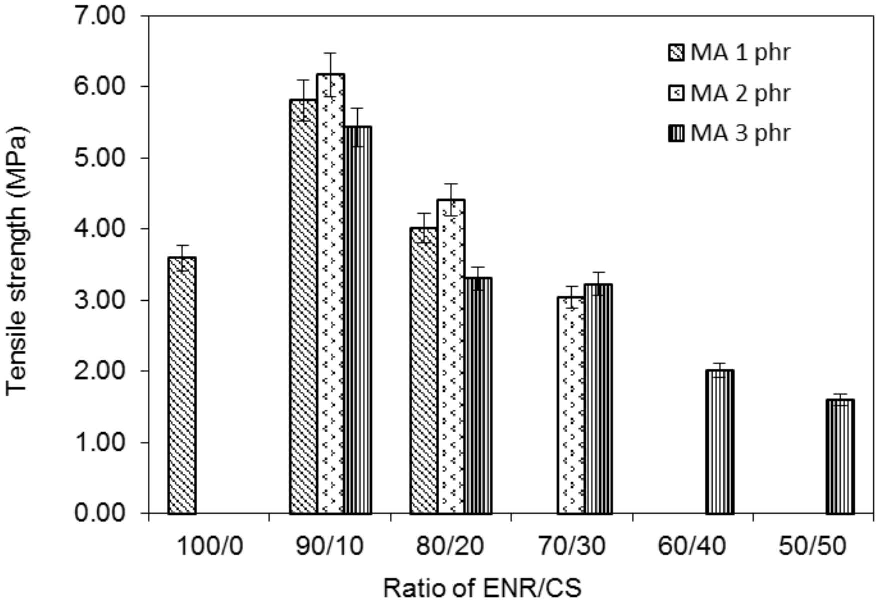


Figure 4.28 Tensile strength of the ENR/CS films at different ENR/CS ratios and with MA of 1, 2 and 3 phr

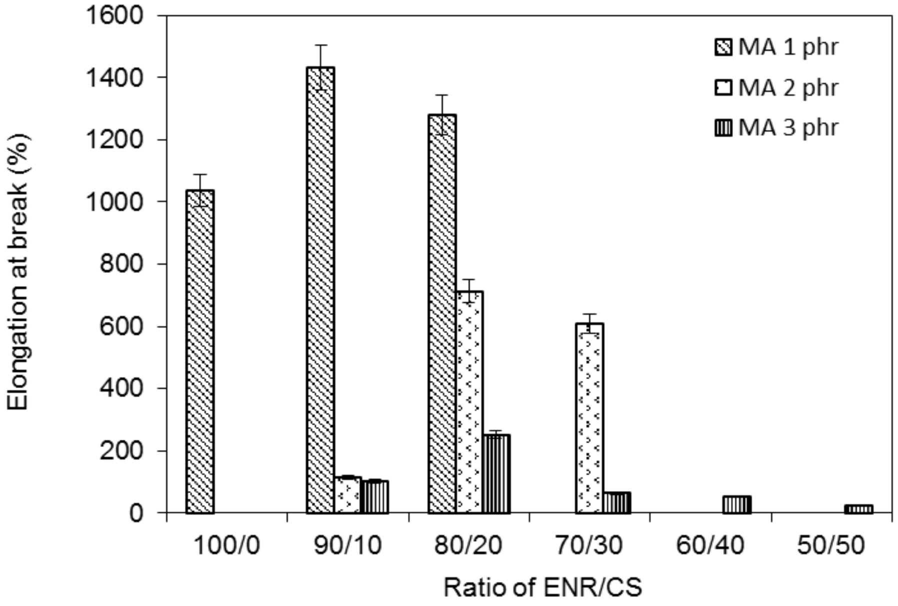


Figure 4.29 Elongation at break of the ENR/CS films at different ENR/CS ratios and with MA of 1, 2, and 3 phr

From **Figure 4.28**, it was seen that the pure ENR film cured with MA of 1 phr had low tensile strength roughly about 3.59 MPa. The pure ENR films cured with MA higher than 1 phr cannot be formed because the obtained film cannot be removed from a casting mold without breaking. In order to understand why tensile strength of the pure ENR film cured with 1 phr of MA was low, the pure ENR film cured with 0.5 phr of MA was prepared. The tensile testing showed that this film had tensile strength around 5.45 MPa and broke at 456 %strain. Explicitly, the reason why the pure ENR film cured with 1 phr of MA had such a low tensile strength was because the crosslink density was too high. At high crosslink level, chain motions become restricted and are incapable of dissipating input energy, resulting brittle fracture at lower strain at break.

For the ENR/CS films with MA of 1 phr, it was found that the ENR/CS films at the ratios of 90/10 and 80/20 showed higher tensile strength than the pure ENR film. Like the NR/CS film, when increasing CS content from 10 to 20 % by weight, the tensile strength of the ENR/CS film clearly drop. When increasing MA loading from 1 to 2 phr, the result showed that at the given ENR/CS ratio, the films with higher MA loading had higher tensile strength. However, when further increasing MA loading to 3 phr, the tensile strength of the film declined. MA can act as a crosslinking agent and also coupling agent between ENR and CS. Initially, increasing in MA loading can increase degree of crosslink as indicated by higher swelling resistance (**Figure 4.27**) and also interaction between ENR and CS as confirmed by the disappearance of macroscopic phase separation, thus resulting the ENR/CS film with MA of 2 phr in having tensile strength higher than the one with MA of 1 phr. However, at higher MA loading, the network became too tight to dissipate input energy, causing the ENR/CS film with MA of 3 phr break easier than the one with MA of 2 phr. For the films with MA of 2 and 3 phr, the ENR/CS ratio giving the film with highest tensile strength was also at the ENR/CS ratio of 90/10. Amongst all ENR/CS films prepared here, the ENR/CS film at the ratio of 90/10 with MA of 2 phr gave the highest tensile strength around 6.17 MPa.

From **Figure 4.29** it can be seen that the elongation at break of films depended on both ENR/CS ratio and MA loading. It was observed that at the given MA loading, %elongation at break of the film passed through the maximum with increasing in the CS content. The film at the ENR/CS ratio of 80/20 showed highest elongation at break. As seen in the previous part, once CS was incorporated into the NR film, the elongation at break of the NR/CS film greatly reduced when compared with that of the pure NR film. However, the ENR/CS film at the ratios of 90/10 and 80/20 can be extended to higher strain than the pure ENR film. This was because the ENR phase of these films was crosslinked at lower level than the ENR phase of the pure ENR. This was evidenced by the higher swelling index. Some part of MA reacted with CS. However, the influence of CS on the decreased elongation at break became pronounced at the ENR/CS ratio higher than 80/20.

4.2.5 Thermal aging resistance of ENR/CS film

Tensile properties of the aged ENR/CS films at different ENR/CS ratios and with MA of 1, 2, and 3 phr were compared with those of unaged ones here. **Figures 4.30- 4.32** showed the TS of the aged and unaged ENR/CS films with MA of 1, 2, and 3 phr, respectively.

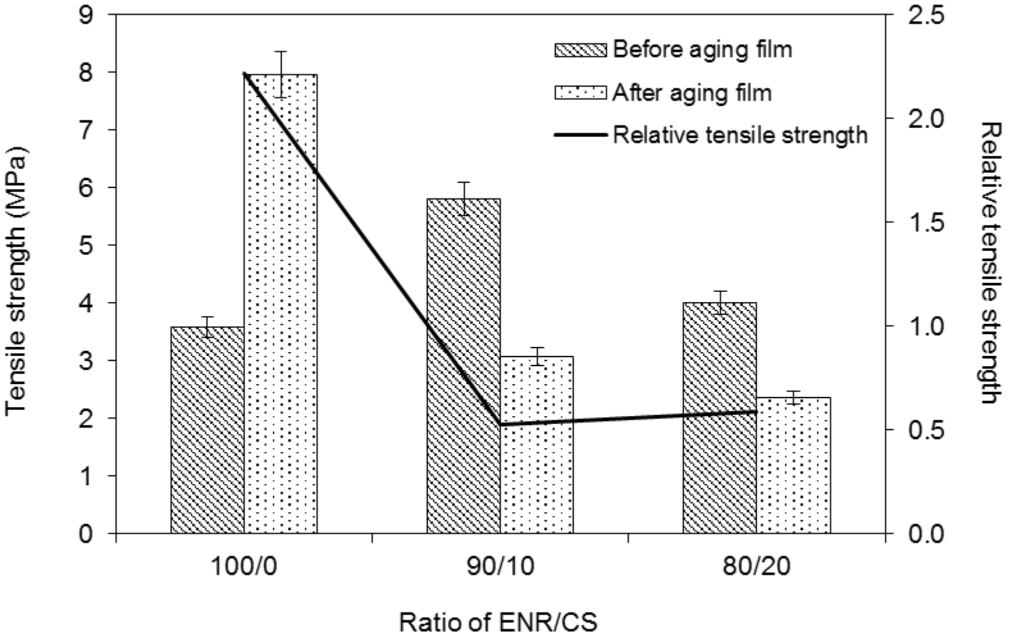


Figure 4.30 Tensile strength and relative tensile strength of the ENR/CS films at different ENR/CS ratios with MA of 1 phr before and after thermal aging

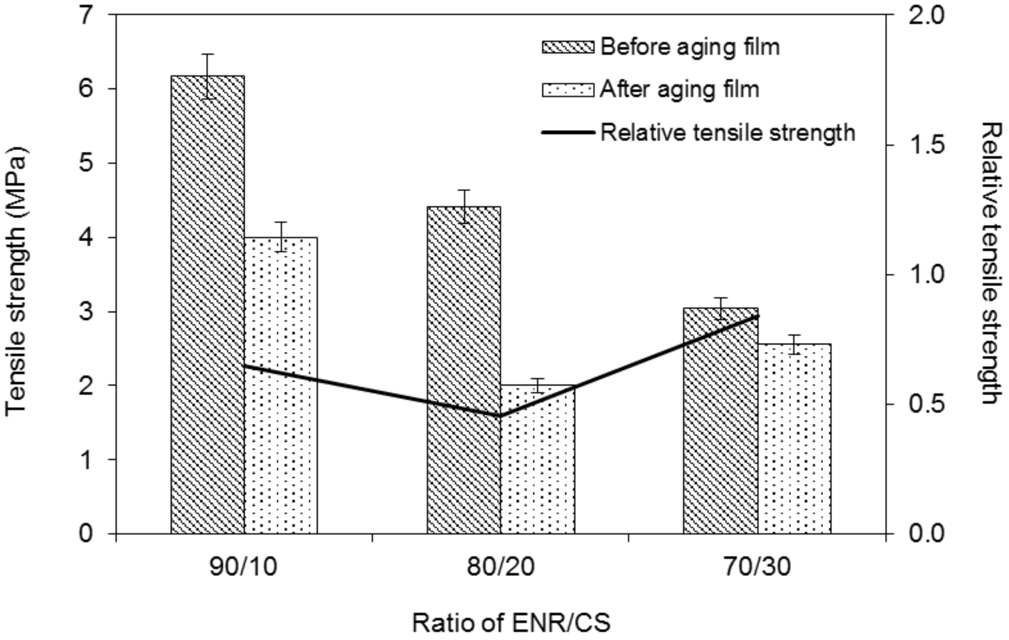


Figure 4.31 Tensile strength and relative tensile strength of the ENR/CS films at different ENR/CS ratios with MA of 2 phr before and after thermal aging

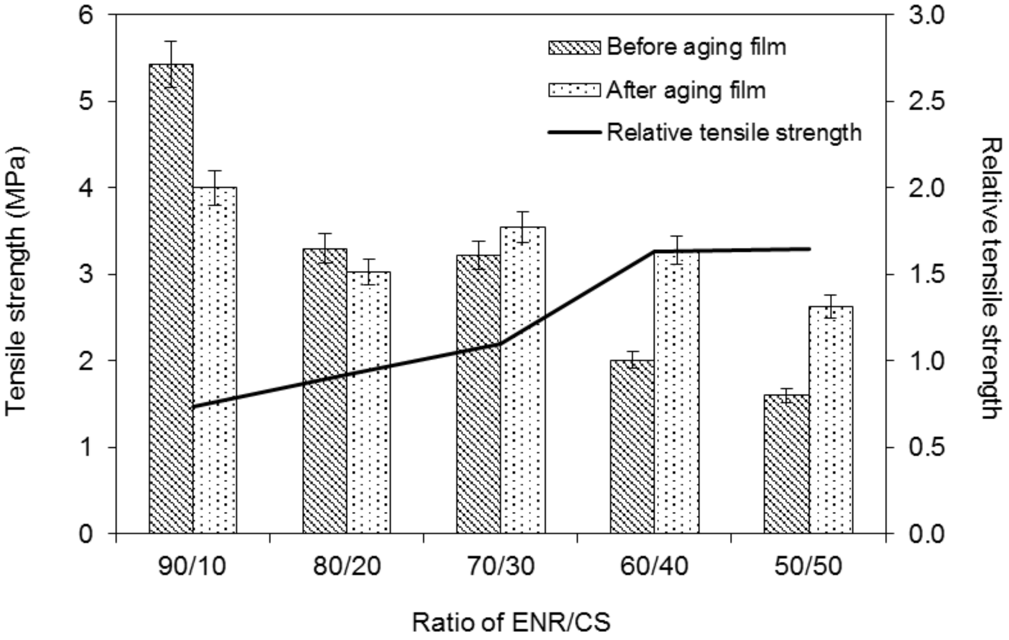


Figure 4.32 Tensile strength and relative tensile strength of the ENR/CS films at different ENR/CS ratios with MA of 3 phr before and after thermal aging

From above results, it was observed that for the ENR/CS films with MA of 1 and 2 phr, after aging their tensile strength decreased. On the other hand, for the ENR/CS films at the ENR/CS ratios of 70/30, 60/40 and 50/50 with MA of 3 phr, the thermal aging caused the samples in having higher tensile strength. The reason that the ENR/CS films containing high curing agent showed the higher tensile strength after aging might be because the film was further crosslinked. To proof this, the swelling index of the aged films with MA of 3 phr were determined and then compared with those of the unaged samples in **Figures 4.33**.

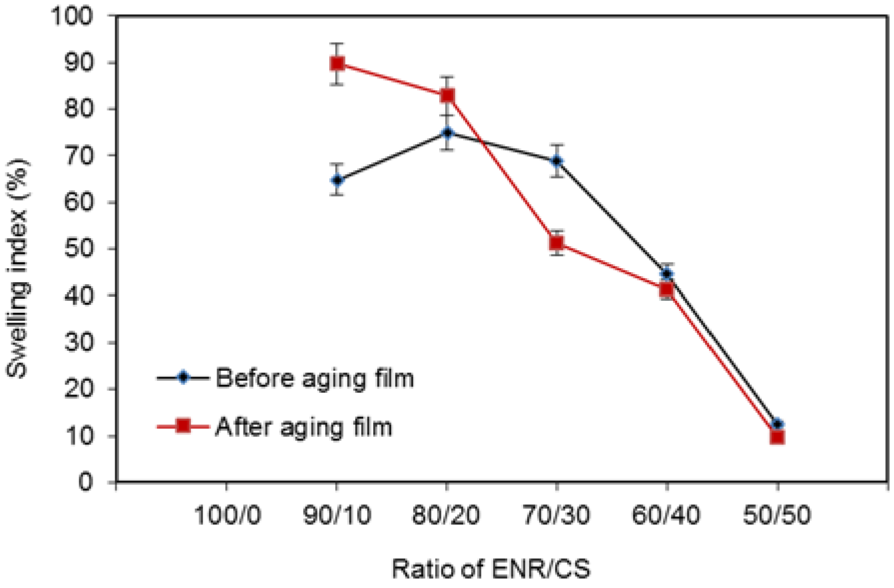


Figure 4.33 Swelling index of the ENR/CS films at different ENR/CS ratios with MA of 3 phr before and after thermal aging

From **Figure 4.33**, it can be clearly seen that for the ENR/CS films at the ENR/CS ratio of 90/10 and 80/20, the thermal aging leading to the oxidative degradation of polymer caused these films in having higher swelling index, thus giving the aged films with lower crosslinking density. Consequently, the decreased crosslink density caused the aged film in having lower strength. However, for the films with ENR/CS ratio of 70/30 and so on, the thermal aging leading not only to the oxidative degradation of polymer but also the post thermal crosslinking. The aged films had swelling index slightly lower than those unaged film. This indicated that the aged film had higher crosslink density. The increased crosslink density caused the aged films in having higher tensile strength.

Figures 4.34-4.36 compared the elongation at break of the aged with those of the unaged ENR/CS films with MA of 1, 2, and 3 phr, respectively.

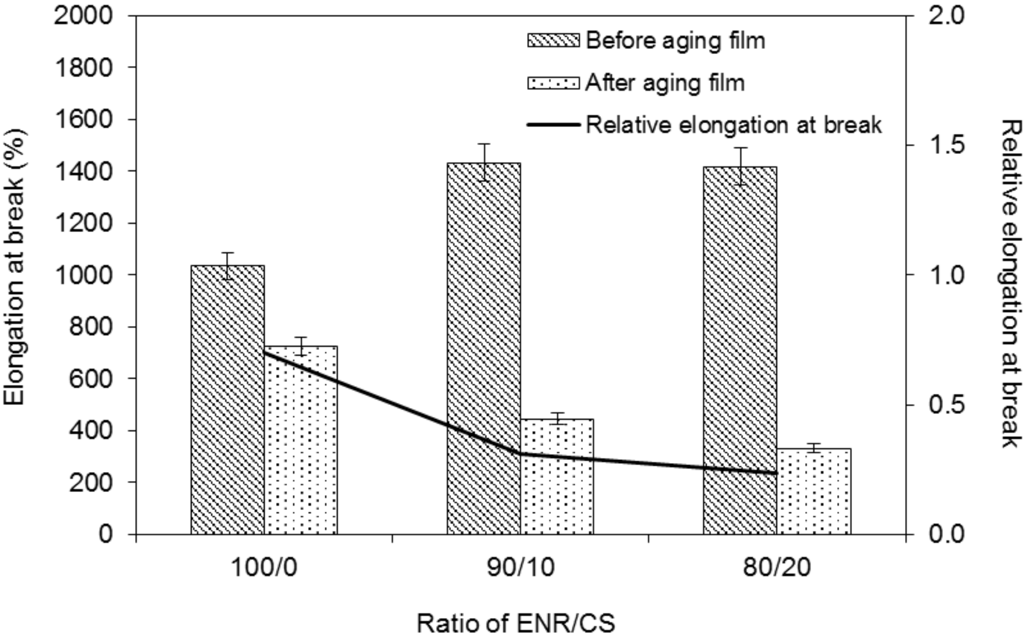


Figure 4.34 Elongation at break and relative elongation at break of the ENR/CS films at different ENR/CS ratios with MA of 1 phr before and after thermal aging

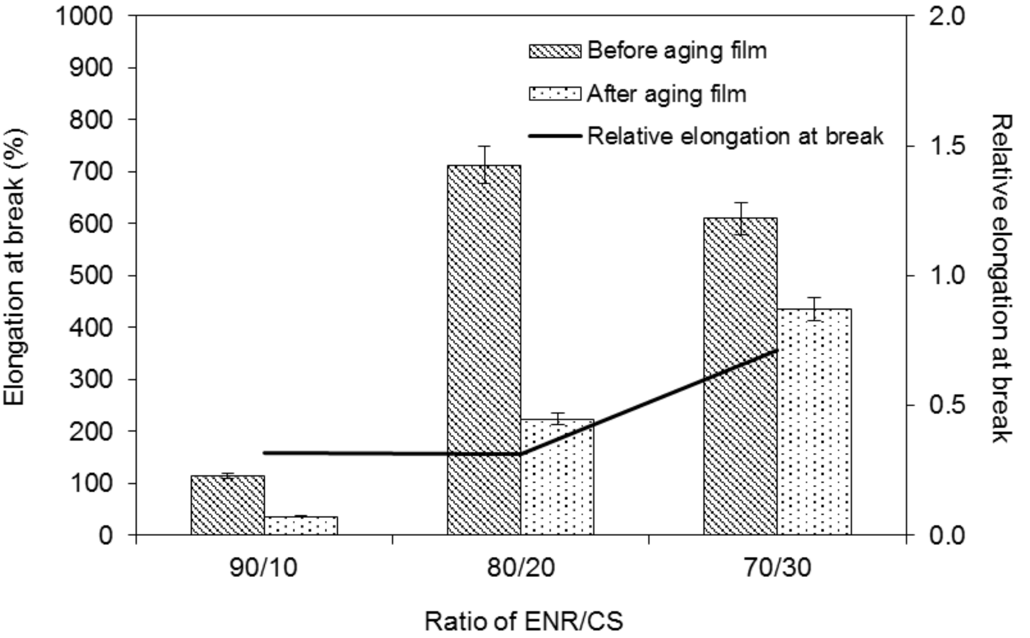


Figure 4.35 Elongation at break and relative elongation at break of the ENR/CS films at different ENR/CS ratios with MA of 2 phr before and after thermal aging

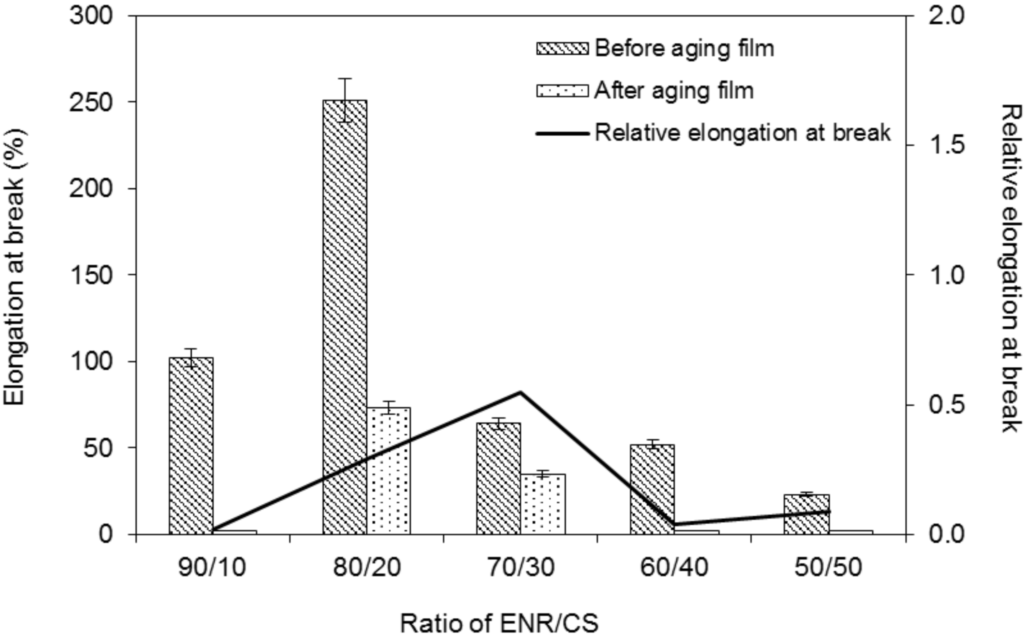


Figure 4.36 Elongation at break and relative elongation at break of the ENR/CS films at different ENR/CS ratios with MA of 3 phr before and after thermal aging

From above results, for overall it can be inferred that the thermal aging caused the samples break at lower strain. The thermally oxidative degradation caused chain scission, thus losing their extensibility.

4.2.6 Thermal decomposition properties of ENR/CS film

Figures 4.37-4.39 show the TGA thermosgrams of the ENR/CS films at different ENR/CS ratios and with MA of 1, 2, and 3 phr, respectively. The onset, endset and differential decomposition temperatures of the ENR/CS films at different ENR/CS ratios and with MA of 1, 2, and 3 phr are given in **Tables 4.6-4.8**.

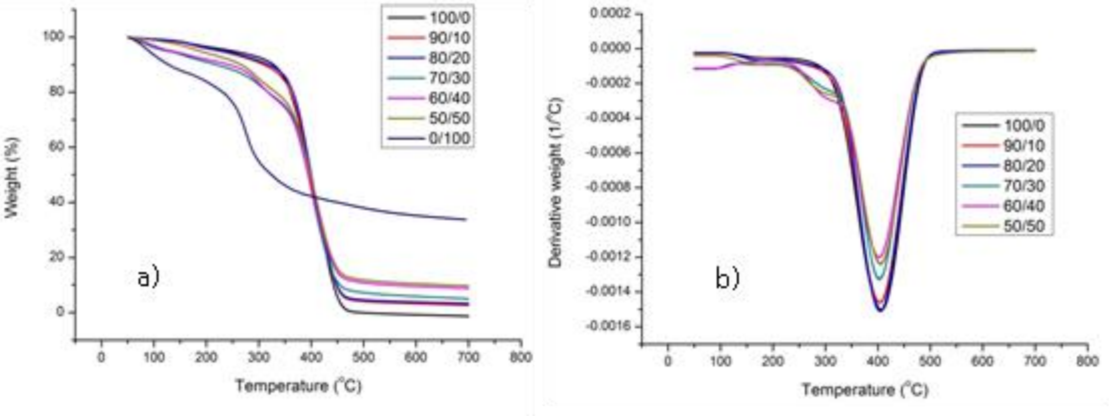


Figure 4.37 a) TGA b) DTA thermograms of the ENR/CS films at different ENR/CS ratios with MA of 1 phr

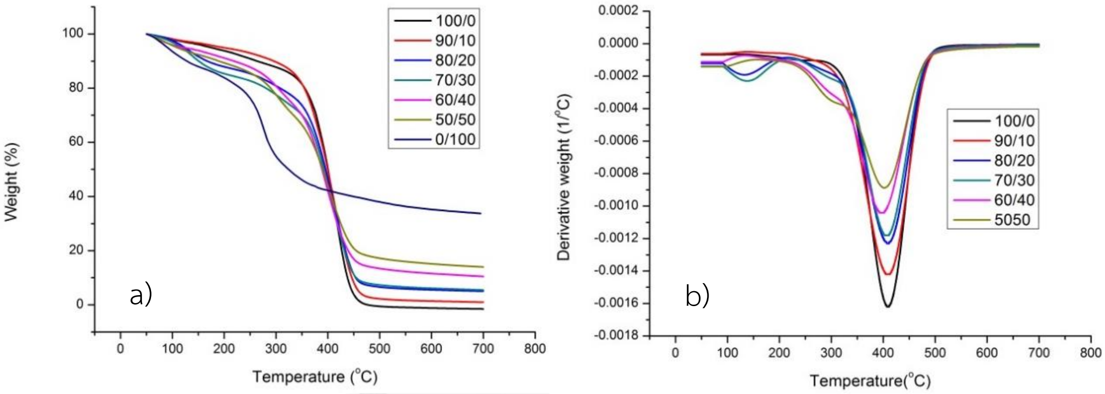


Figure 4.38 a) TGA b) DTA thermograms of the ENR/CS films at different ENR/CS ratios with MA of 2 phr

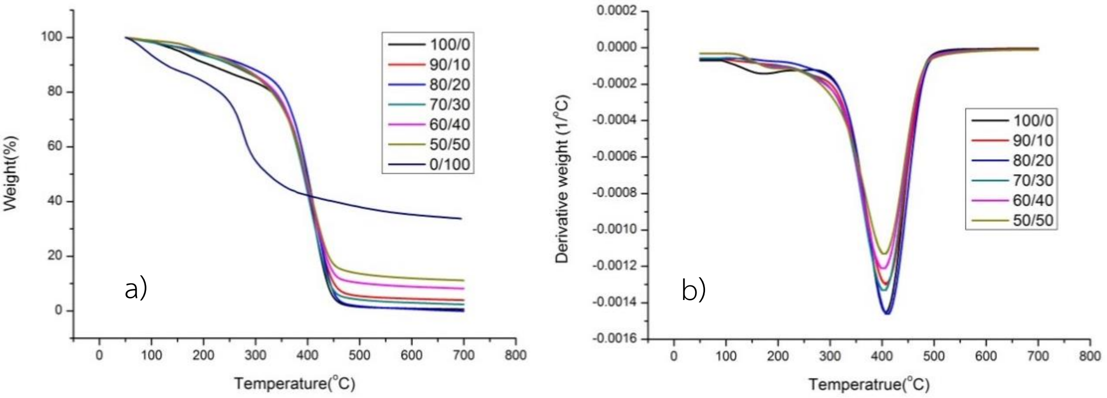


Figure 4.39 a) TGA b) DTA thermograms of the ENR/CS films at different ENR/CS ratios with MA of 3 phr

Table 4.6 Thermal decomposition temperatures of the ENR/CS films with MA of 1 phr

ENR/CS	Onset temperature of mass loss (°C)		Endset temperature of mass loss (°C)	Peak temperature from DTA curve	
	1st peak	2nd peak		1st peak	2nd peak
100/0	356.74		438.19	408.29	
90/10	354.30		444.15	403.87	
80/20	356.42		443.92	403.87	
70/30*	264.11	358.03	442.08	294.63	403.87
60/40*	261.34	355.24	442.38	296.84	401.67
50/50*	267.04	362.37	445.09	290.40	403.87
0/100	250.73		324.54	275.71	

* The film cannot be formed. The result was taken from the dried sample of the mixture.

Table 4.7 Thermal decomposition temperatures of the ENR/CS films with MA of 2 phr

ENR/CS	Onset Temperature of mass loss (°C)		Endset temperature of mass loss (°C)	Peak temperature from DTA curve	
	1st peak	2nd peak		1st peak	2nd peak
100/0[a]	368.51		444.82	407.37	
90/10	359.25		449.03	421.25	
80/20	345.18		450.15	411.78	
70/30*	278.63	363.61	447.39	277.90	405.16
60/40*	272.75	348.45	442.07	288.93	394.31
50/50*	258.41	342.98	447.86	293.35	402.95
0/100	250.73		324.54	275.71	

[a] The obtained film was very brittle.

* The film cannot be formed. The result was taken from the dried sample of the mixture.

Table 4.8 Thermal decomposition temperatures of the ENR/CS films with MA of 3 phr

ENR/CS	Onset Temperature of mass loss (oC)		Endset temperature of mass loss (oC)	Peak temperature from DTA curve	
	1st peak	2nd peak		1st peak	2nd peak
100/0[a]	364.51		443.61	407.95	
90/10	355.23		447.56	407.36	
80/20	361.79		450.17	409.57	
70/30	349.22		445.86	402.95	
60/40	344.53		445.41	402.95	
50/50	343.73		444.45	405.16	
0/100	250.73		324.54	275.71	

[a] The obtained film was very brittle.

From Part I, it was observed that the pure NR film initially decomposed at temperature of 351.99°C. By introducing the epoxide ring onto isoprene unit 20% of the NR chain, the decomposition of rubber shifted to higher temperature. This indicated that the ENR had higher thermal resistance than the pure NR. The reduction of susceptibly thermally oxidative diene may be a reason that enhances the thermal resistance of the ENR. Moreover, it was found that the obtained ENR/CS films showed only one decomposition peak. Although some compositions cannot not form film indicated by the asterisk in **Tables 4.6** and **4.7**, the decomposition temperatures of those mixtures also were determined. The results showed that those samples showed two decomposition temperatures, one close to that of pure ENR and another one close to that of pure CS. Therefore, the single decomposition temperature of the obtained ENR/CS film confirmed that there was a chemical interaction between the ENR chain and CS chain via MA molecule.

For the pure ENR, the increase in MA loading increased the onset decomposition temperature. The result showed that the onset decomposition temperature of the pure ENR shifted from 356.74°C to 368.51°C and 364.51°C when increasing MA loading from 1 phr to 2 and 3 phr, respectively. The increased onset decomposition temperature was due to the higher crosslink density. The increase in MA loading also caused the complete decomposition of the pure ENR shift to the higher temperature. However, the differential decomposition temperature seemed to be independent of the MA loading. For the ENR/CS film at the given ratio, the influence of MS loading on the thermal decomposition behavior of film cannot be concluded. The value of onset, endset and differential decomposition temperature scattered.

At the given MA loading, the presence of 10% CS by weight slightly caused the onset decomposition shift to lower temperature, but no significant difference in endset and differential decomposition temperature were observed. Although for MA loading at 1 and 2 phr, the increase in CS loading did not clearly change thermal decomposition behavior of the film, for MA loading at 3 phr the increase in CS loading seemed to cause thermal decomposition at lower temperature.

4.2.7 Oxygen permeability (OP) of ENR/CS film

The OP values of the pure ENR, pure CS and the ENR/CS films at the ENR/CS ratio of 80/20 with MA of 1, 2, and 3 phr are listed in **Table 4.9**. It was found that the pure ENR film with MA of 1 phr had an OP of 1577 cc / (m^2 - day) which was lower than the pure CS film having an OP of 2610 cc / (m^2 - day). This was because ENR was crosslinked with MA, inhibiting the transportation of oxygen through the film. Once introducing CS into the ENR, oxygen permeation of the film was further reduced. When comparing with the NR film, the opposite behavior was observed here. In the case of the NR/CS, the OP of the NR/CS film was higher than both the pure NR and CS film *(from 4.1.6).* The reason was due to the increase in free volume at the boundary between two heterogeneous phases. However, the ENR/CS film showed lower OP than the pure ENR and CS film. This indicated that there was no boundary between two phases, reducing the oxygen permeation. The further increase in MA loading gave the ENR/CS film with lower OP. This was not only due to higher crosslinking density but also higher interaction between ENR and CS chain.

Table 4.9 Oxygen permeability of the pure ENR, pure CS and ENR/CS films at the ENR/CS ratio of 80/20 with MA of 1, 2, and 3 phr.

ENR/CS	MA (phr)	OP (cc/m^2-day)
100/0	1	1577
80/20	1	1284
	2	524
	3	250
0/100	-	2610

CHAPTER V

CONCLUSIONS

The various NR/CS films were prepared here from the NR latex and CS solution using a solution casting method. Two types of rubber latex including pristine NR and epoxidized NR latex were used here. For Part I, the NRLs with and without sulfur curing agents was mixed with CS at different NR/CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 0/100. For Part II, the ENR latex prepared by in-situ epoxidation was mixed with CS solution at different ENR/CS ratios of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 0/100 and with different MA loadings at 1, 2 and 3 phr. The effects of type of rubber, rubber to chitosan weight ratio, and the presence of network on the properties of the obtained films were investigated. The overall results can be concluded as follows:

5.1 The uncured and cured NR/CS films

The pure uncured and cured NR films were highly flexible while the pure CS film was brittle. The introducing CS into the NR films caused the film less flexible and became rigid at the high CS loading. For the cured NR/CS film, when increasing the CS content, no macroscopic phase separation was observed due to the formation of semi-interpenetration network. However, for the uncured NR/CS films, the initial phase separation was observed at the NR/CS ratio of 70/30. At higher CS, phase separation became more serious.

When considering the presence of networks on the properties of films, it was found that the presence of network significantly enhanced the solvent resistance and mechanical and thermal aging properties but reduced the thermal decomposition property and oxygen permeability of the NR/CS film. When considering the effect of the NR/CS ratios on the properties of films, for both uncured and cured NR/CS films, the swelling index decreased with increasing in CS content, while modulus at 100% and 300% strain and tensile strength passed through the maximum with the increase in CS loading. For both uncured and cured NR/CS films, the maximum modulus and tensile strength were observed at the NR/CS ratio of 70/30 and 90/10, respectively. The presence of CS reduced the ability to elongate. The higher CS loading, the lower elongation at break. All NR/CS films showed two thermal decomposition peaks. The one at lower temperature was attributed to the decomposition of CS, while the higher temperature was due to the decomposition of the NR phase. Although the initial decompositions of CS and NR of the NR/CS films slightly shifted to higher temperature than the pure polymer, the effect of the NR/CS ratio on thermal decomposition was not clearly observed. Due to the lower glass transition temperature, the pure NR had oxygen permeability higher than the pure CS. However, blending NR with CS gave the mixed film with highest oxygen permeability.

5.2 The ENR/CS films

The ENR latex with 22 mol% epoxidation was successfully prepared here using in-situ epoxidation. The pure ENR and ENR/CS mixture without MA cannot form film. It was proposed here that MA can act as a crosslinking agent for ENR and coupling agent, thus resulting in forming the ENR/CS film. To obtain the ENR/CS film, the optimal MA loading depended strongly on the ENR/CS ratio. The more CS content, the more MA loading.

When considering the effect of the ENR/CS ratio and MA loading on the solvent resistance of films, it was found that at the given MA loading of 1 and 2 phr, the swelling index of the film increased with increasing of CS loading, while at the given MA loading of 3 phr, the swelling index of the film passed through maximum with increasing of CS loading. At the given ENR/CS ratio, the film with MA of 3 phr had lowest swelling index. Similar to the previous part, it was found that the maximum tensile strength was found at the rubber to CS ratio of 90/10. At higher CS content, the tensile strength was reduced and eventually became lower than the pure ENR. The ENR/CS film at the ratio of 90/10 with MA of 2 phr showed highest tensile strength. After thermal aging, it was found that the ENR/CS films at the ratios of 70/30, 60/40 and 50/50 with MA of 3 phr had higher tensile strength. It was proposed here that the increased tensile strength was due to further thermal crosslinking during aging. This hypothesis was supported by the lower swelling index of these films. Unlike the NR/CS films, the obtained homogenous ENR/CS films without phase separation showed only one thermal decomposition peaks. This can be implied that the CS chains were chemically bound to the NR chains. The effect of the ENR/CS ratio and MA loading on the thermal decomposition of films could not be clearly concluded. Even though the previous part found that the NR/CS films had higher oxygen permeability than both pure NR and CS film, here the ENR/CS films clearly showed lower oxygen permeability than both pure ENR and CS film.

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APPENDICES

APPENDIX A

SWELLING PROPERTIES

Table A-1 Swelling index of the uncured NR/CS film

NR/CS	Weight of dried samples (g)	Weight of swollen samples (g)	Swelling ratio (%)
100/0	0.2987	N/A	N/A
90/10	0.1302	1.9425	1391
80/20	0.0975	0.5792	494
70/30	0.0681	0.2557	275
60/40	0.0857	0.3117	263
50/50	0.0668	0.1973	195

Table A-2 Swelling index of the cured NR/CS film

NR/CS	Weight of dried samples (g)	Weight of swollen samples (g)	Swelling ratio (%)
100/0	0.1488	0.8002	437
90/10	0.0423	0.1413	234
80/20	0.0779	0.2330	199
70/30	0.0865	0.2492	188
60/40	0.0590	0.1400	137
50/50	0.0458	0.0767	67

Table A-3 Swelling index of the ENR/CS film with MA of 1 phr

ENR/CS	Weight of dried samples (g)	Weight of swollen samples (g)	Swelling ratio (%)
100/0	0.0504	0.1015	101
90/10	0.0509	0.1864	266
80/20	0.0667	0.4444	566
70/30	N/A	N/A	N/A
60/40	N/A	N/A	N/A
50/50	N/A	N/A	N/A

Table A-4 Swelling index of the ENR/CS film with MA of 2 phr

ENR/CS	Weight of dried samples (g)	Weight of swollen samples (g)	Swelling ratio (%)
100/0	0.0505	0.0705	**40**
90/10	0.0720	0.1417	**97**
80/20	0.0469	0.2086	**345**
70/30	0.0413	0.2218	**437**
60/40	N/A	N/A	**N/A**
50/50	N/A	N/A	**N/A**

Table A-5 Swelling index of the ENR/CS film with of MA of 3 phr

ENR/CS	Weight of dried samples (g)	Weight of swollen samples (g)	Swelling ratio (%)
100/0	0.1020	0.1593	**56**
90/10	0.0643	0.1060	**65**
80/20	0.0888	0.1555	**75**
70/30	0.0438	0.0740	**69**
60/40	0.0336	0.0486	**45**
50/50	0.0370	0.0416	**12**

Table A-6 Swelling index of the ENR/CS film with of MA of 3 phr after thermal aging

ENR/CS	Weight of dried samples (g)	Weight of swollen samples (g)	Swelling ratio (%)
100/0	N/A	N/A	**N/A**
90/10	0.0903	0.1713	**90**
80/20	0.0937	0.1538	**83**
70/30	0.0501	0.0758	**51**
60/40	0.0304	0.043	**41**
50/50	0.0443	0.0486	**10**

APPENDIX B

MECHANICAL PROPERTIES OF NR/CS FILMS

Table B-1 Mechanical properties of the uncured 100/0 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.38	0.40	0.37	1291	0.80
2	0.41	0.42	0.40	1100	0.85
3	0.37	0.40	0.40	1444	0.80
4	0.38	0.40	0.40	1280	0.88
5	0.38	0.41	0.41	1313	0.92
Average	**0.39**	**0.40**	**0.40**	**1286**	**0.85**
SD	**±0.01**	**±0.01**	**±0.01**	**±110**	**±0.05**

Table B-2 Mechanical properties of the uncured 90/10 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	1.16	1.46	1.82	1269	10.42
2	1.05	1.36	1.71	1370	12.06
3	1.15	1.49	1.86	1152	10.24
4	1.21	1.53	1.96	1212	12.13
5	1.43	1.92	2.37	1247	12.92
Average	**1.20**	**1.55**	**1.94**	**1250**	**11.55**
SD	**±0.14**	**±0.21**	**±0.26**	**±80**	**±1.17**

Table B-3 Mechanical properties of the uncured 80/20 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	2.27	2.75	3.25	972	7.98
2	2.02	2.50	2.97	997	7.90
3	2.08	1.77	2.14	1044	7.89
4	1.41	1.77	3.04	991	7.00
5	1.95	2.51	4.07	922	8.63
Average	**1.95**	**2.26**	**3.09**	**985**	**7.88**
SD	**±0.32**	**±0.46**	**±0.69**	**±39**	**±0.58**

Table B-4 Mechanical properties of the uncured 70/30 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	3.96	4.05	4.95	435	5.10
2	4.47	5.13	6.01	508	4.48
3	4.05	4.71	5.63	518	5.25
4	4.66	5.30	6.20	427	6.00
5	4.47	5.18	6.12	432	4.43
Average	**4.32**	**4.88**	**5.78**	**464**	**5.05**
SD	**±0.30**	**±0.51**	**±0.51**	**±40**	**±0.64**

Table B-5 Mechanical properties of the uncured 60/40 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.66	0.83	1.01	269	5.47
2	0.62	0.81	1.01	274	5.25
3	0.59	0.75	0.90	247	4.33
4	0.55	0.71	0.88	355	4.81
5	0.61	0.78	0.95	370	5.06
Average	**0.60**	**0.77**	**0.95**	**303**	**4.98**
SD	**±0.04**	**±0.05**	**±0.06**	**±50**	**±0.44**

Table B-6 Mechanical properties of the uncured 50/50 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	2	2.40
2	-	-	-	2	2.60
3	-	-	-	2	2.80
4	-	-	-	2	2.90
5	-	-	-	2	2.50
Average	**-**	**-**	**-**	**2**	**2.64**
SD	**-**	**-**	**-**	**0**	**±0.21**

Table B-7 Mechanical properties of the cured 100/0 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.42	0.60	0.75	1618	12.58
2	0.41	0.58	0.73	1488	10.84
3	0.42	0.59	0.74	1705	13.35
4	0.46	0.64	0.81	1599	13.27
5	0.37	0.54	0.68	1646	12.51
Average	**0.42**	**0.59**	**0.74**	**1611**	**12.51**
SD	**±0.03**	**±0.04**	**±0.05**	**±79**	**±1.01**

Table B-8 Mechanical properties of the cured 90/10 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	1.65	2.22	2.85	1134	15.10
2	2.01	2.38	3.45	1021	15.57
3	2.07	2.81	3.65	966	15.37
4	1.97	2.64	3.39	1049	16.27
5	1.98	2.63	3.40	1060	16.40
Average	**1.94**	**2.54**	**3.35**	**1046**	**15.74**
SD	**±0.16**	**±0.23**	**±0.30**	**±61**	**±0.57**

Table B-9 Mechanical properties of the cured 80/20 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	2.81	3.62	4.59	777	12.57
2	3.06	3.93	5.03	734	12.84
3	2.76	3.56	4.56	766	12.43
4	2.90	3.71	4.71	795	13.37
5	2.81	3.66	4.70	761	13.33
Average	**2.87**	**3.70**	**4.72**	**767**	**12.91**
SD	**0.12**	**0.14**	**0.19**	**±22**	**±0.43**

Table B-10 Mechanical properties of the cured 70/30 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	3.07	3.89	4.90	613	9.65
2	2.59	3.47	4.51	633	9.68
3	2.72	3.61	4.71	719	12.05
4	2.71	3.63	4.75	677	11.15
5	3.02	3.98	5.15	572	9.49
Average	**2.82**	**3.72**	**4.81**	**643**	**10.41**
SD	**±0.21**	**±0.21**	**±0.24**	**±57**	**±1.41**

Table B-11 Mechanical properties of the cured 60/40 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	54	4.60
2	-	-	-	52	4.40
3	-	-	-	65	4.90
4	-	-	-	61	4.89
5	-	-	-	58	4.51
Average	**-**	**-**	**-**	**58**	**4.66**
SD	**-**	**-**	**-**	**±5**	**±0.23**

Table B-12 Mechanical properties of the cured 50/50 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	2	2.50
2	-	-	-	2	4.20
3	-	-	-	2	3.50
4	-	-	-	2	3.50
5	-	-	-	2	2.60
Average	**-**	**-**	**-**	**2**	**3.26**
SD	**-**	**-**	**-**	**0**	**±0.71**

MECHANICAL PROPERTIES OF ENR/CS FILMS

Table B-13 Mechanical properties of the 100/0 ENR/CS film with MA of 1 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.70	0.60	1.13	1054	4.00
2	0.45	0.67	0.87	1105	3.69
3	0.36	0.52	0.66	1076	3.36
4	0.40	0.60	0.80	958	3.24
5	0.50	0.75	1.01	987	3.64
Average	**0.48**	**0.63**	**0.89**	**1036**	**3.59**
SD	**±0.13**	**±0.09**	**±0.18**	**±62**	**±0.30**

Table B-14 Mechanical properties of the 90/10 ENR/CS film with MA of 1 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.40	0.51	0.65	1469	5.74
2	0.48	0.76	1.06	1432	5.24
3	0.69	0.92	1.13	1460	6.50
4	0.38	0.51	0.62	1404	4.78
5	0.43	0.56	0.68	1400	6.80
Average	**0.48**	**0.65**	**0.83**	**1433**	**5.81**
SD	**±0.13**	**±0.18**	**±0.25**	**±31**	**±0.84**

Table B-15 Mechanical properties of the 80/20 ENR/CS film with MA of 1 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.39	0.48	0.57	1247	3.63
2	0.38	0.47	0.56	1272	4.13
3	0.42	0.57	0.72	1288	3.62
4	0.46	0.63	0.81	1299	4.79
5	0.36	0.45	0.54	1291	3.87
Average	**0.40**	**0.52**	**0.64**	**1279**	**4.01**
SD	**±0.04**	**±0.08**	**±0.12**	**±21**	**±0.48**

Table B-16 Mechanical properties of the 90/10ENR/CS film with MA of 2 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	115	6.43
2	-	-	-	110	6.32
3	-	-	-	112	6.15
4	-	-	-	117	6.79
5	-	-	-	115	5.15
Average	**-**	**-**	**-**	**114**	**6.17**
SD	**-**	**-**	**-**	**±3**	**±0.62**

Table B-17 Mechanical properties of the 80/20 ENR/CS film with MA of 2 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.68	0.83	0.98	714	4.42
2	0.68	0.81	0.86	713	4.33
3	0.69	0.75	0.87	715	4.54
4	0.64	0.73	0.82	712	4.40
5	0.66	0.86	0.93	713	4.36
Average	**0.67**	**0.80**	**0.89**	**713**	**4.41**
SD	**±0.02**	**±0.05**	**±0.06**	**±1**	**±0.08**

Table B-18 Mechanical properties of the 70/30 ENR/CS film with MA of 2 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	638	3.09
2	-	-	-	605	3.03
3	-	-	-	605	3.00
4	-	-	-	602	3.04
5	-	-	-	601	3.05
Average	**-**	**-**	**-**	**610**	**3.04**
SD	**-**	**-**	**-**	**±16**	**±0.03**

Table B-19 Mechanical properties of the 90/10 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	4.51	-	-	99	6.22
2	5.13	-	-	133	5.85
3	4.14	-	-	91	5.72
4	-	-	-	133	4.87
5	-	-	-	102	4.50
Average	**4.59**	**-**	**-**	**112**	**5.43**
SD	**±0.50**	**-**	**-**	**±20**	**±0.72**

Table B-20 Mechanical properties of the 80/20 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	1.88	2.77	-	247	2.98
2	2.00	2.89	-	270	2.74
3	1.78	2.66	-	277	3.86
4	2.14	3.10	-	216	3.39
5	2.14	-	-	244	3.55
Average	**1.99**	**2.85**	**-**	**251**	**3.30**
SD	**±0.16**	**±0.19**	**-**	**±24**	**±0.45**

Table B-21 Mechanical properties of the 70/30 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	66	3.13
2	-	-	-	65	3.43
3	-	-	-	67	3.24
4	-	-	-	60	3.23
5	-	-	-	61	3.04
Average	**-**	**-**	**-**	**64**	**3.22**
SD	**-**	**-**	**-**	**±3**	**±0.15**

Table B-22 Mechanical properties of the 60/40 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	52	3.06
2	-	-	-	50	2.16
3	-	-	-	52	2.10
4	-	-	-	51	2.10
5	-	-	-	54	2.10
Average	-	-	-	52	**2.30**
SD	-	-	-	±1	**±0.42**

Table B-23 Mechanical properties of the 50/50 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	25	2.06
2	-	-	-	22	1.16
3	-	-	-	25	1.05
4	-	-	-	22	2.10
5	-	-	-	23	1.63
Average	-	-	-	23	1.60
SD	-	-	-	±1	±0.49

APPENDIX C

THERMAL AGING ON MECHANICAL PROPERTIES OF NR/CS FILMS

Table C-1 Mechanical properties of the uncured 100/0 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.33	0.33	0.32	1916	0.83
2	0.28	0.29	0.27	1933	0.78
3	0.91	1.05	1.19	610	1.80
4	0.25	0.28	0.25	1880	0.71
5	0.33	0.32	0.29	1100	1.00
Average	**0.42**	**0.45**	**0.47**	**1488**	**1.02**
SD	**±0.27**	**±0.34**	**±0.40**	**±603**	**±0.45**

Table C-2 Mechanical properties of the uncured 90/10 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.98	1.40	1.84	975	9.50
2	0.87	1.24	1.61	977	9.48
3	0.85	1.22	1.61	978	9.51
4	0.85	1.20	1.54	978	9.52
5	0.87	1.21	1.56	975	9.51
Average	**0.89**	**1.25**	**1.63**	**977**	**9.50**
SD	**±0.05**	**±0.07**	**±0.11**	**±1**	**±0.01**

Table C-3 Mechanical properties of the uncured 80/20 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.54	0.58	0.66	854	2.61
2	0.64	0.76	0.91	844	2.92
3	0.52	0.59	0.68	869	2.89
4	0.55	0.62	0.72	857	2.30
5	0.53	0.62	0.74	850	2.00
Average	**0.55**	**0.63**	**0.74**	**855**	**2.55**
SD	**±0.05**	**±0.07**	**±0.10**	**±9**	**±0.39**

Table C-4 Mechanical properties of the uncured 70/30 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	58	3.25
2	-	-	-	58	3.19
3	-	-	-	47	3.05
4	-	-	-	80	3.40
5	-	-	-	33	3.49
Average	**-**	**-**	**-**	**55**	**3.28**
SD	**-**	**-**	**-**	**±17**	**±0.17**

Table C-5 Mechanical properties of the uncured 60/40 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	2.43	2.94	-	69	3.02
2	3.37	-	-	66	3.59
3	-	-	-	69	3.24
4	1.83	2.21	2.61	67	2.96
5	-	-	-	69	3.24
Average	**2.54**	**2.57**	**2.61**	**68**	**3.21**
SD	**±0.78**	**±0.52**	**-**	**±1**	**±0.24**

Table C-6 Mechanical properties of the uncured 50/50 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	2	1.70
2	-	-	-	2	0.50
3	-	-	-	2	0.60
4	-	-	-	2	1.00
5	-	-	-	2	0.90
Average	**-**	**-**	**-**	**2**	**0.94**
SD	**-**	**-**	**-**	**0**	**±0.47**

Table C-7 Mechanical properties of the cured 100/0 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.40	0.56	0.71	1530	11.59
2	0.36	0.53	0.66	1594	11.82
3	0.40	0.56	0.70	1504	11.53
4	0.37	0.54	0.68	1500	10.00
5	0.40	0.57	0.73	1433	12.06
Average	**0.39**	**0.55**	**0.69**	**1512**	**11.40**
SD	**±0.02**	**±0.02**	**±0.02**	**±58**	**±0.81**

Table C-8 Mechanical properties of the cured 90/10 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	1.90	2.58	3.30	1135	18.57
2	1.90	2.56	3.31	1091	17.66
3	1.88	2.56	3.33	1094	18.08
4	1.88	2.56	3.33	1094	18.08
5	2.12	2.85	3.68	1073	19.14
Average	**1.94**	**2.62**	**3.39**	**1097**	**18.31**
SD	**±0.10**	**±0.13**	**±0.16**	**±23**	**±0.57**

Table C-9 Mechanical properties of the cured 80/20 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	2.53	3.41	4.44	919	15.63
2	2.62	3.55	4.65	802	14.80
3	2.53	3.42	4.53	774	15.31
4	2.56	3.47	4.55	877	15.86
5	2.90	3.90	5.10	849	15.93
Average	**2.63**	**3.55**	**4.65**	**844**	**15.50**
SD	**±0.16**	**±0.20**	**±0.26**	**±58**	**±0.46**

Table C-10 Mechanical properties of the cured 70/30 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	3.02	4.05	5.25	643	16.48
2	2.87	3.83	4.96	647	16.47
3	2.54	3.47	4.56	649	16.21
4	2.89	3.86	4.99	642	15.38
5	3.03	4.05	5.23	642	15.64
Average	**2.87**	**3.85**	**5.00**	**645**	**16.04**
SD	**±0.20**	**±0.24**	**±0.28**	**±3**	**±0.50**

Table C-11 Mechanical properties of the cured 60/40 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	36	12.77
2	-	-	-	33	12.67
3	-	-	-	30	12.42
4	-	-	-	36	12.60
5	-	-	-	31	12.45
Average	**-**	**-**	**-**	**33**	**12.58**
SD	**-**	**-**	**-**	**±3**	**±0.15**

Table C-12 Mechanical properties of the cured 50/50 NR/CS film

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	22	6.84
2	-	-	-	26	6.54
3	-	-	-	23	5.63
4	-	-	-	22	5.55
5	-	-	-	25	5.45
Average	**-**	**-**	**-**	**24**	**6.00**
SD	**-**	**-**	**-**	**±2**	**±0.64**

THERMAL AGING ON MECHANICAL PROPERTIES OF ENR/CS FILMS

Table C-13 Mechanical properties of the 100/0 ENR/CS film with MA of 1 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.55	0.88	1.24	728	8.00
2	0.52	0.85	1.24	722	7.95
3	0.53	0.87	1.28	726	7.99
4	0.51	0.85	1.22	725	7.93
5	0.59	0.96	1.38	723	7.94
Average	**0.54**	**0.88**	**1.27**	**725**	**7.96**
SD	**±0.03**	**±0.05**	**±0.06**	**±2**	**±0.03**

Table C-14 Mechanical properties of the 90/10 ENR/CS film with MA of 1 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	1.05	1.66	1.95	439	2.80
2	1.00	1.67	2.25	456	3.20
3	1.01	1.64	2.05	441	3.12
4	1.06	1.62	1.98	440	3.05
5	1.08	1.69	2.23	449	3.16
Average	**1.04**	**1.66**	**2.09**	**445**	**3.07**
SD	**±0.03**	**±0.03**	**±0.14**	**±7**	**±0.16**

Table C-15 Mechanical properties of the 80/20 ENR/CS film with MA of 1 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	0.88	1.38	1.91	310	2.00
2	1.95	1.49	2.07	316	2.15
3	0.84	1.33	1.85	339	2.07
4	0.97	1.53	2.11	369	2.57
5	0.73	1.18	1.64	323	3.03
Average	1.07	1.38	1.92	331	2.36
SD	±0.50	±0.14	±0.19	±24	±0.43

Table C-16 Mechanical properties of the 90/10 ENR/CS film with MA of 2 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	36	4.40
2	-	-	-	35	3.60
3	-	-	-	40	3.92
4	-	-	-	34	4.07
5	-	-	-	32	4.03
Average	-	-	-	**35**	**4.00**
SD	-	-	-	**±3**	**±0.29**

Table C-17 Mechanical properties of the 80/20 ENR/CS film with MA of 2 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	1.59	1.93	0.14	272	2.10
2	1.43	1.79	-	216	1.75
3	1.55	1.88	-	256	2.02
4	1.67	2.00	2.22	243	2.23
5	1.62	-	-	235	1.89
Average	**1.57**	**1.90**	**1.18**	**244**	**2.00**
SD	**±0.09**	**±0.09**	**±1.47**	**±21**	**±0.19**

Table C-18 Mechanical properties of the 70/30 ENR/CS film with MA of 2 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	1.15	1.47	1.87	419	2.31
2	1.74	2.21	2.65	432	2.85
3	1.33	1.71	2.11	446	2.70
4	1.61	2.02	-	440	2.37
5	1.26	2.13	2.46	443	2.56
Average	**1.42**	**1.91**	**2.27**	**436**	**2.56**
SD	**±0.25**	**±0.31**	**±0.35**	**±11**	**±0.22**

Table C-19 Mechanical properties of the 90/10 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	2	4.21
2	-	-	-	3	3.98
3	-	-	-	3	3.88
4	-	-	-	2	3.90
5	-	-	-	3	4.10
Average	-	-	-	2	4.01
SD	-	-	-	±0	±0.14

Table C-20 Mechanical properties of the 80/20 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	83	2.72
2	-	-	-	53	3.18
3	-	-	-	73	2.68
4	-	-	-	63	3.08
5	-	-	-	93	3.48
Average	-	-	-	73	3.03
SD	-	-	-	±16	±0.33

Table C-21 Mechanical properties of the 70/30 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	3	3.50
2	-	-	-	2	3.55
3	-	-	-	2	3.56
4	-	-	-	2	3.53
5	-	-	-	2	3.55
Average	-	-	-	2	3.54
SD	-	-	-	0	±0.02

Table C-22 Mechanical properties of the 60/40 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	33	3.22
2	-	-	-	36	3.03
3	-	-	-	33	3.11
4	-	-	-	36	3.67
5	-	-	-	36	3.38
Average	**-**	**-**	**-**	**35**	**3.28**
SD	**-**	**-**	**-**	**±2**	**±0.25**

Table C-23 Mechanical properties of the 50/50 ENR/CS film with MA of 3 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	%Elongation	Tensile strength (MPa)
1	-	-	-	2	2.69
2	-	-	-	2	2.64
3	-	-	-	2	2.58
4	-	-	-	2	2.65
5	-	-	-	3	2.59
Average	**-**	**-**	**-**	**2**	**2.63**
SD	**-**	**-**	**-**	**0**	**±0.05**

APPENDIX D

THERMAL PROPERTIES OF NR/CS FILMS

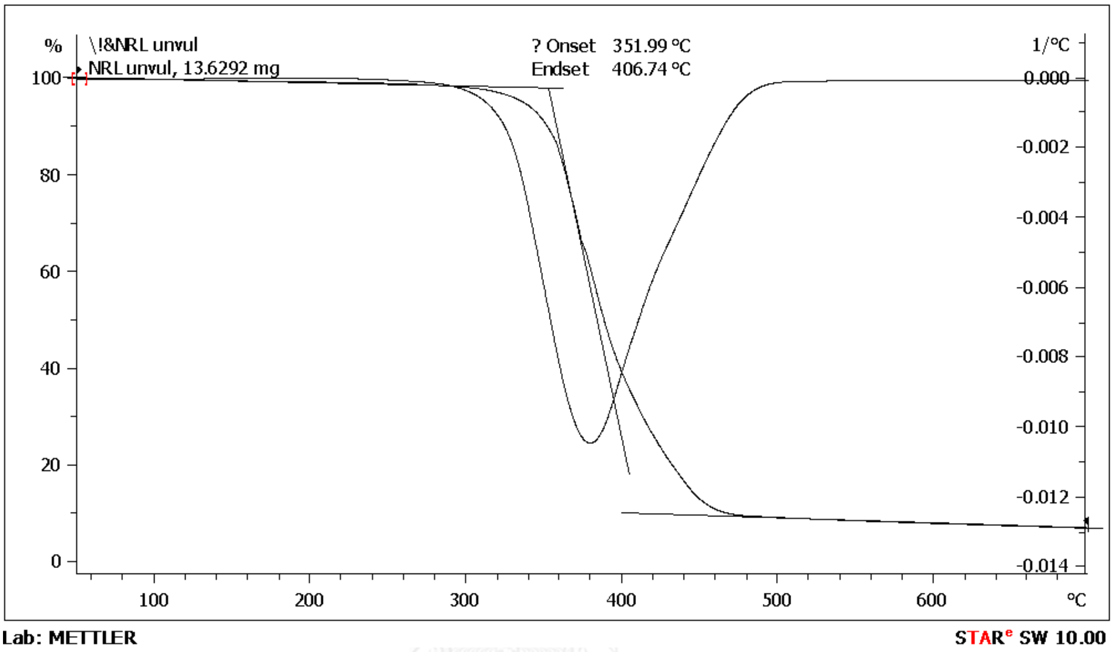

Figure D-1 TGA thermogram of the uncured 100/0 NR/CS film

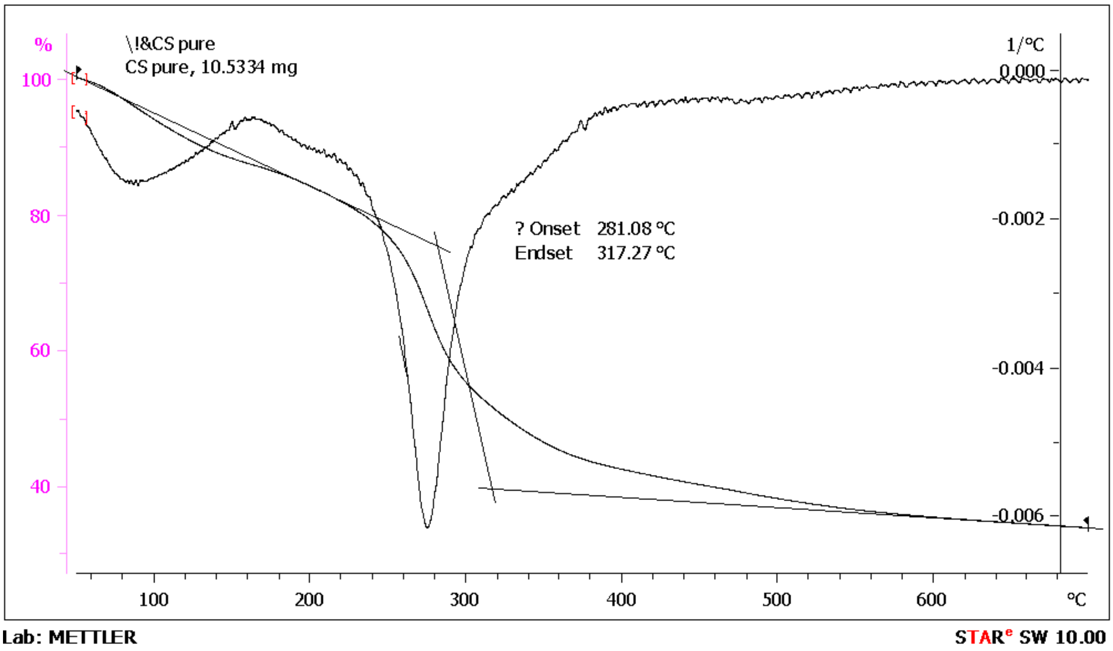

Figure D-2 TGA thermogram of 0/100 NR/CS film

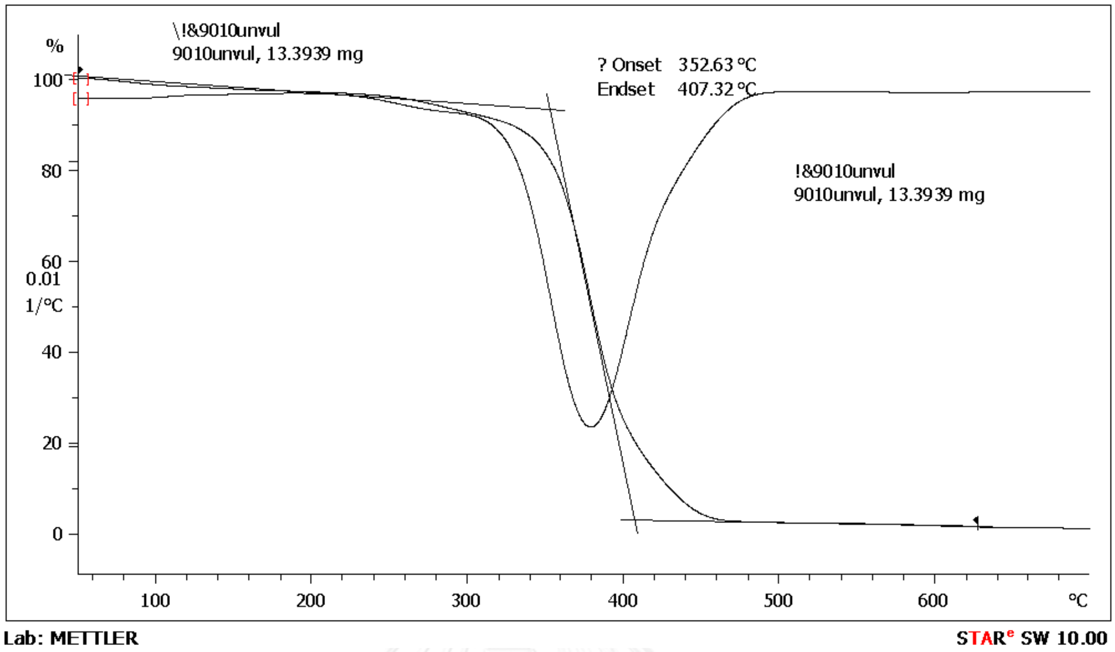

Figure D-3 TGA thermogram of the uncured 90/10 NR/CS film

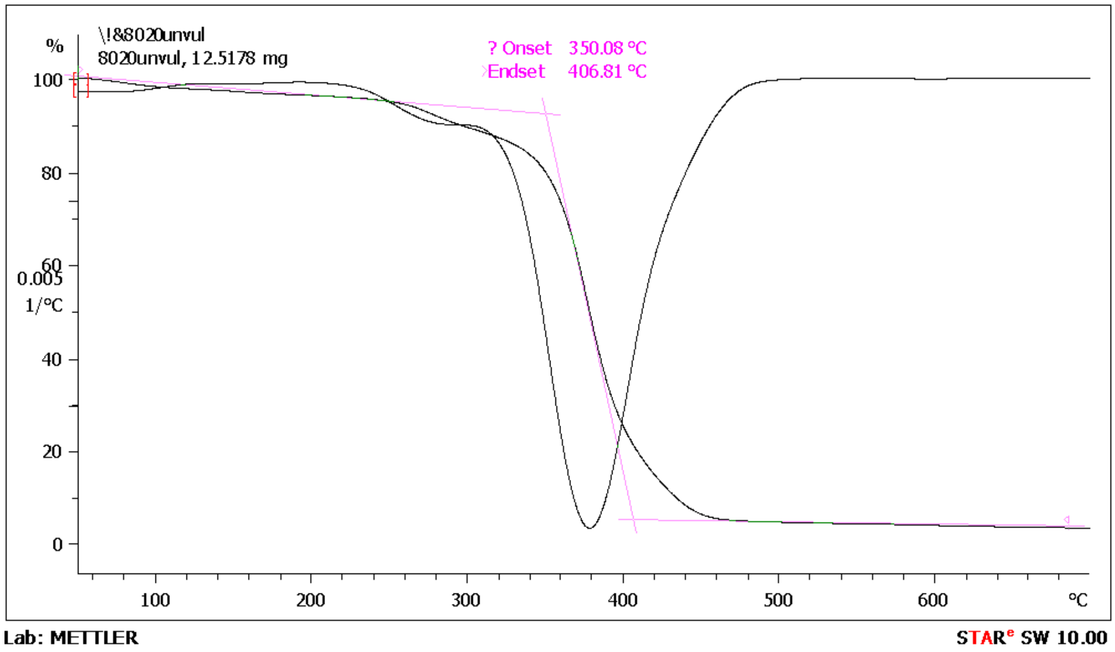

Figure D-4 TGA thermogram of the uncured 80/20 NR/CS film

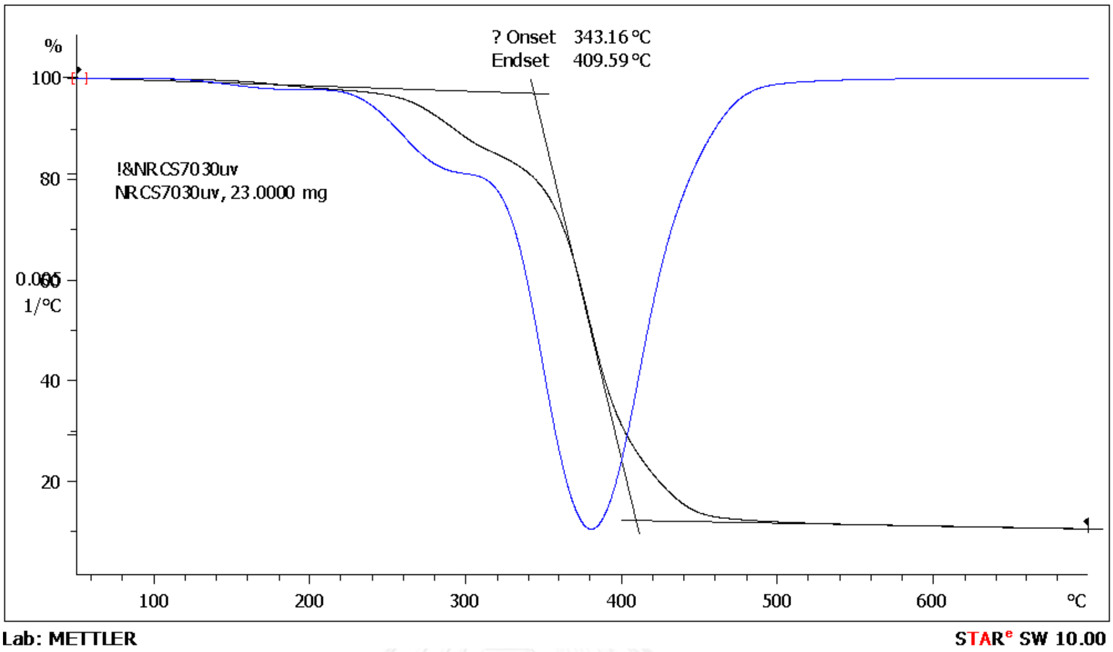

Figure D-5 TGA thermogram of the uncured 70/30 NR/CS film

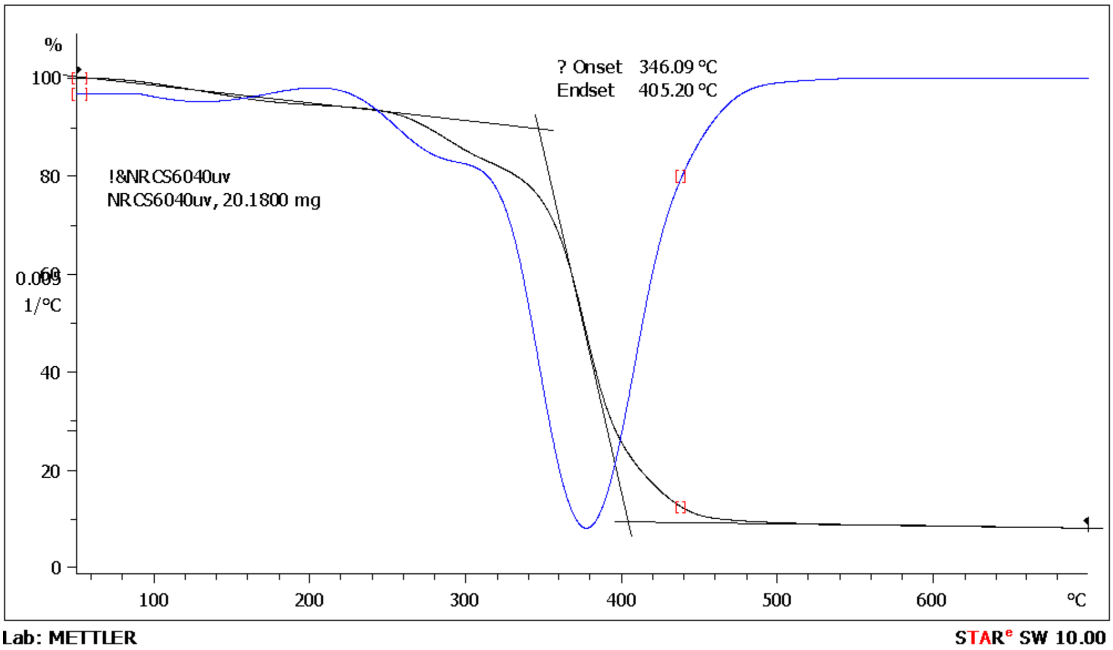

Figure D-6 TGA thermogram of the uncured 60/40 NR/CS film

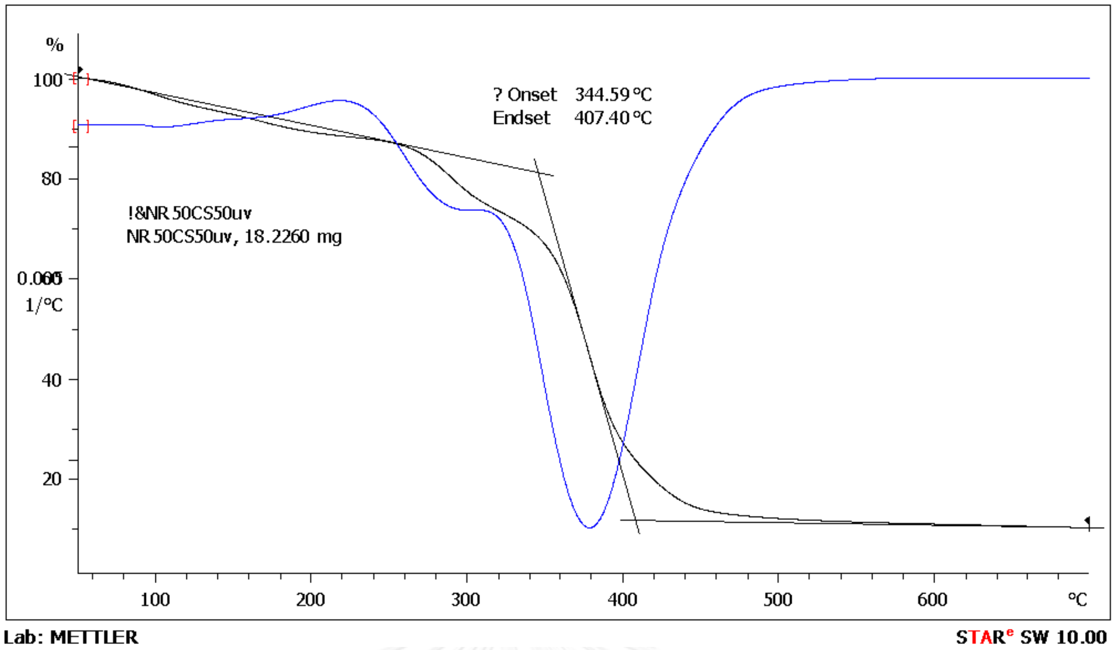

Figure D-7 TGA thermogram of the uncured 50/50 NR/CS film

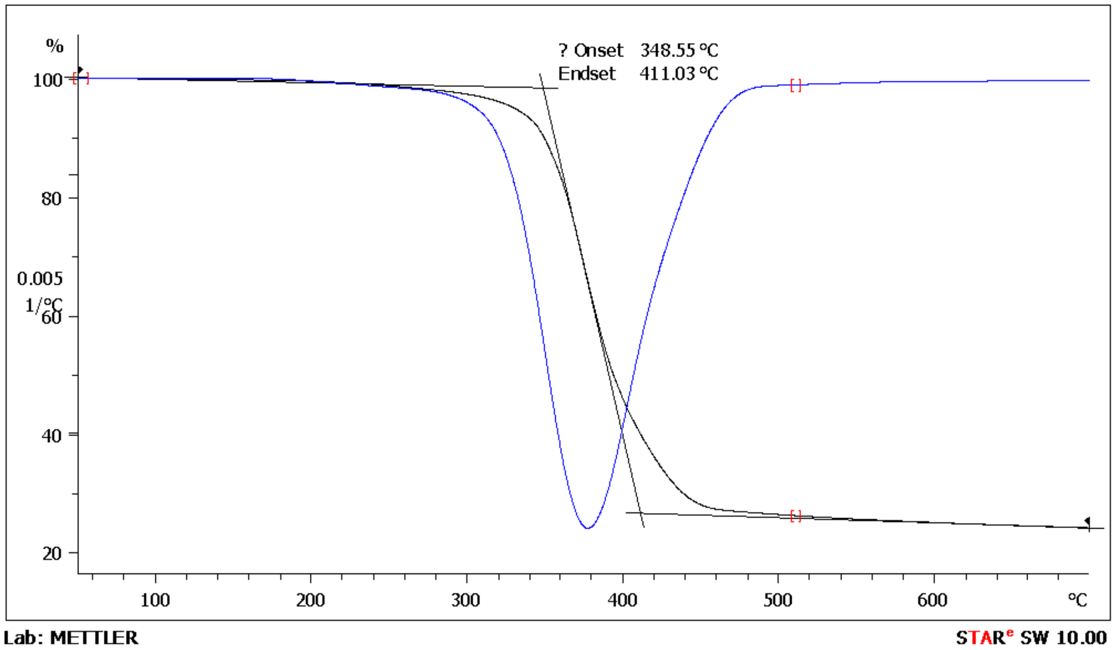

Figure D-8 TGA thermogram of the cured 100/0 NR/CS film

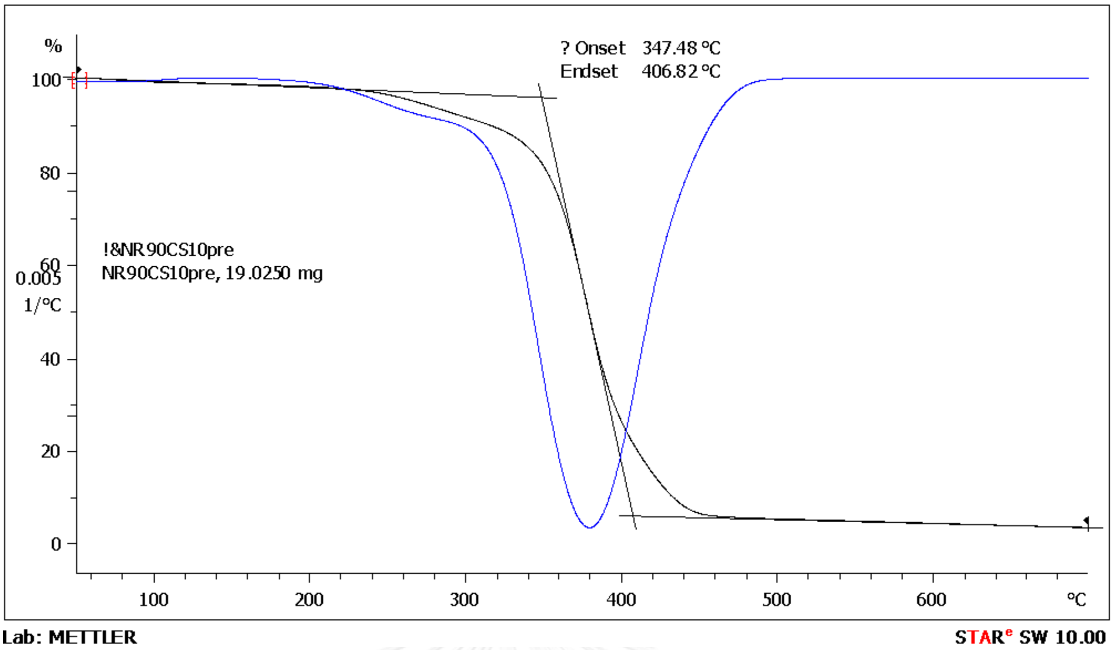

Figure D-9 TGA thermogram of the cured 90/10 NR/CS film

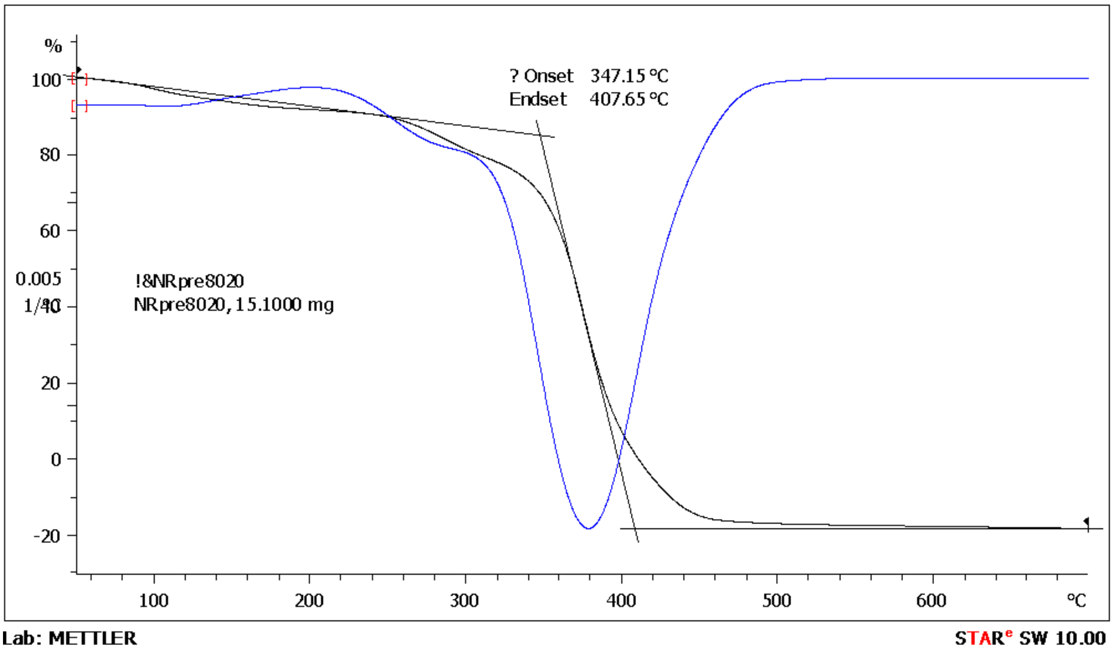

Figure D-10 TGA thermogram of the cured 80/20 NR/CS film

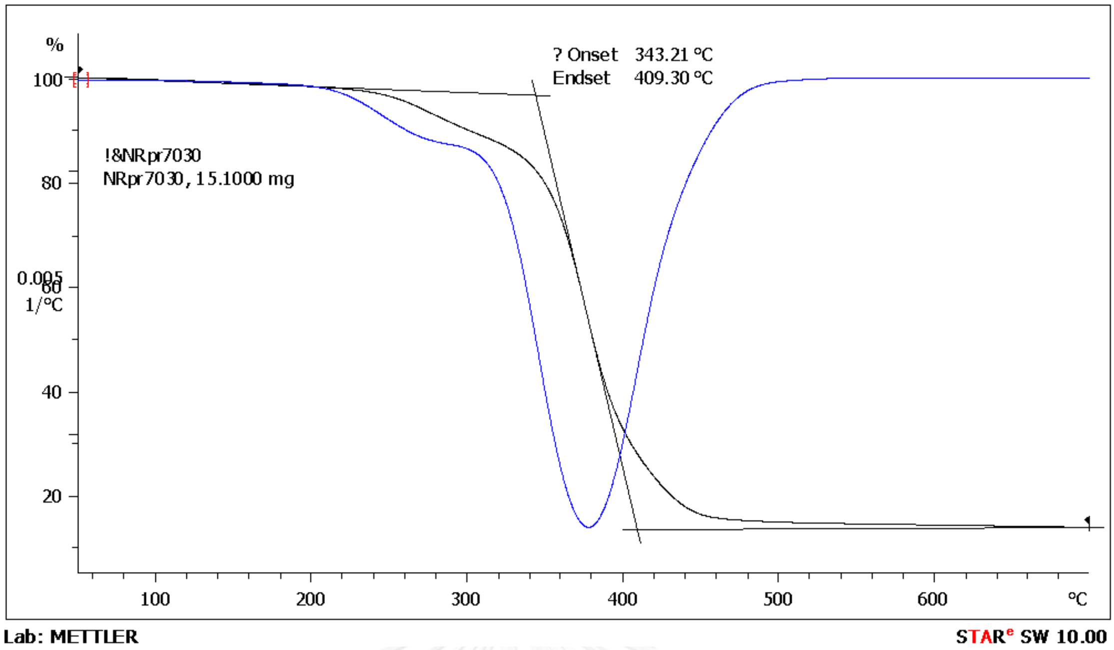

Figure D-11 TGA thermogram of the cured 70/30 NR/CS film

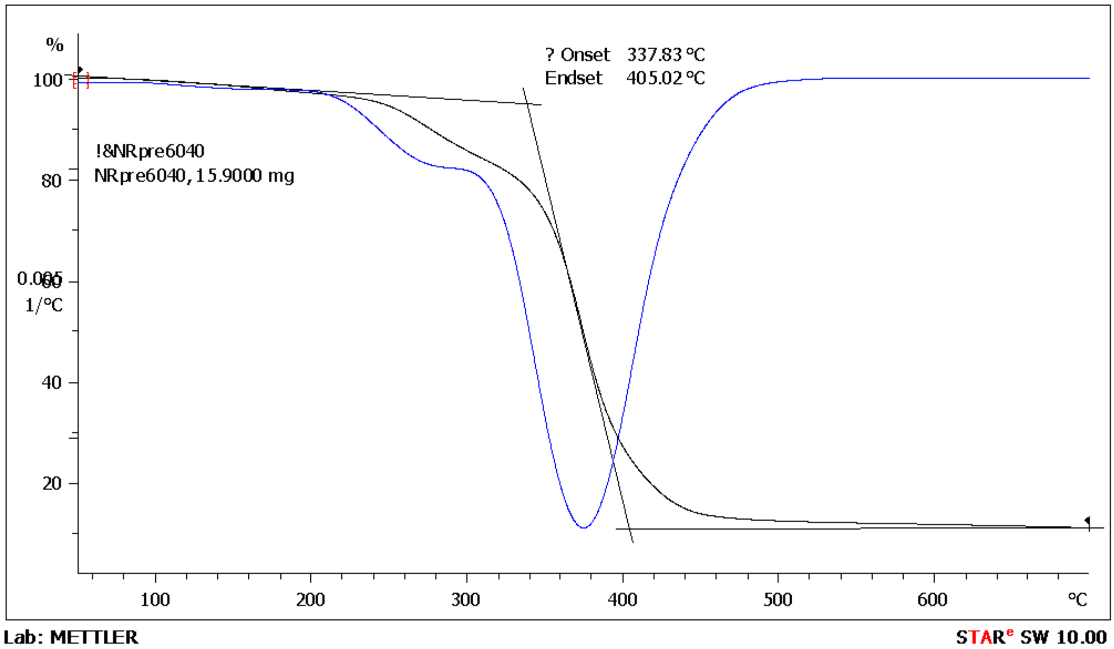

Figure D-12 TGA thermogram of the cured 60/40 NR/CS film

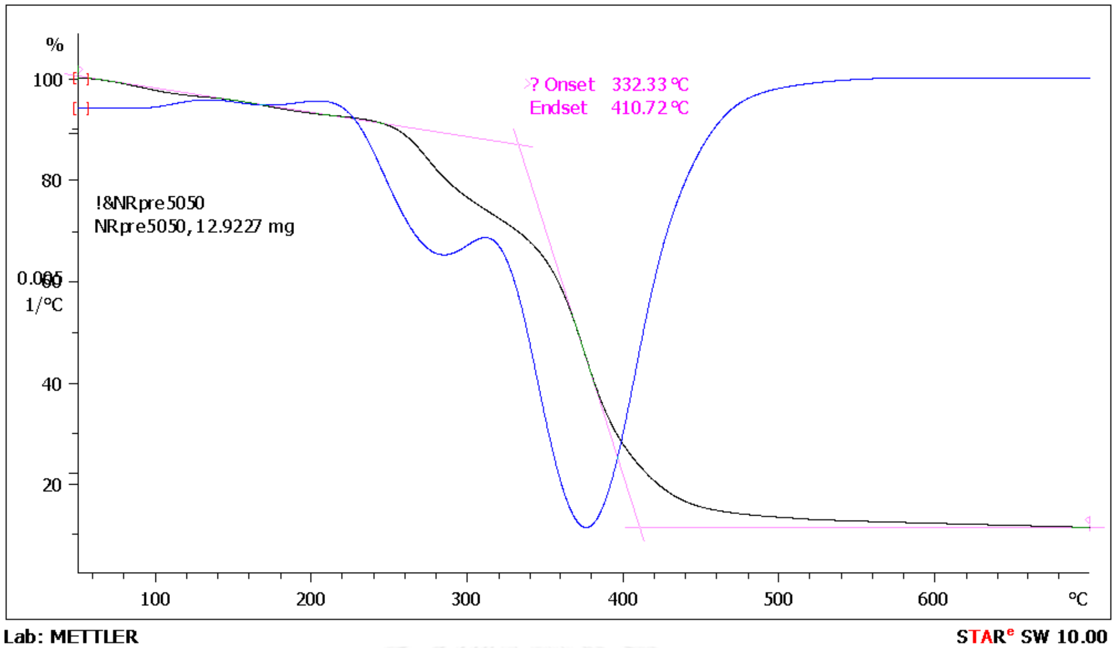

Figure D-13 TGA thermogram of the cured 50/50 NR/CS film

THERMAL PROPERTIES OF ENR/CS FILMS

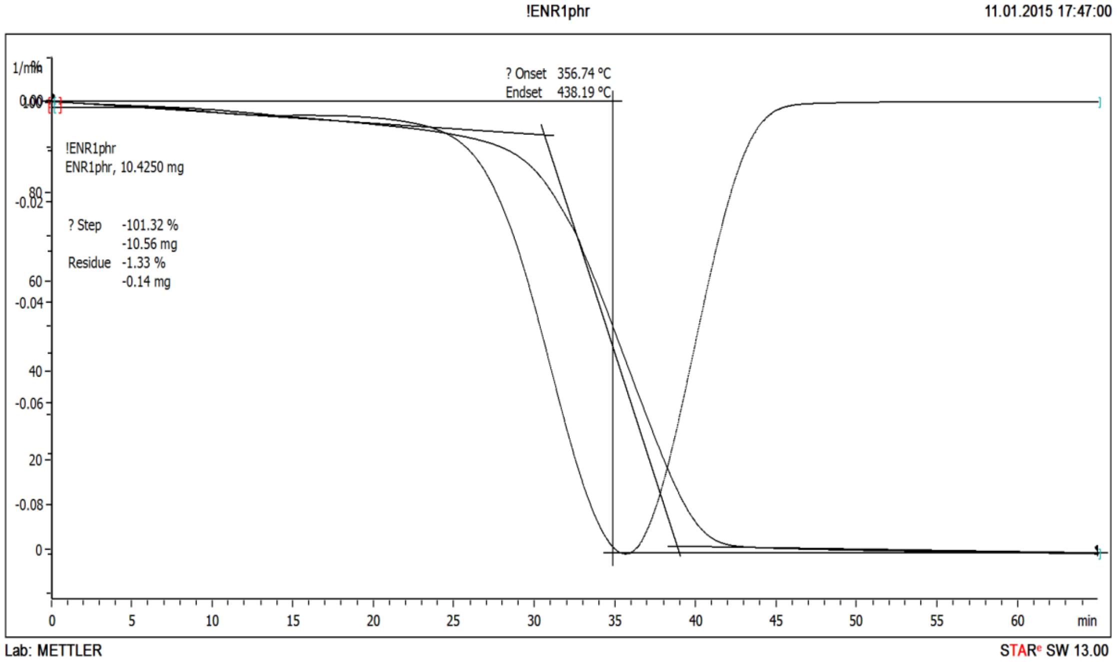

Figure D-14 TGA thermogram of the 100/0 ENR/CS film with MA of 1 phr

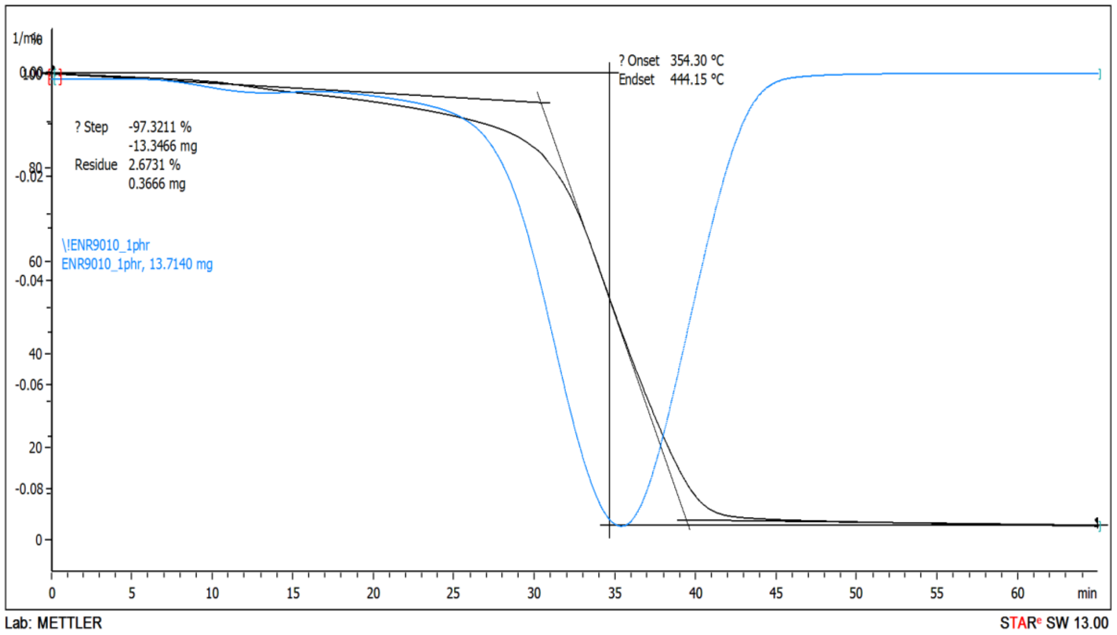

Figure D-15 TGA thermogram of the 90/10 ENR/CS film with MA of 1 phr

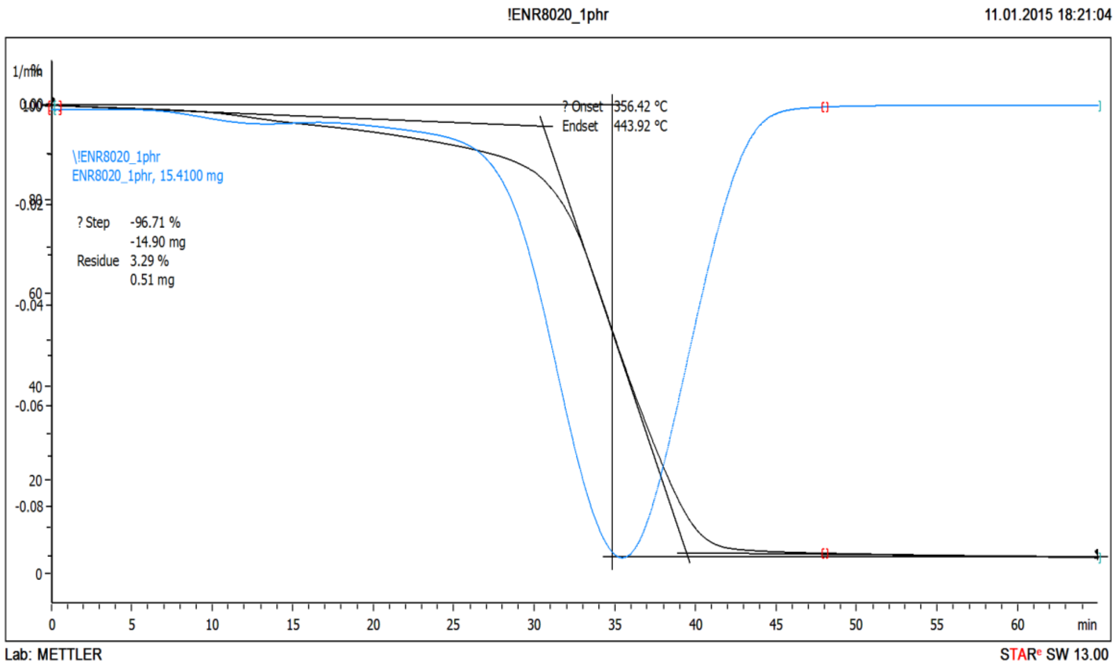

Figure D-16 TGA thermogram of the 80/20 ENR/CS film with MA of 1 phr

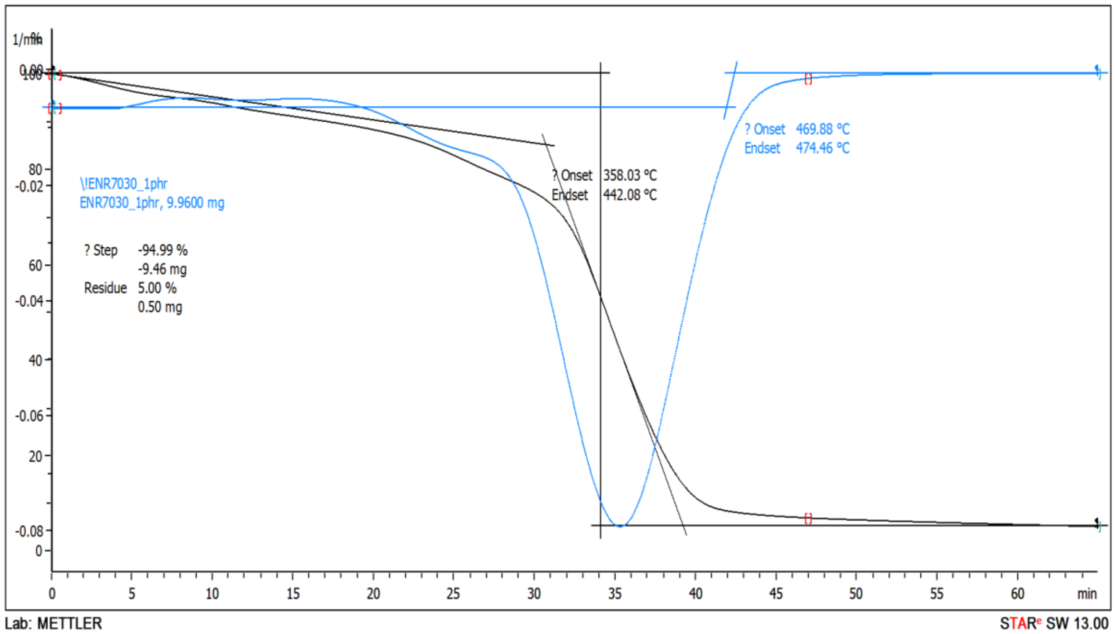

Figure D-17 TGA thermogram of the 70/30ENR/CS film with MA of 1 phr

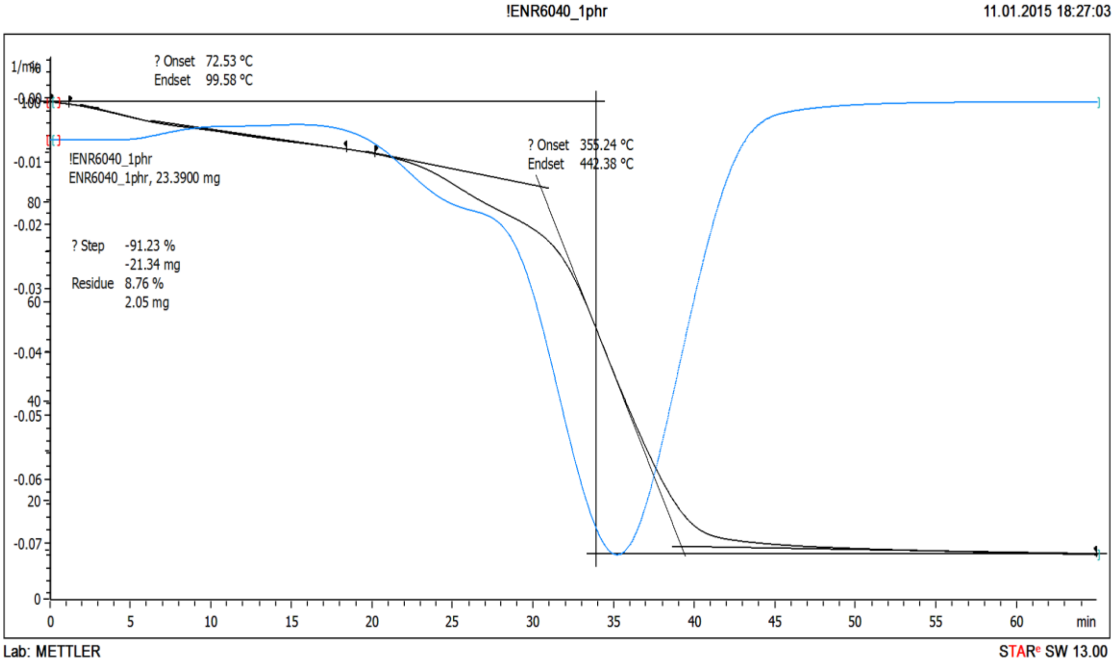

Figure D-18 TGA thermogram of the 60/40 ENR/CS film with MA of 1 phr

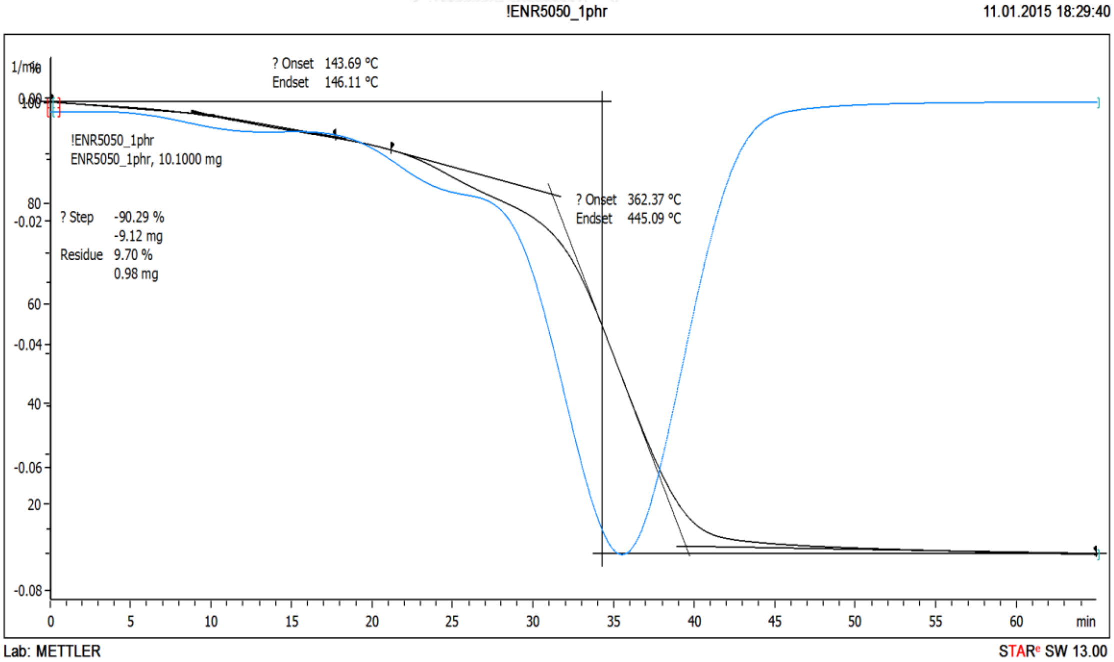

Figure D-19 TGA thermogram of the 50/50 ENR/CS film with MA of 1 phr

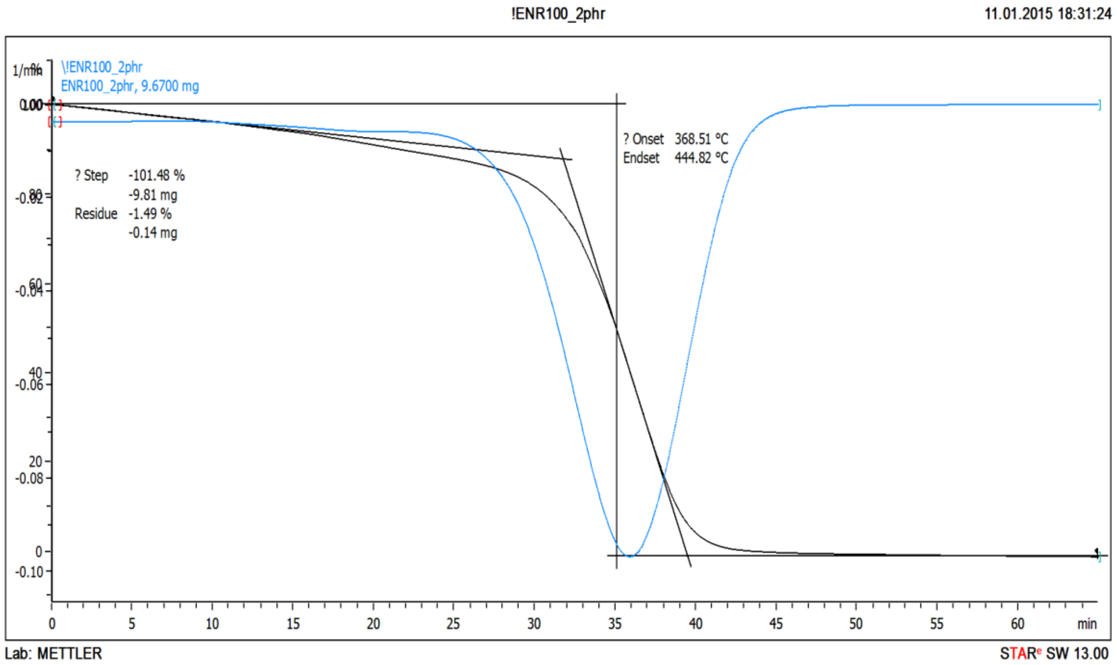

Figure D-20 TGA thermogram of the 100/0 ENR/CS film with MA of 2 phr

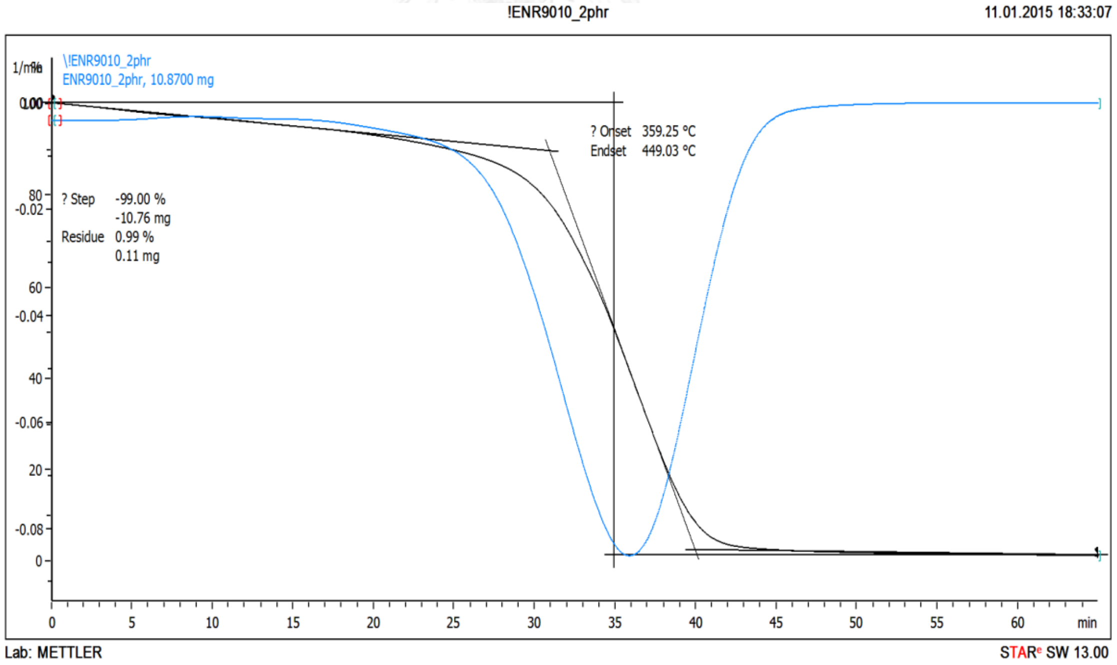

Figure D-21 TGA thermogram of the 90/10 ENR/CS film with MA of 2 phr

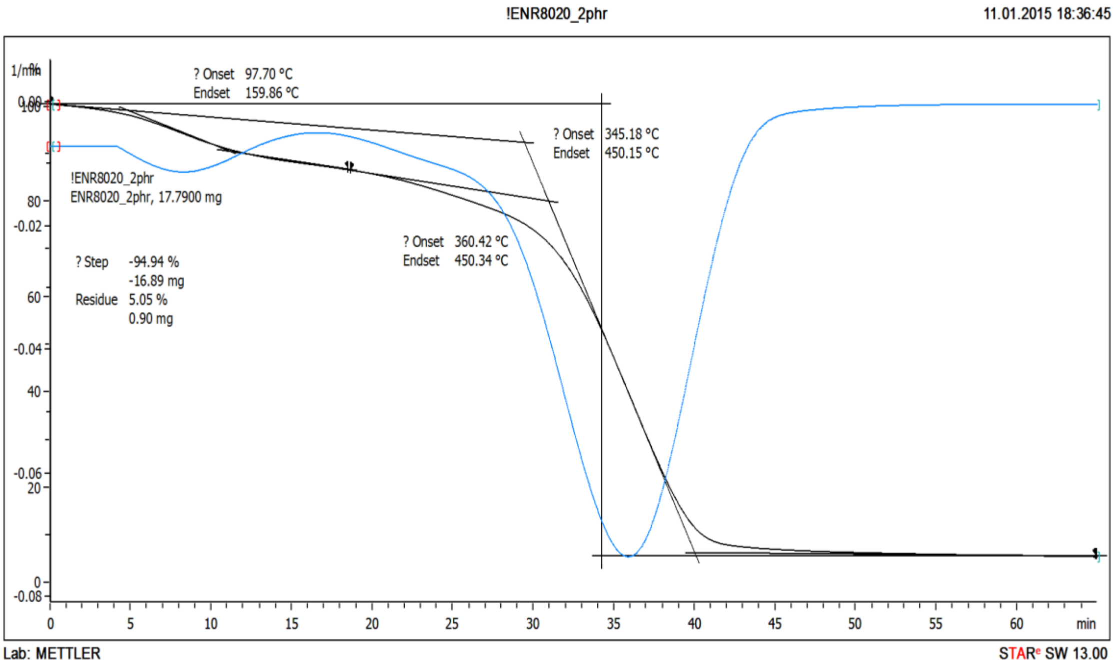

Figure D-22 TGA thermogram of the 80/20 ENR/CS film with MA of 2 phr

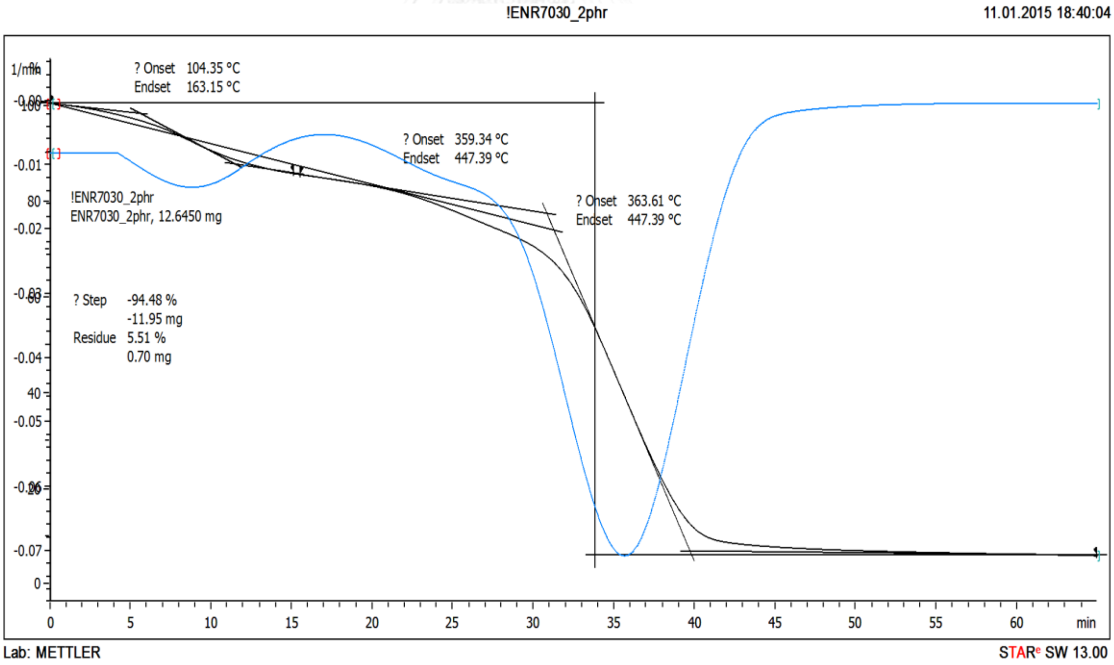

Figure D-23 TGA thermogram of the 70/30ENR/CS film with MA of 2 phr

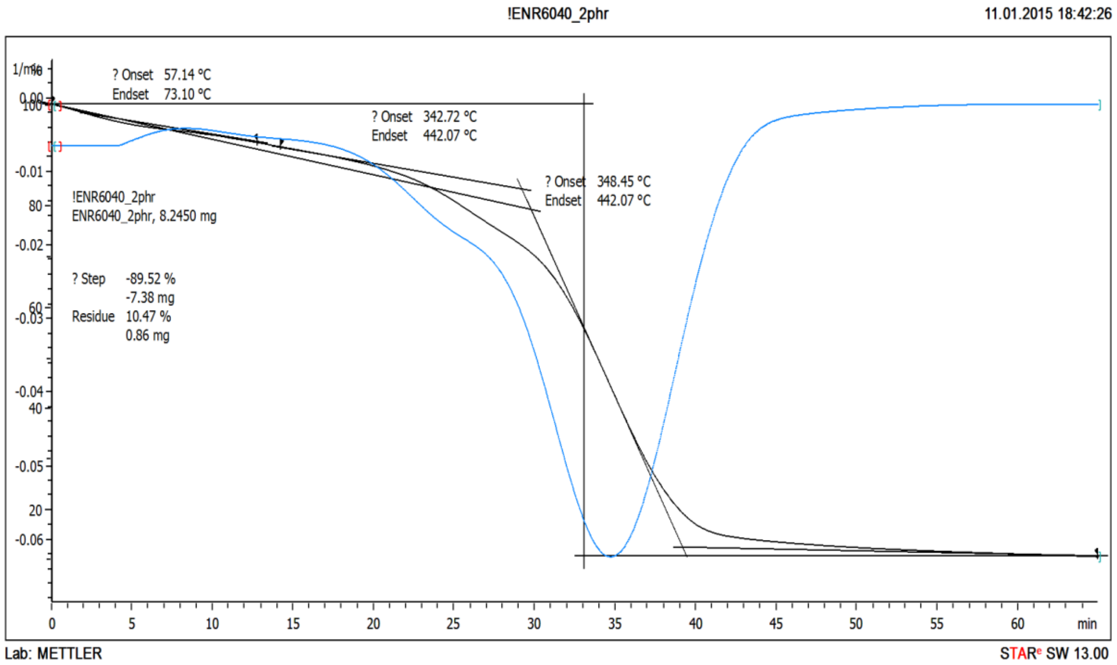

Figure D-24 TGA thermogram of the 60/40 ENR/CS film with MA of 2 phr

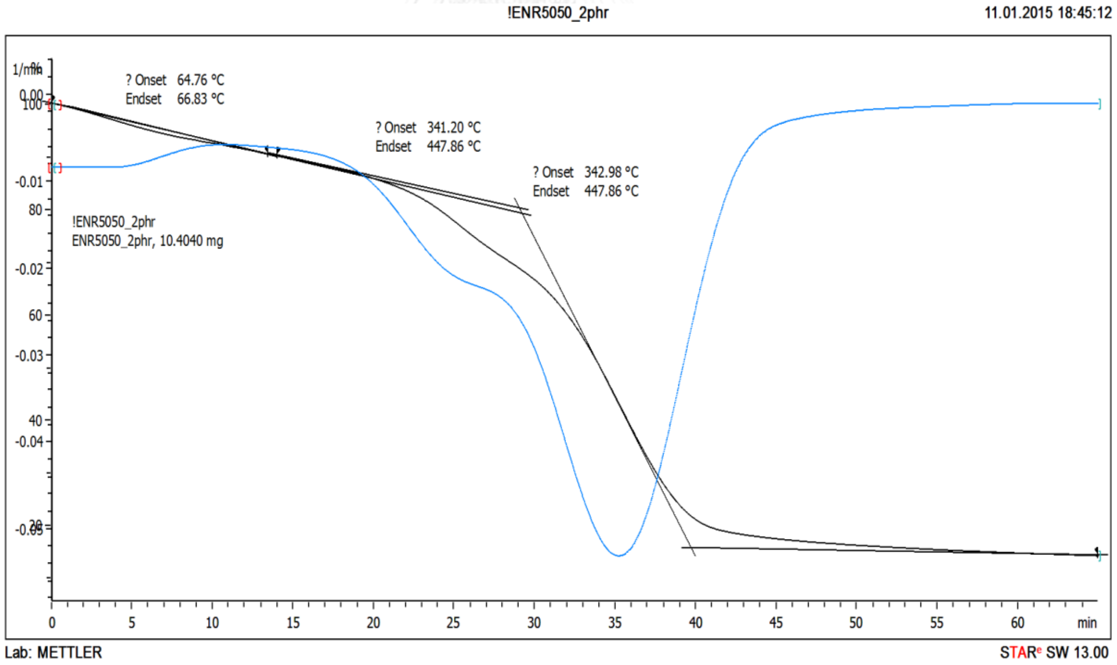

Figure D-25 TGA thermogram of the 50/50 ENR/CS film with MA of 2 phr

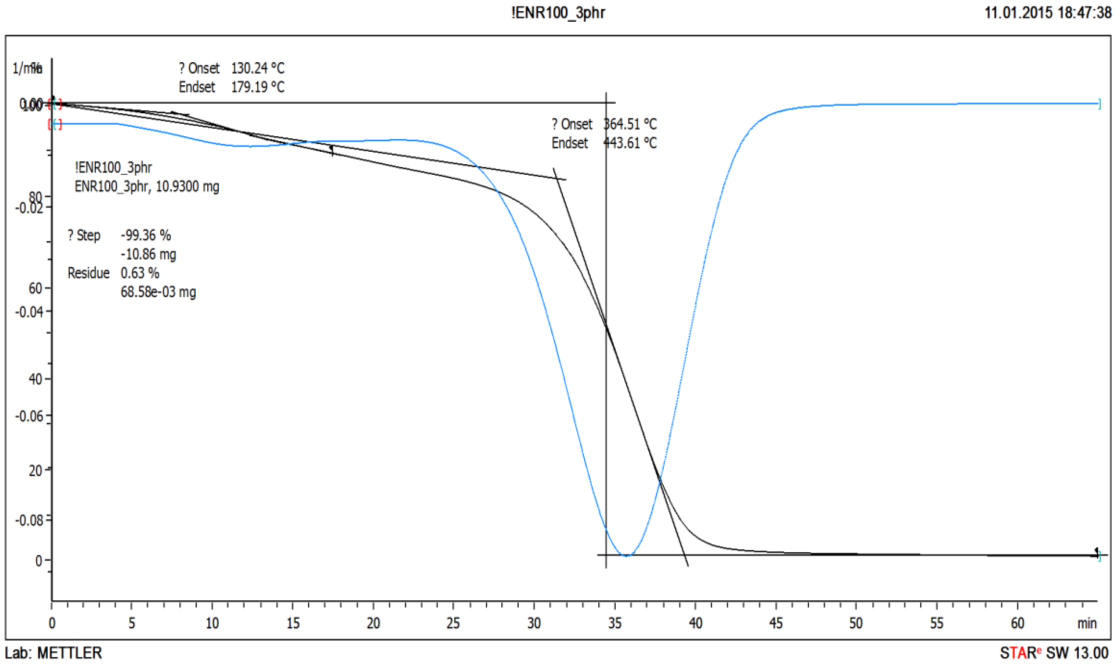

Figure D-26 TGA thermogram of the 100/0 ENR/CS film with MA of 3 phr

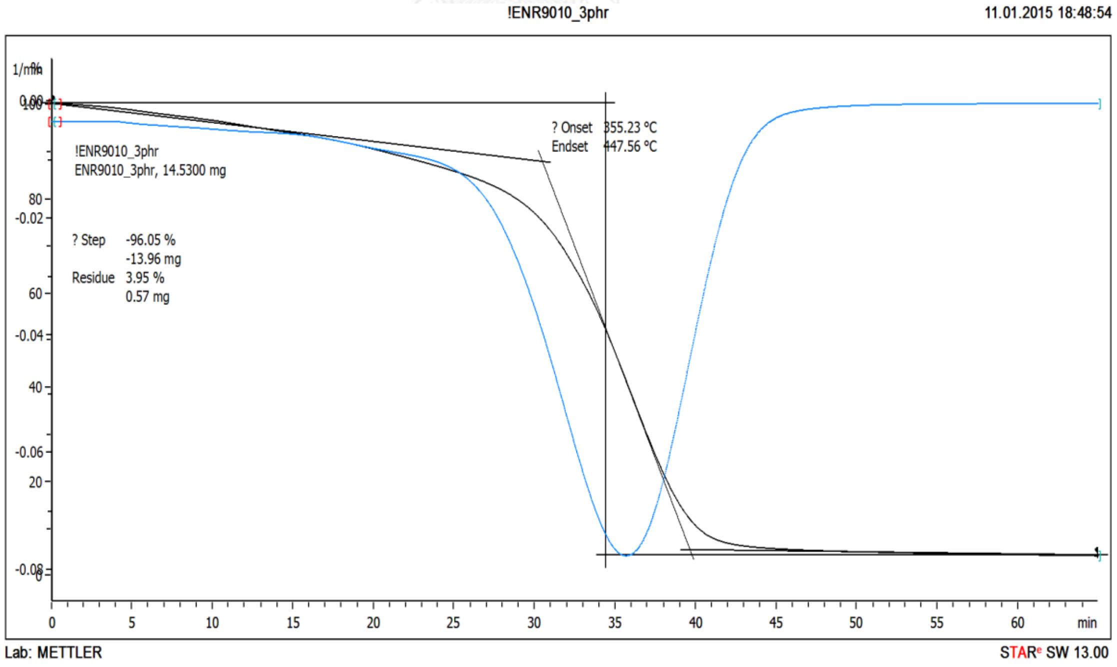

Figure D-27 TGA thermogram of the 90/10 ENR/CS film with MA of 3 phr

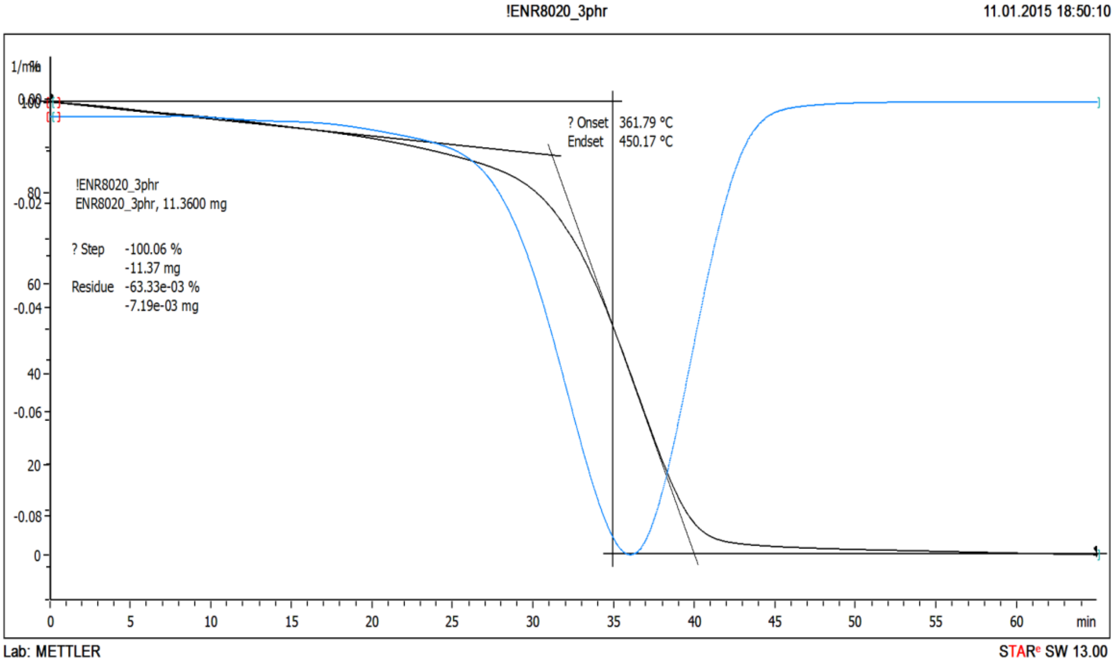

Figure D-28 TGA thermogram of the 80/20 ENR/CS film with MA of 3 phr

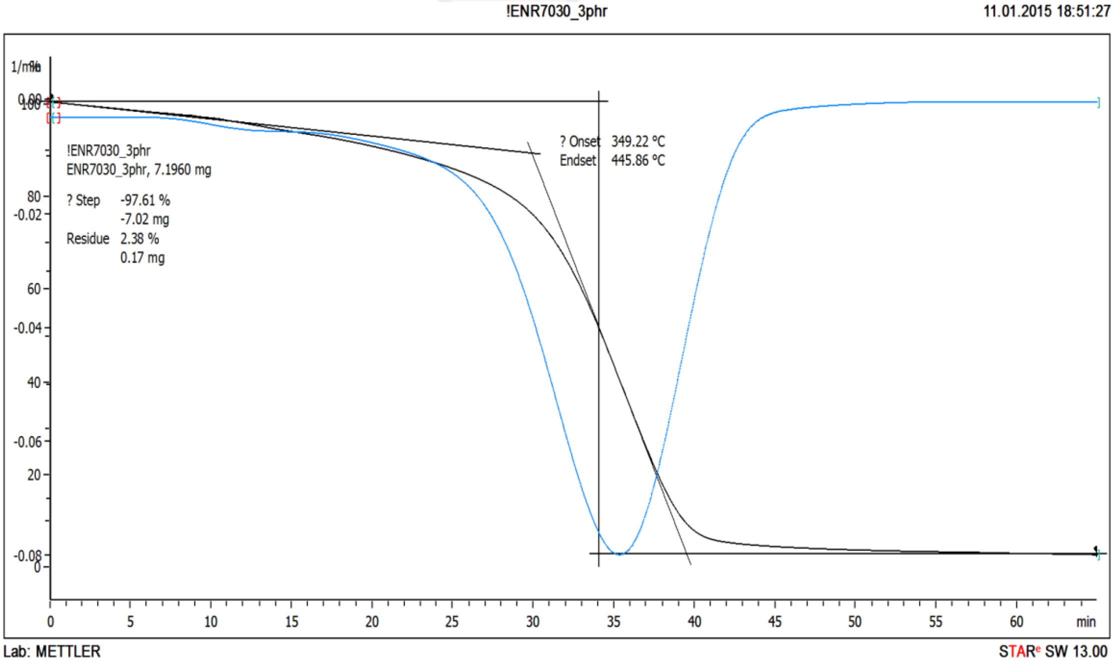

Figure D-29 TGA thermogram of the 70/30 ENR/CS film with MA of 3 phr

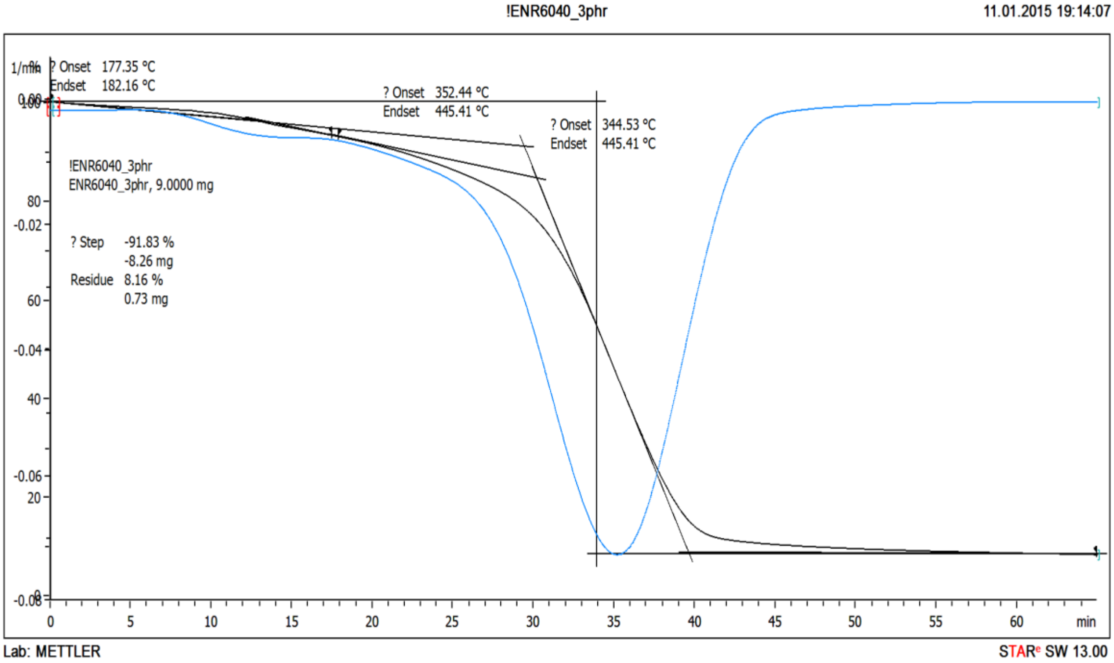

Figure D-30 TGA thermogram of the 60/40 ENR/CS film with MA of 3 phr

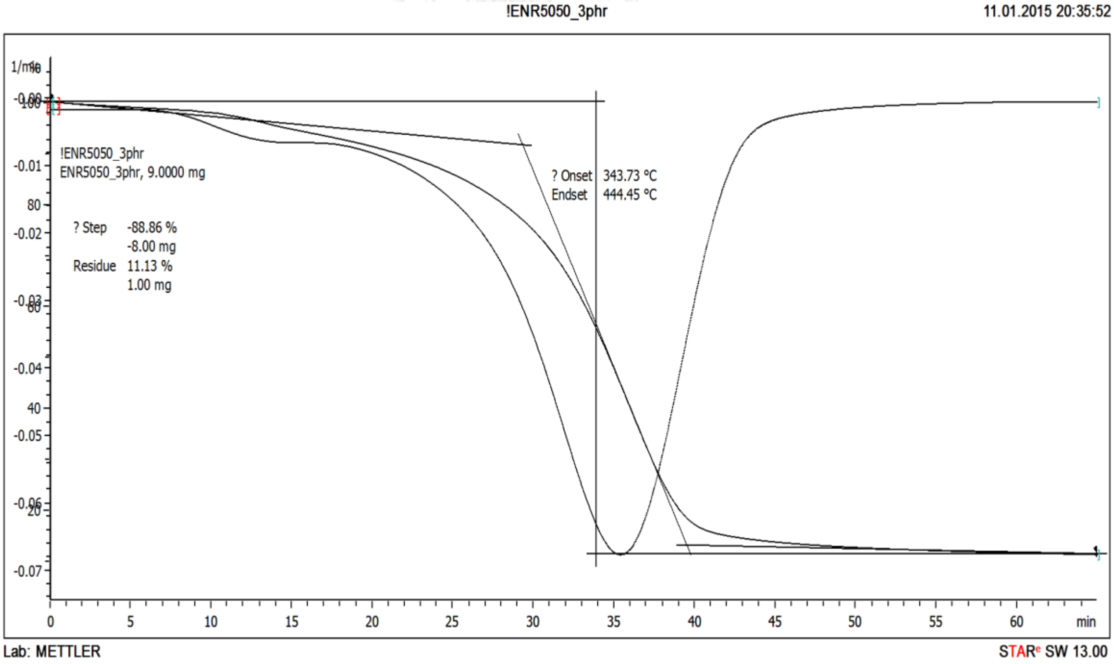

Figure D-31 TGA thermogram of the 50/50 ENR/CS film with MA of 3 phr

VITA

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