EFFECT OF SURFACE MODIFICATION ON PHYSICAL PROPERTIES OF SISAL FIBER/NATURAL RUBBER COMPOSITES

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ผลของการดัดแปรพื้นผิวต่อสมบัติทางกายภาพของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติ

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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EFFECT OF SURFACE MODIFICATION ON PHYSICAL PROPERTIES OF SISAL FIBER/NATURAL RUBBER COMPOSITES

Suranaree University of Technology has approved this thesis submitted in partial fulfillments of the requirement for a Master's Degree.

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วิทวัส วงษ์โสรัจ : ผลของการดัดแปรพื้นผิวต่อสมบัติทางกายภาพของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติ (EFFECT OF SURFACE MODIFICATION ON PHYSICAL PROPERTIES OF SISAL FIBER/NATURAL RUBBER COMPOSITES) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.กษมา จารุกำจร, 117 หน้า.

ในวิทยานิพนธ์นี้ เส้นใยป่านศรนารายณ์ถูกใช้ในการเสริมแรงยางธรรมชาติ ปริมาณเส้นใยคือ 10 20 และ 30 ส่วนในหนึ่งร้อยส่วนของยางธรรมชาติ พอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติถูกเตรียมโดยเครื่องผสมแบบสองลูกกลิ้ง ชิ้นงานสำหรับทดสอบถูกเตรียมโดยเครื่องกดอัด สมบัติทางกล สัณฐานวิทยา และสมบัติการคงรูปของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติได้ถูกตรวจสอบ การทำอัลคาไลน์เซชัน และการใส่สารช่วยให้เข้ากัน ได้แก่ ยางธรรมชาติอิพ็อกซิไดซ์ และยางธรรมชาติกราฟท์มาเลอิกแอนไฮไดรด์ ถูกใช้ในการเพิ่มความเข้ากันได้ระหว่างเส้นใยและยางธรรมชาติ

ยางธรรมชาติกราฟท์มาเลอิกแอนไฮไดรด์ถูกเตรียมโดยเครื่องบดผสมภายใน อินฟราเรดสเปกโตรสโคปี และการไทเทรตถูกใช้เพื่อยืนยันการกราฟท์ของมาเลอิกแอนไฮไดรด์บนยางธรรมชาติ และเพื่อวิเคราะห์ปริมาณการกราฟท์ของมาเลอิกแอนไฮไดรด์บนโมเลกุลของยางธรรมชาติ ปริมาณการกราฟท์ของมาเลอิกแอนไฮไดรด์บนยางธรรมชาติที่สูงที่สุดเตรียมโดยใช้มาเลอิกแอนไฮไดรด์ 6 ส่วนในหนึ่งร้อยส่วนของยางธรรมชาติและไดคิวมิวเปอร์ออกไซด์ 1 ส่วนในหนึ่งร้อยส่วนของยางธรรมชาติ

จากผลการทดลองพบว่า เมื่อเพิ่มปริมาณของเส้นใย ค่ามอดุลัสที่ 100 เปอร์เซ็นต์การดึงยืด ค่ามอดุลัสที่ 300 เปอร์เซ็นต์การดึงยืด ค่าการทนทานต่อการฉีกขาด และค่าความแข็งของพอลิเมอร์เชิงประกอบของยางธรรมชาติที่ใส่เส้นใยที่ไม่ผ่านการปรับปรุงและเส้นใยที่ผ่านการทำอัลคาไลน์เซชันมีค่าเพิ่มขึ้น ในขณะที่ค่าการทนทานต่อแรงดึง และค่าเปอร์เซ็นต์การยืดตัวก่อนขาดมีค่าลดลง แต่อย่างไรก็ตามเวลาการคงรูปของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติมีค่าลดลงเมื่อเพิ่มปริมาณของเส้นใย นอกจากนี้ปริมาณของเส้นใยไม่ส่งผลกระทบอย่างมากต่อเวลาการสกอร์ช

พอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์ที่มีการทำอัลคาไลน์เซชันกับยางธรรมชาติ แสดงสมบัติทางกลที่สูงกว่าเมื่อเปรียบเทียบกับพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์ที่ไม่มีการปรับปรุงกับยางธรรมชาติที่ทุกปริมาณเส้นใย เนื่องมาจากการปรับปรุงแรงยึดติดระหว่างเส้นใย และยางธรรมชาติผ่านกลไกแบบการเชื่อมต่อกันทางกล แต่อย่างไรก็ตาม

เวลาการคงรูปและเวลาการสกอร์ช ของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์ที่มีการทำอัลคาไลน์เซชันกับยางธรรมชาติและพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์ที่ไม่มีการปรับปรุงกับยางธรรมชาติพบว่ามีค่าไม่ต่างกันมาก

เมื่อเปรียบเทียบระหว่างการทำอัลคาไลน์เซชัน และการใส่สารช่วยให้เข้ากัน พบว่าการใส่ยางธรรมชาติกราฟท์มาเลอิกแอนไฮไดรด์ให้ผลที่มีประสิทธิภาพมากที่สุดในการปรับปรุงสมบัติทางกลของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติ เนื่องมาจากการยึดติดระหว่างเส้นใย และยางธรรมชาติที่ดีกว่า เมื่อใส่ยางธรรมชาติกราฟท์มาเลอิกแอนไฮไดรด์เข้าไปในพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติ ส่งผลให้เวลาการสกอร์ช และเวลาคงรูปเพิ่มขึ้น แต่อย่างไรก็ตามเมื่อเพิ่มปริมาณของยางธรรมชาติกราฟท์มาเลอิกแอนไฮไดรด์ สมบัติทางกล เวลาการสกอร์ช และเวลาคงรูปของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติเพิ่มขึ้น

นอกจากนี้สมบัติการทนทานต่อแรงดึงของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติที่ปรับปรุงความเข้ากันได้ด้วยยางธรรมชาติกราฟท์มาเลอิกแอนไฮไดรด์ที่ปริมาณ 10 ส่วนในหนึ่งร้อยส่วนของยางธรรมชาติ ถูกเปรียบเทียบกับพอลิเมอร์เชิงประกอบระหว่างซิลิกากับยางธรรมชาติ และพอลิเมอร์เชิงประกอบระหว่างผงเขม่าดำกับยางธรรมชาติ ที่ปริมาณสารเสริมแรง 10 ส่วนในหนึ่งร้อยส่วนของยางธรรมชาติ พอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับยางธรรมชาติ ที่มีการปรับปรุงความเข้ากันได้ด้วยยางธรรมชาติกราฟท์มาเลอิกแอนไฮไดรด์แสดงค่ามอดุลัสจำเพาะ และค่าการทนทานต่อแรงดึงจำเพาะที่สูงกว่าทั้งพอลิเมอร์เชิงประกอบของยางธรรมชาติที่ใส่ซิลิกา และเขม่าดำ

สาขาวิชา วิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา____________________
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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม____________________

WITTAWAT WONGSORAT : EFFECT OF SURFACE MODIFICATION ON PHYSICAL PROPERTIES OF SISAL FIBER/NATURAL RUBBER COMPOSITES. THESIS ADVISOR : ASST. PROF. KASAMA JARUKUMJORN, Ph.D., 117 PP.

NATURAL RUBBER/SISAL FIBER/COMPOSITE/ALKALIZATION/
EPOXIDIZED NATURAL RUBBER/NATURAL RUBBER GRAFTED WITH MALEIC ANHYDRIDE

In this study, sisal fiber was used to reinforce natural rubber (NR). The fiber loadings were 10, 20, and 30 phr. Sisal fiber/NR composites were prepared using a two-roll mill. The specimens were molded using a compression molding machine. Mechanical properties, morphology, and cure characteristics of the sisal fiber/NR composites were investigated. Fiber alkalization and addition of compatibilizers, i.e. epoxidized natural rubber (ENR) and natural rubber grafted with maleic anhydride (NR-g-MA), were used to enhance the compatibility between the fiber and NR matrix.

NR-g-MA was prepared using an internal mixer. Fourier Transform Infrared Spectroscopy (FTIR) and a titration method were used to confirm the MA grafted onto NR molecule and to determine the level of MA grafted onto the NR molecule. The highest grafting level of NR-g-MA was obtained with maleic anhydride content of 6 phr and dicumyl peroxide content of 1 phr.

It was found that modulus at 100% strain (M100), modulus at 300% strain (M300), tear strength, and hardness of the NR composites filled with untreated and alkali treated fibers increased with increasing fiber loading whereas tensile strength and elongation at break of the NR composites decreased. Nonetheless, cure time of sisal fiber/NR composites decreased with increasing fiber loading but scorch time was not much affected by fiber loading.

Alkali treated sisal fiber/NR composites exhibited higher mechanical properties compared with untreated sisal fiber/NR composites at all fiber loadings due to improved interfacial adhesion between the fiber and NR matrix through the mechanical interlocking mechanism. However, cure time and scorch time of the untreated sisal fiber/NR composites and alkali treated sisal fiber/NR composites were not much different.

In comparison between alkalization and addition of the compatibilizers, NR-g-MA provided the most effective improvement of the mechanical properties of the sisal fiber/NR composites due to better adhesion between the sisal fiber and NR matrix. The prolonged scorch time and cure time of the composites were observed at the presence of NR-g-MA. However, with increasing NR-g-MA loading, the mechanical properties, scorch time, and cure time of the sisal fiber/NR composites were increased.

In addition, the tensile properties of NR-g-MA compatibilized NR composite containing 10 phr of NR-g-MA were compared with silica/NR and carbon black/NR composites at the filler loading of 10 phr. The NR-g-MA compatibilized NR composite showed higher specific modulus and tensile strength than the NR composites filled with silica and carbon black.

School of Polymer Engineering — Student's Signature ____________________

Academic Year 2010 — Advisor's Signature ____________________

Co-advisor's Signature ____________________

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Wittawat Wongsorat

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SYMBOLS AND ABBREVIATIONS

NR = Natural rubber

ENR = Epoxidized natural rubber

% = Percent

^{o} = Degree

^{o}C = Degree Celsius

mol = Mole

mol% = Percent by mole

wt% = Percent by weight

phr = Part per hundred of rubber

rpm = Revolution per minute

FTIR = Fourier Transform Infrared Spectrometer

MDR = Moving die rheometer

UTM = Universal testing machine

DCP = Dicumyl peroxide

NR-g-MA = Natural rubber grafted with maleic anhydride

STR = Standard thai rubber

IRHD = International rubber hardness degrees tester

SEM = Scanning electron microscope

OM = Optical microscope

hrs = hours

SYMBOLS AND ABBREVIATIONS (Continued)

wt/wt = Weight by weight

wt/v = Weight by volume

v/v = Volume by volume

cm^{-1} = Reciprocal centrimeter

MA = Maleic anhydride

CBS = N-cyclohexyl-2-benzothiazole-2-sulphenamide

UT = Untreated fiber

AT = Alkali treated fiber

ml = Milliliter

mm = Millimeter

g = Gram

cm^3 = Cubic centrimeter

min = Minute

dN-m = Deci newton meter

MPa = Mega Pascal

$\overline{L}_n$ = Number average fiber length

$\overline{L}_w$ = Weight average fiber length

V_e = Crosslink density

kN = Kilo Newton

kN/m = Kilo Newton per meter

keV = Kilo electron volt

CHAPTER I

INTRODUCTION

1.1 Background

Natural rubber (NR) is one of the versatile materials widely used in many applications. The main producers of NR are Thailand, Indonesia, Malaysia, and China. NR has several advantages such as low cost, low hysteresis, high resilience, excellent dynamic properties, and fatigue resistance (Teh, Mohd Ishak, Hashim, Karger-Kocsis, and Ishiaku, 2004). However, raw NR has poor mechanical properties. To improve its mechanical properties, ingredients such as accelerators, activators, crosslinking agents, and fillers are commonly mixed into rubber to obtain suitable properties (Ismail and Turky, 2001). In particular, the incorporation of fillers in NR matrix leads to significant improvement in mechanical properties of the NR composites (Dutta et al., 2001). Conventional fillers used in rubber industries are carbon black and silica. Carbon black is the most efficient reinforcing filler for rubber composites. However, the carbon black is a product produced from a nonrenewable resource (petroleum) and it always makes rubber products black. Besides carbon black, silica, and calcium carbonate ($CaCO_3$) are conventional fillers used in the rubber industry. However, they give lower level of reinforcement than carbon black of the same particle size (Hernandez, Ichazo, Gonzalez, and Albano, 2004).

Nowadays, natural fibers are received much more attention as alternative fillers for plastic and rubber products. The advantages of natural fibers over the traditional fillers for NR composites are low cost, low density, renewability, and environmental friendly (Ismail, Rusli, and Rashid, 2005). Sisal fiber is one of the most interesting candidates for reinforcing natural rubber due to its high specific strength and modulus, low density, renewability, and no health risk. In addition, sisal fiber is a tropical plant which can cultivate in a wide range of area in Thailand.

Short fiber reinforced natural rubber composites have gained more interest due to improvement of their mechanical properties, ease of processing, and economic advantages (Lopattananon, N., Panawarangkul, K., Sahakaro, K., and Ellis, B., 2006). The properties of short natural fiber reinforced rubber composites depend on several factors such as fiber aspect ratio, fiber length, fiber content, fiber-rubber adhesion, fiber orientation, and dispersion (Geethamma, Thomas, and Kuriakose, 1995). The main problem of using natural fiber to reinforce NR is the incompatibility between a hydrophilic natural fiber and a hydrophobic NR, leading to poor mechanical properties of the composites.

The interfacial adhesion between the natural fiber and NR can be improved by various methods such as fiber surface treatment (Ismail and Hasliza, 1999), matrix modification (Pattamaprom, C., Bandidchutikun, K., Sotananan, S., and Phrommedetch, S., 2008), and addition of compatibilizer (Ismail and Haw, 2008). Alkalization is a common method to clean up and modify fiber surfaces by which the critical surface tension is lower and interfacial adhesion between natural fibers and polymer matrices is enhanced. In addition, the effective fiber surface area available for interaction with the matrix would be increased, too (Lopattananon, N. et al., 2006). Natural rubber grafted with maleic anhydride (NR-g-MA) is found to be an effective compatibilizer for paper sludge/NR composites (Ismail, Rusli, and Rashid, 2005). Natural rubber segments of NR-g-MA should be miscible with the bulk natural rubber and maleic anhydride segments of NR-g-MA may form hydrogen bonds with the hydroxyl groups of natural fibers. Therefore, the interfacial adhesion between the natural fiber and NR can be improved by use of NR-g-MA. Since NR does not contain polar groups in its structure, epoxidized natural rubber (ENR) is used as a compatibilizer to enhance natural fiber and NR adhesion. As the NR is epoxidized, its chemical and physical properties change according to the extent to which the mol% of modification is introduced. When the degree of epoxidation is increased the NR becomes more polar. This may be made ENR more compatible to sisal fiber than NR. When the ENR is added into the NR composites, the polar part of ENR may interact with sisal fiber and the NR part of ENR may be miscible with NR. These lead to the improvement of interfacial interaction between sisal fiber and NR matrix.

1.2 Research objectives

The aims of this research are as follows:

(i) To investigate effect of initiator content on a level of grafted MA onto NR molecule of natural rubber grafted with maleic anhydride (NR-g-MA).

(ii) To investigate effect of interfacial modifications by fiber alkalization and adding compatibilizers, and fiber loading on mechanical properties and cure characteristics of sisal fiber/NR composites.

(iii) To investigate effect of NR-g-MA loading on mechanical properties and cure characteristics of sisal fiber/NR composites.

(iv) To comparatively study the effect of sisal fiber, silica, and carbon black on mechanical properties and cure characteristics of NR composites.

1.3 Scope and limitation of the study

Natural rubber grafted with maleic anhydride (NR-g-MA) was prepared using an internal mixer. Maleic anhydride content was 6 phr and initiator (dicumyl peroxide) contents were varied as 0.5, 1.0, and 1.5 phr. Fourier Transform Infrared Spectroscopy (FTIR) was used to confirm the MA grafted onto natural rubber (NR) molecule and a titration method was used to determine the level of MA grafted onto NR molecules.

NR of STR 5L was used. Sisal fiber contents used in this study were 10, 20, and 30 phr. Fiber alkalization and addition of compatibilizers were used to enhance the compatibility between the sisal fiber and NR matrix. The compatibilizers were epoxidized natural rubber with 50 mol% of epoxide groups (ENR50) and NR-g-MA. The compatibilizer content was 5 phr. The concentration for sisal fiber alkalization was 2 wt% of sodium hydroxide (NaOH) solution. The sisal fiber/NR composites were prepared using a two-roll mill and test specimens were made using a compression molding machine. A conventional sulfur vulcanization system was used in this study.

Cure characteristics of sisal fiber/NR composites were determined using a moving die rheometer (MDR). Tensile and tear properties of sisal fiber/NR composites were investigated by a universal testing machine (UTM). Hardness of sisal fiber/NR composites were measured using an international rubber hardness degrees tester (IRHD). Morphologies of sisal fiber/NR composites were examined using a scanning electron microscope (SEM). Fiber length distribution was measured based on 200 samples using an optical microscope (OM). Crosslink density of sisal fiber/NR composites was investigated on the basis of rapid solvent-swelling measurements.

Based on the mechanical properties and cure characteristics of the compatibilized NR composites, either NR-g-MA or ENR was selected to further study the effect of compatibilizer content on the mechanical properties, cure characteristics, and morphology of the NR composites. The compatibilizer contents were 0, 2.5, 5.0, 7.5, and 10.0 phr.

The compatibilized NR composite giving the optimum mechanical properties and cure characteristics was chosen to compare its properties with NR composites filled conventional fillers, i.e. carbon black and silica of equal filler loading.

CHAPTER II

LITERATURE REVIEW

Natural fiber reinforced natural rubber composites have gained more attention due to low specific weight, renewable resource, and economic advantage. The advantages of natural fiber include low cost, non-abrasive to processing equipment, acceptable specific strength, biodegradability, and renewable resource. However, the main problem of using natural fiber to reinforce natural rubber is incompatibility between a hydrophilic natural fiber and a hydrophobic natural rubber leading to poor mechanical properties. To solve this problem, it is necessary to improve the interfacial adhesion between the natural fiber and natural rubber which can be carried out by various methods such as fiber surface treatment, matrix modification, and addition of compatibilizer.

2.1 Sisal fiber

Sisal fiber is obtained from the leaves of the plant *Agave sisalana,* which is originated from Mexico and is now mainly cultivated in East Africa, Brazil, Haiti, India, Indonesia, and Thailand (Nilsson, 1975; Mattoso, Ferreira, and Curvelo, 1997). The characteristics of the sisal fibers depend on the properties of the individual constituents, the fibrillar structure, and the lamellae matrix. The fiber is composed of numerous elongated fusiform fiber cells that narrow towards each end. The fiber cells are linked together by means of middle lamellae, which contain hemicellulose, lignin, and pectin. Figure 2.1 shows a schematic sketch of a sisal fiber cell. The cell walls consist of several layers of fibrillae structure. In the primary wall, the fibrillae have a reticulated structure. In the outer secondary wall (S_1), which is located inside the primary wall, the fibrillae are arranged in spirals with a spiral angle of 40^o in relation to the longitudinal axis of the cell. The fibrillae in the inner secondary wall (S_2) of sisal fibers have a sharper slope, 18 to 25^o. The thin, innermost, tertiary wall has a parallel fibrillar structure and encloses the lumen.

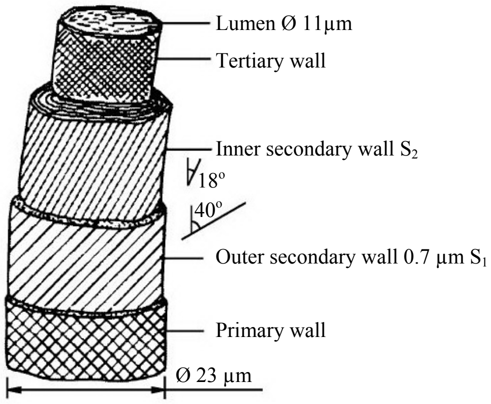


Figure 2.1 Schematic sketch of sisal fiber cell (Gram, 1983).

Natural fibers compose of cellulose, hemicellulose, lignin, pectin, and waxes. Cellulose is a natural polymer consisting of D-anhydro-glucose ($C_6H_{11}O_5$) repeating units connected by β-1,4-glyco-sidic linkages at C_1 and C_4 position (Nevell and Zeronian, 1985). Each repeating unit has three hydroxyl groups. These hydroxyl groups and their ability to form hydrogen bond play a major role in directing the crystalline packing and also control the physical properties of cellulose. Hemicellulose contains several different sugar units while cellulose contains only 1,4-β-D-glucopyranose units. Moreover, it exhibits a significant degree of chain branching giving rise to its noncrystalline nature. Lignin is totally amorphous and hydrophobic in nature. It is the three-dimensional copolymer of aliphatic and aromatic constituents that gives rigidity to the plants. Pectin is a collective name for heteropolysaccarides. It provides flexibility to plants. Waxes make up the last part of fibers and they consist of different types of alcohols. The structure, microfibrillar angle, cell dimensions, defects, and the chemical composition of fibers are the important variables that determine the overall properties of the fibers (Murherjee and Satyanarayana, 1984). Chemical composition and tensile properties of the sisal fiber reported by many researchers are listed in Table 2.1 and 2.2 respectively.

Table 2.1 Chemical composition of sisal fiber reported by many researchers.

Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)	Waxes (%)	References
65	12	9.9	-	2	John and Anandjiwala (2008)
47-78	10-24	7-11	-	-	Mohanty, Misra, and Drzal (2001)
73.8	11	9.7	-	-	Bledzki and Gassan (1999)
73	13	11	2	-	Mwaikambo and Ansell (2002)
78	10	8	-	2	Bledzki and Reihmane (1996)

Table 2.2 Tensile properties of sisal fiber reported by many researchers.

Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	References
604	9.40-15.80	-	Satyanarayana et al. (1990)
530-630	17-22	3.64-5.12	Murherjee and Satyanarayana (1984)
400-700	9-20	5-14	Kalaprasad, Joseph, and Thomas (1997)
450-700	7-13	4-9	Manikandan, Nair, and Thomas (1996)
155-471	12.74-34.30	1.60-10.47	Kaewkuk (2010)

2.2 Fiber surface treatment

Fiber surface treatment can be classified into chemical method and physical method. Both methods are different efficiencies for improving the adhesion between fiber and matrix.

2.2.1 Chemical methods

2.2.1.1 Alkalization

The interest in alkali treated natural fibers has increased dramatically in the past decade. Alkali treatment is a common method to clean and modify fiber surfaces to lower surface tension and enhance interfacial adhesion between natural fibers and polymer matrices. Bisanda (2000) studied the effect of alkali treatment on the adhesion characteristics of sisal fiber/epoxy composites. The treatment of sisal fibers with 0.5N of NaOH solution improved adhesion characteristics due to increased surface roughness and surface tension of the fiber. In addition, the removal of lignin and other surface waxy substances by alkali solution increased the chance for mechanical interlocking between matrix and fiber.

This resulted in the composites with improvements in the compressive strength and water resistance.

Ray, Sarkar, Basak, and Rana (2002) treated jute fibers with 5% NaOH for 2, 4, 6, and 8 hrs. Thermal analysis results showed the moisture desorption was observed at a lower temperature in all treated fibers due to the increased fineness of the fiber which offered more surface area for moisture evaporation. In all treated fibers, the percentage degradation of the hemicellulose decreased considerably. This confirmed that the hemicellulose content was lowered on the alkali treatment. The decomposition temperature for α-cellulose was lowered to 348°C from 362.2°C for all treated fibers and the residual char formation increased to a significant extent. The enthalpy for the thermal degradation of α-cellulose showed a decreasing trend for 2 and 4 hrs treated fibers, which could be caused by the initial loosening of the structure.

Sydenstricker, Mochnaz, and Amico (2003) examined the thermal properties of NaOH treated sisal fibers. NaOH treatment gave a decrease in density of sisal fibers and lignin content. This was attributed to a reduction in moisture absorption of sisal fiber. TGA results showed that NaOH treated sisal fiber became more thermally resistant as compared to untreated fiber.

Lopattananon, N. et al. (2006) treated pineapple leaf fibers with 1, 3, 5, 7% wt/v of NaOH solution. FTIR results showed that after alkalization the peaks of lignin (1436 cm^{-1}) was reduced and hemicellulose (1254 cm^{-1}) structure was absent due to complete decomposition of hemicellulose and partial leaching out of lignin by the NaOH. This indicated that the ester type in hemicellulose was more easily removed by an alkali solution. SEM micrograph of treated fiber showed the separation of the microfibrillar structure of fiber due to the removal of lignin and hemicellulose. The extraction of alkali soluble materials (lignin and hemicellulose) observed from SEM analysis clearly confirmed the FTIR spectra of treated fiber. The removal of lignin and hemicellulose appeared to increase with higher concentrations of alkali solution. The other impurities, e.g., waxes, had also been removed from the fiber surface. Consequently, the effective fiber surface area which was available for bonding with the matrix would be increased.

Das and Chakraborty (2006) examined the influence of alkali treatment on the structure and morphology of bamboo fibers. Bamboo fibers were treated with NaOH solution of various concentrations (10, 15, and 20%). X-ray diffraction results showed that a lattice transformation from cellulose-I to cellulose-II took place. Swelling test in NaOH found considerable changes in crystallinity and orientation angle. When the concentration of NaOH increased, degree of crystallinity and crystallinity index of bamboo strips increased and fell off after 15% concentration of NaOH. SEM micrograph indicated the fibrillation of bamboo fibers at higher alkali concentration.

Mwaikambo and Ansell (2006) reported the potential of alkali treated sisal fiber as reinforcement material. The fibers were treated with 0.03, 0.08, 0.16, 0.24, and 0.32% of NaOH solution for 48 hrs. SEM micrograph of alkali treated sisal fibers showed rough and void regions between individual fiber cells. The rough surface of fiber enhanced interface and improved packing order of the crystalline regions. Tensile test showed that Young's modulus and tensile strength of sisal fiber bundles depended on physical characteristics of fiber's internal structure such as the cellulose content, crystallinity index, and micro-fibril angle. The optimum Young's modulus and tensile strength were obtained at 0.16% of NaOH solution. The tensile strength and stiffness of the alkali treated sisal fiber made it suitable as reinforcement for the manufacture of composites.

Mohd Edeerozey, Md Akil, Azhar, and Zainal Ariffin (2007) treated kenaf fibers with different concentrations of NaOH solution (3, 6, and 9% NaOH). SEM micrograph showed that 3% NaOH was ineffective to remove the impurities on the fiber surface and 9% NaOH treatment showed the cleanest fiber surface. However, the fibers with 9% NaOH showed the worse results on tensile strength. This may be due to damage of the fiber resulting in lower tensile strength. It was found that at 6% NaOH gave the highest tensile strength. So, at 6% NaOH was an optimum concentration for kenaf fibers.

Mathew and Joseph (2007) treated isora fiber with 5% NaOH solution for 4 hrs. SEM micrograph showed strong evidence for the physical microcellular structural changes occurring in the fiber surface on alkalization. The pores became clearer and fibers became thinner. This might be due to the dissolution and leaching out of fatty acids and lignin components of the fiber. This rendered roughness to the fiber and thereby enhanced mechanical interlocking at the interface. The development of a rough surface topography offered better fiber-rubber interface adhesion and increased mechanical properties.

2.2.1.2 Silanization

Silane coupling agents are hydrophilic compounds with different groups attached to silicon. One end can interact with matrix and the other end can react with hydrophilic fiber. This reaction performs as a bridge between them. Gonzalez, Cervantes Uc, Olayo, and Herrera Franco (1999) treated henequen fibers with a 0.5% wt/wt dicumyl peroxide and 1% wt/wt vinyltris (2-methoxy-ethoxy) silane coupling agent. The fibers were immersed in silane solution for 1 hr. FTIR results showed that silane treated fibers showed the absorption bands at 700, 1030, 1145 and 1187 cm^{-1}, which were assigned to -Si-O-Si- bond. The shoulders at 965 and 1200 cm^{-1} implied the characteristic of the -Si-O-C- bond that came from the reaction of silane and the henequen fibers. The absorption bands at 860 and 930 cm^{-1} corresponding to the -Si-OH bond revealed the presence of residual hydrolyzed silane. The tensile test results showed that the composite with silane coupling agent had higher tensile strength than the composite without silane coupling agent. The interaction between the fiber and the matrix was enhanced when the fiber surface was modified with the silane coupling agent.

Ismail, Shuhelmy, and Edyham (2002) treated bamboo fiber with 3 phr of bis(triethoxysilyl propyl) tetra sulphide (Si69). SEM micrographs of the composites without Si69 showed many holes remaining after the fibers were pulled out from the rubber matrix and unwetted fibers on the surface particularly. However, the composites with Si69 showed a better adhesion between bamboo fibers and rubber matrix. The fibers were well wetted by the rubber matrix and the pulled out of fibers from rubber matrix was minimum. This may be because the silane coupling agent improved the surface functionality of the bamboo fibers and subsequently enabled bamboo fibers to bond chemically to the rubber matrix. Consequently, interfacial adhesion on the surface of the fiber increased and composites exhibited increased strength.

Pothan, Thomas, and Groeninckx (2006) investigated the role of fiber-matrix interactions in chemically modified banana fiber/polyester composites. Banana fibers were treated with 0.6% of γ-methacryloxypropyl trimethoxy silane (silane A174). DMA results showed that dynamic modulus values were increased and low damping values showed the improved interactions between the fiber and the matrix. The damping peaks were found to be dependent on the nature of chemical treatment. Both storage modulus and damping values measured experimentally were consistent and attributed to the effectiveness of silane A174 for improved fiber matrix adhesion

Abdelmouleh, Boufi, Belgacem, and Dufresne (2007) investigated the effect of various silane coupling agents on mechanical properties and water uptake ability of natural fiber reinforced polyethylene and natural rubber composites. The fibers were treated with 3% of three different silane coupling agents, namely γ-methacryloxypropyltrimethoxy (MPS), γ-mercaptoproyltrimethoxy (MRPS), and hexadecyltrimethoxy-silanes (HDS). The composites filled with MPS and MRPS treated fibers showed good mechanical properties. Both MPS and MRPS included of functional groups that can react with radical species to generate a covalent bond. The radical species might be created through peroxide decomposition which took place by thermal oxidation during the processing of the composites. Consequently, this reaction gave rise to chemical bonding between the fibers and matrix that led the enhancement in interfacial adhesion. The treatment of the fibers with HDS did not bring about significant reduction in water absorption compared to MPS or MRPS, despited the marked hydrophobic character of the ensuing modified fiber.

2.2.1.3 Acetylation

The main principle of acetylation is to react the hydroxyl group of the fiber with acetyl groups, therefore the fiber surface is more hydrophobic. Albano, Gonzalez, Ichazo, and Kaiser (1999) examined the effect of acetylation on thermal degradation of sisal fiber. TGA results showed that hemicellulose decomposition of acetylated fiber was missing and weight loss at the major degradation step (385ºC) increased. This implied that the acetylation increased the thermal stability of the fiber. The residue left at 427ºC of acetylated fiber was less than the untreated fiber because of the loss of volatile products that did not contribute to char formation.

Ichazo, Albano, and Gonzalez (2000) investigated the influence of acetylation on the surface morphology of sisal fiber reinforced polypropylene composites. The microfibers forming of acetylated sisal fibers could be seen clearly. An enhancement in aspect ratio of the acetylated fiber gave better fiber-matrix interface adhesion leading to an increase in mechanical properties. Moreover, this treatment provided an enhancement in wettability property and number of small void on the fiber surface that led mechanical interlocking between the fiber and matrix.

Rong, Zhang, Liu, Yang, and Zeng (2001) reported the effect of acetylation on the mechanical properties of unidirectional sisal reinforced epoxy composites. The tensile test showed that acetylation can improve tensile strength of sisal fibers. The improvement of interfacial bonding in sisal fiber reinforced epoxy composites was the results of (i) hydrogen bonds between acetyl groups and hydroxyl or amine groups in epoxy resin and (ii) mechanical interlocking between epoxy and the caved fiber surface due to the alkali pretreatment before acetylation.

2.2.2 Physical methods

2.2.2.1 Thermal treatment

Heating cellulose fiber at higher temperatures than normal drying conditions has been shown to appreciably reduce the hygroscopicity and the subsequent swelling and shrinking of the lingo-cellulosic material. The thermal modifications of wood result in changes of lignin and hemicelluloses that become less hygroscopic, while the crystallinity of fiber increases. Rusche (1973) studied the strength properties of dried wood fiber after thermal treatment. Wood fibers were heated at temperature range 100 to 200°C. The decrease in the strength properties was related to the rate of thermal degradation. The modulus of elasticity decreased significantly only when the losses of substance caused by the thermal treatment.

Hakkou, Petrissana, Zoulalian, and Gerardin (2005) investigated the change of wettability of wood during thermal treatment. Wood blocks were thermal treatment in an oven at different temperature (20-240^{o}C) for 8 hrs. FTIR results showed that thermal treatment led to an important decrease of the carbonyl band at 1730 cm^{-1} indicating hemicelluloses degradation. The hydrophilic wood became rather hydrophobic after thermal treatment in a range of temperatures between 130 and 160^{o}C.

Saikia (2008) reported the effect of heat on the structural characteristics of sisal fiber. X-ray diffraction and IR results showed that sisal fiber had a cellulosic structure in nature. The cellulosic structure of the fiber was unchanged on heating up to 177°C. TG, DTG, and DSC studies showed that three distinct thermal processes occurred in the fiber under heating at temperature from 37°C to 487°C. The first step took place in a temperature range from approximate

37°C to 107°C due to a dehydration process. No decomposition of the fiber took place up to about 227°C. The second thermal process of the sample was under heating in the temperature above 227°C. Thermal decomposition led to incomplete carbonization of the fibers. The original structural features of the cellulosic were not completely lost in temperature above 227°C. The third thermal process was representative of combustion of the fibers to carbonized material.

2.2.2.2 Corona treatment

The corona treatment of the natural fibers leads to an increase in the polar component of the free surface energy, mainly due to increasing the content of carboxyl and hydroxyl groups. Gassan and Gutowski (2000) improved the properties of tossa jute fibers reinforced epoxy composites by treatment of tossa jute fibers with corona discharge. Corona treated fibers showed higher polar components of free surface energy with increasing treatment energy output. It was found that at the optimum treatment condition, an increase in the composite flexural strength of about 30% was achieved.

Gassan, Gutowski, and Bledzki (2000) studied the surface characteristics of corona treated jute fibers. The corona treatment increased the polarity of jute fibers, while the non-polar component was constant over the whole range of corona energy output. The adhesion at the fiber-matrix interface may be increased due to the increase of the number of carboxyl and hydroxyl groups, as confirmed by the increase in the surface polarity. The strength and fracture performance of the composite lowered when fibers were over-treated.

2.3 Matrix modification

Epoxidized natural rubber (ENR) has been introduced as a modified form of natural rubber (NR). As the NR is epoxidized, its chemical and physical properties change according to the extent to which the mole % of modification is introduced. When the degree of epoxidation is increased the rubber becomes more polar. This may be made ENR more compatible to natural fiber than NR. Mohd Ishak and Bakar (1995) investigated the mechanical properties of oil palm wood flour reinforced ENR composites. With increasing oil palm wood flour content, the tensile strength, tear strength, and hardness of ENR composites showed an increase. This may be attributed to good filler dispersion and good bonding quality between the fillers and ENR matrix.

Pattamaprom, C. et al. (2008) examined the effect of matrix modification on physical properties of rice husk ash (RHA) reinforced NR composites. The ENR composite had lower % mass loss as compared to NR composite. This indicated that ENR composite showed good abrasion resistance due to the better compatibility with RHA.

2.4 Addition of compatibilizer

A compatibilizer is added into the incompatible composites to enhance the degree of compatibility. The compatibilizer attends at the interface during blending and plays the roles of reducing the interfacial tension and strengthening interfacial adhesion resulting into improvement of the physical and mechanical properties of the composites. Ismail et al. (2005) examined the addition of maleated natural rubber as a compatibilizer for paper sludge/natural rubber composites. The rubber-filler interaction was studied by Lorenz and Park equation. The maleated natural rubber was prepared in internal mixer at 135^{o}C at 60 rpm for 10 min. The incorporation of maleated natural rubber into NR composites gave lower values of rubber-filler interaction, which confirmed that better interactions between fiber and matrix occured in the presence of maleated natural rubber. SEM micrographs showed that adding maleated natural rubber caused a reduction in filler pull-out and less aggregates.

2.5 Properties of natural fiber/natural rubber composites

2.5.1 Effect of alkalization on cure characteristics and mechanical properties of natural fiber/natural rubber composites

De, Debas., De, Debap., and Adhikari (2006) investigated the effect of alkali treatment on cure characteristics, mechanical properties, and morphological properties of grass fiber/natural rubber composites. The fibers were treated with 5% NaOH for 15 min. The composites with alkali treated fibers showed higher maximum torque than those of the composites with untreated fiber due to the better adhesion between the fibers and the rubber matrix. The cure time decreased for the alkali treated grass fiber based composites with increasing filler loading. This decrease in the cure time of the alkali treated grass fiber filled compounds compared to that of the control compounds can be attributed mostly to the influence of pH on the grass fillers. It is known that a vulcanization reaction becomes faster in an alkaline pH. The mechanical properties of the composites filled with alkali treated fibers were higher than those filled with untreated fibers at similar loadings. From these results, it was clear that the alkali treatment of grass fiber improved the fiber adhesion to rubber matrix. SEM micrograph of the composites filled with alkali treated fibers showed the fiber breakage because of strong adhesion between the fibers and the rubber matrix.

Lopattananon, N. et al. (2006) prepared pineapple leaf fiber/natural rubber composites. Pineapple leaf fibers were treated with 1, 3, 5, and 7% NaOH for 18 hrs. It was found that alkali treatment enhanced adhesion between the fiber and matrix and tensile properties of the composites. The treatment with 5% NaOH provided the best improvement (28%) of strength of the composites when compared with untreated fiber composites. The alkali treatment removed lignin and other surface waxy substances so the possibility for mechanical interlocking between the fiber and natural rubber increased. This resulted in improvement of the mechanical properties of the composites. After thermal aging, the % retention in tensile strength of composites filled with 5% NaOH treated fiber was greater than composites filled with untreated fiber. This may be attributed to the existence of good interfacial adhesion which provided the protection against void formation during aging. SEM micrograph of the composites filled with alkali treated fibers showed better adhesion between the fibers and rubber matrix, as indicated by the presence of rubber phase wetting to the fibers.

Mathew and Joseph (2007) reported the cure characteristics, mechanical properties, and morphological properties of isora fiber reinforced natural rubber composites. The isora fiber was treated with a 5% NaOH for 4 hrs. The treatment of the fiber resulted in the improvement of maximum torque because the treated fiber may provide a better surface for reinforcement. However, cure time was not very much affected by the modification of fiber surface. The mechanical properties of the composites filled with treated fibers were higher than those filled with untreated fibers at similar loadings. SEM micrograph of treated isora fiber showed a strong evidence for the physical microcellular structural changes occurring in the fiber surface on alkalization. The pores became clearer, and fibers became thinner. This may due to the dissolution and leaching out of fatty acids and lignin components of the fiber. This rendered roughness to the fiber and thereby enhanced mechanical interlocking at the interface. The development of a rough surface topography offered better fiber rubber interface adhesion and increased mechanical properties. From these results, it was clear that the alkali treatment of isora fiber improved the fiber adhesion to rubber matrix.

2.5.2 Effect of silanization on cure characteristics and mechanical properties of natural fiber/natural rubber composites

Ismail, Nasaruddin, and Ishiaku (1999) studied the effect of silane coupling agent on cure characteristics, mechanical properties, rubber-filler interaction, and morphological properties of white rice husk ash/natural rubber composites. The silane used was bis(triethoxysilyl propyl) tetra sulphide (Si69). The scorch time and cure time of the composites with silane coupling agent decreased when compared to the composites without silane coupling agent. The incorporation of silane coupling agent also increased the maximum torque and improved the mechanical properties of the composites. SEM micrograph indicated that silane coupling agent enhanced filler dispersion of the composites.

Ismail et al. (2002) investigated the effect of silane coupling agent on cure characteristics, mechanical properties, and morphological properties of bamboo fiber filled natural rubber composites. Silane coupling agent used to treat the fiber was bis(triethoxysilyl propyl) tetra sulphide (Si69). The Si69 was added at 3 phr.

The composites with the silane coupling agent had shorter scorch time and cure time than the composites without the silane coupling agent. The cure enhancement was due to improvement in filler dispersion in a rubber matrix by the silane coupling agent. The composites with silane coupling agent exhibited higher tensile and tear strengths compared to the composites without silane coupling agent. This may be attributed to improved surface functionality of the bamboo fibers and subsequently enabled bamboo fibers to bond chemically to the rubber matrix. Consequently, interfacial adhesion on the surface of the fiber increased and composites exhibited increased strength. The tensile fracture surface of composites showed a better adhesion between bamboo fibers and rubber matrix. The fibers were well wetted by the rubber matrix and the pulled out of fibers from rubber matrix was minimum. The enhancement of the mechanical properties of the composites with adding silane coupling agent can be attributed to the better wetting and dispersion of bamboo fibers in rubber matrix.

2.5.3 Effect of bonding agent on cure characteristics and mechanical properties of natural fiber/natural rubber composites

Ismail, Edyham, and Wirjosentono (2002) reported the effect of bonding agent on cure characteristics, mechanical properties, and morphological properties of bamboo fiber filled natural rubber composites. Tricomponent systems consisting of phenol formaldehyde, hexamethylene tetramine, and silica were used as the bonding agent. The scorch and cure times of the composites with the bonding agent were shorter than the composites without the bonding agent. This was because adhesion between the fiber and rubber matrix was increased and more energy needed to incorporate the fibers due to increased viscosity. Tensile modulus and hardness of the composites increased with presence of bonding agent because the adhesion between the fiber and rubber matrix was enhanced. SEM micrographs showed very low pull-out of fibers on the fracture surface due to strong adhesion between fiber and rubber matrix.

De et al. (2006) studied the effect of resorcinol formaldehyde latex (RFL) as a bonding agent on cure characteristics, mechanical properties, and morphological properties of grass fiber filled natural rubber composites. The composites with the bonding agent treated fiber showed higher torque than the composites with untreated fiber because of better adhesion at the fiber-matrix interface. Bonding agent treated fibers showed higher tensile strength in composites at all levels of fiber loading. Stress transfer became more efficient and consequently, the tensile strength was enhanced. SEM micrograph of the composites with bonding agent showed that the fibers were well wetted by the rubber matrix and there was fiber breakage because of strong adhesion between fibers and matrix.

Mathew and Joseph (2007) investigated the effect of bonding agent on mechanical properties and morphological properties of isora fiber reinforced natural rubber composites. Tricomponent system containing of resorcinol formaldehyde resin, hexamethylene tetramine, and precipitated silica were used as a bonding agent. Addition of the bonding agent in the composites improved the modulus, tensile strength, tear strength, and hardness. This may be attributed to strong adhesion between the fiber and matrix. Consequently, the mechanical properties of the composites were improved. SEM micrographs showed that the failure of the composites with the bonding agent occurred at the fiber due to strong adhesion between the fibers and matrix.

2.5.4 Effect of thermal treatment on swelling characteristics and mechanical properties of natural fiber/natural rubber composites

Jacob, Thomas, and Varughese (2006) reported the tensile properties and swelling characteristics of sisal fabric reinforced natural rubber composites. Sisal fabric was heated in an oven at 150°C for 8 hrs. Tensile strength, tear strength, and hardness of heat treated sisal fabric composites were higher than those of untreated composites. This may be attributed to an increase in the crystallinity of cellulose due to the rearrangement of molecular structure at elevated temperatures. The heat treatment also resulted in moisture loss of the fabric and thereby enhanced the extent of bonding between the fabric and rubber. Crosslink density values showed that the composites containing heat treated fabric exhibited the maximum crosslink density indicating that the extent of interaction was maximum in heat treated fabric composite. SEM micrograph result showed that the adhesion between the rubber matrix and the sisal fabric increased.

2.5.5 Effect of matrix modification on cure characteristics and mechanical properties of natural fiber/natural rubber composites

Mohd Ishak and Bakar (1995) investigated the potential of rice husk ash (RHA) as fillers for epoxidized natural rubber (ENR). Epoxidized natural rubber was ENR50. The scorch and cure time of the composites increased with increasing rice husk ash content. The enhancement of the scorch and cure time can be associated to the filler parameters such as surface area, surface reactivity, particle size, and moisture content. The tensile and tear strength increased with increasing filler content until a filler level was reached at 20 phr, then decreased. As the filler loading was increased, finally a level was reached whereby the filler particles or aggregates were no longer adequately separated or wetted by rubber phase. So, the reduction in strength may be due to agglomeration of the filler particles to form a domain that acted like a foreign body or simplify the result of physical contact between adjacent aggregates.

Pattamaprom, C. et al. (2008) reported the effect of natural rubber (NR) modification on physical properties of rice husk ash (RHA) composites. The modified natural rubbers were maleated natural rubber (MNR) and epoxidized natural rubber (ENR). The composite of epoxidized natural rubber (ENR-RHA) showed the highest crosslink density and the shortest scorch time, followed by natural rubber (NR-RHA) and maleated natural rubber (MNR-RHA) respectively. This was because the epoxy group in ENR tended to activate the adjacent double bonds in the rubber molecules yielding free radicals. The radicals created from the reaction can quickly react and form crosslinks with sulphur. For the composite of maleated natural rubber (MNR-RHA), the scorch time was delayed. This may be due to the acidity of maleic acid and the interaction between maleic anhydride and the accelerator. The tensile modulus of epoxidized natural rubber composites (ENR-RHA) and maleated natural rubber composites (MNR-RHA) were higher than natural rubber composites (NR-RHA) but the ultimate tensile strengths were still lower.

2.5.6 Effect of addition of compatibilizer on cure characteristics and mechanical properties of natural fiber/natural rubber composites

Ismail et al. (2005) examined the influence of maleated natural rubber (MNR) on cure characteristics and tensile properties of paper sludge filled natural rubber composites. Scorch time and cure time of the composites with MNR were longer than the composites without MNR. The modulus and tensile strength of the composites with the addition of MNR was better than the composites without MNR. The enhancement of scorch time and cure time and the improvement in tensile properties of the composites can be attributed to the improvement in the interfacial adhesion between paper sludge and natural rubber by MNR. It is believed that the natural rubber segments of MNR form miscible blends with the bulk natural rubber and the polar part of MNR forms hydrogen bonds with the hydroxyl group of fibers in the interfacial region. SEM micrographs showed that the dispersion and wettability of the composites worsen with increasing filler loading but the presence of MNR caused reduction in filler pull-out and less aggregates were formed.

Ismail and Haw (2008) investigated the effect of MNR as a compatibilizer on cure characteristics and mechanical properties of palm ash/natural rubber composites. The addition of MNR into the composites decreased scorch time and cure time due to the good interaction between the palm ash and rubber matrix. MNR also increased the maximum and minimum torque of the composites. This indicated that the using of MNR reduced the damping characteristics of the composites. The modulus at 100% strain, modulus at 300% strain, tensile strength, and elongation at break of the composites increased with increasing MNR loading. This may be attributed to the improvement in the interfacial adhesion between palm ash and natural rubber matrix by MNR. SEM micrographs of the composites with MNR showed less pullout of palm ash from natural rubber matrix due to the strong interaction between the fiber and rubber matrix.

CHAPTER III

EXPERIMENTAL

3.1 Materials

Natural rubber (NR, STR 5L) was supplied from Thai Hua Rubber Co., Ltd. Epoxidized natural rubber with 50 mol% of epoxide groups (ENR50) was purchased from Muang Mai Guthrie Co., Ltd. Sisal fiber was purchased from Sisal-Handicraft OTOP group, Nakhon Ratchasima, Thailand. Carbon black (N330) was supplied from Thai Tokai Carbon Product Co., Ltd. Silica (Tokusil®UR-T) was obtained from Tokuyama Siam Silica Co., Ltd. Polyethylene glycol (PEG-4000) was supplied from Imperial Industrial Chemicals (Thailand) Co., Ltd. Maleic anhydride (MA, Sigma-Aldrich) and dicumyl peroxide (DCP, Aldrich Chemicals) were used. Other ingredients used to vulcanize natural rubber were stearic acid, zinc oxide, N-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS), and sulfur.

3.2 Experimental

3.2.1 Preparation of sisal fiber

Sisal fiber was cut into an approximate length of 2 mm then dried in an oven at 60°C overnight. This fiber was called untreated fiber (UT). In order to eliminate hemicellulose, waxes, and low molecular weight species, the UT fiber was treated with 2 wt% sodium hydroxide (NaOH) solution for 2 hrs. Then, the UT fiber was washed with water and dried at 60°C overnight. This fiber was called alkali treated fiber (AT).

3.2.2 Preparation of natural rubber grafted with maleic anhydride

The natural rubber grafted with maleic anhydride (NR-g-MA) was prepared in an internal mixer (HAKKE RHEOMIX 3000P) at a temperature of 130°C for 10 min and a rotor speed of 60 rpm. The maleic anhydride content used was 6 phr (Nakason, C., Kaesaman, A., and Supasanthitikul, P., 2004). The dicumyl peroxide contents used in this study were 0.5, 1.0, and 1.5 phr.

3.2.3 Characterization of natural rubber grafted with maleic anhydride

3.2.3.1 Determination of maleic anhydride content

The quantity of maleic anhydride content on natural rubber was determined by titrating carboxylic acid groups derived from the anhydride functional groups. NR-g-MA solution for the titration was prepared by dissolution of 1 g of NR-g-MA in 100 ml of toluene at its boiling temperature. To remove unreacted maleic anhydride, excess amount of acetone was added to NR-g-MA solution and filtrated. The precipitant product was dried in the vacuum oven at 40°C for 24 hrs. The sample was redissolved in toluene. Then 0.2 ml of water was added to hydrolyze anhydride functional groups into carboxylic acid functional groups. The solution was refluxed for 2 hrs to complete the hydrolysis. The carboxylic acid concentration was determined by titration of the NR solution with 0.025 N potassium hydroxide in methanol/benzyl alcohol 1/9 (v/v). The solution of 1% phenolphthalein in methanol was used as an indicator. The carboxylic acid concentration was converted to the MA content as follows (Nakason, C., et al., 2004):

$$\mathrm{MA\,(wt\%)} = \frac{(V_1 - V_0)}{2w} \times N \times 98 \times 100\% \tag{3.1}$$

where N is the concentration (mol/l) of potassium hydroxide dissolved in methanol/ benzyl alcohol. V_o and V_1 are volumes of the KOH used in the blank test and in the test with samples respectively. w is weight (g) of the NR-g-MA sample.

3.2.3.2 Determination of gel fraction

NR-g-MA, after removing unreacted maleic anhydride, was extracted using boiling toluene for 24 hrs and the extracted NR-g-MA were dried to constant weight. The gel fraction was calculated as follows (Nakason, C., et al., 2004):

$$\text{Gel fraction} = \frac{W}{W_0} \times 100 \tag{3.2}$$

where W and W_0 are the weight of the dried sample after extraction and the weight of the sample before extraction respectively.

3.2.3.3 Fourier Transform Infrared Spectroscopy

FTIR spectra of NR-g-MA, NR, and MA were investigated using a Fourier Transform Infrared Spectrometer (FTIR, BRUKER). The spectra were recorded in the range of 4000-600 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}. For FTIR measurement, NR and purified NR-g-MA were casted on the KBr disc.

In addition, to estimate the level of grafted MA onto NR molecule, the absorbance ratios (peak area) of peaks at 1790 and 1867 cm^{-1} (C=O stretching peak of five-membered cyclic anhydride) to 835 cm^{-1} (-C-H stretching peak on *cis* C=C bonds of *cis*-1,4-polyisoprene) can be calculated as shown in Appendix A. (Nakason, C., et al., 2004).

3.2.4 Preparation of natural rubber composites

Formulations for compounding are shown in Table 3.1. The compounds were mixed using a two-roll mill (CHAICHAREON) at room temperature. The fiber contents used in this study were 10, 20, and 30 phr. Firstly, NR was masticated for 5 min then zinc oxide was added after that the fiber (UT or AT) was added. The vulcanization ingredients were added to the compound after the incorporation of the fiber and, lastly, sulfur was added. The total mixing time was 25 min. The test specimens were prepared using a compression molding machine (GOTECH/GT-7014-A30) under a pressure of 130 MPa and a temperature of 150^{o}C.

In cases of compatibilized NR composites, NR-g-MA or ENR of 5 phr was added at the same time as NR was added. Based on the mechanical properties and cure characteristics of the compatibilized NR composites, NR-g-MA or ENR was selected to study effect of compatibilizer content on the properties of the NR composites. The compatibilizer contents were varied (2.5, 5.0, 7.5, and 10.0 phr). In addition, the sisal fiber/NR composite giving the optimum mechanical properties and cure characteristics was chosen to compare its cure characteristics and tensile properties with NR composites filled conventional fillers, i.e. carbon black and silica of equal filler content. The added vulcanization ingredients were incorporated with the same amount as shown in Table 3.1.

Table 3.1 Formulation of natural rubber composites.

Materials	**Contents (phr)**		
Natural rubber	100	100	100
Zinc oxide	5	5	5
Stearic acid	1.5	1.5	1.5
CBS$^{(1)}$	0.5	0.5	0.5
Sulfur	2.5	2.5	2.5
Untreated sisal fiber	-	x	-
Alkali treated sisal fiber	-	-	x

Remark: x : 10, 20, 30 phr
(1) : N-cyclohexyl-2-benzothiazole-2-sulphenamide

3.2.5 Characterization of NR and NR composites

3.2.5.1 Cure characteristics

Maximum torque (MH), minimum torque (ML), scorch time (t_{s1}), and cure time (t_{90}) of the NR and NR composites at 150°C were investigated with a moving die rheometer (MDR, GOTECH/GT-M200F).

3.2.5.2 Mechanical properties

Tensile properties of NR and NR composites were tested according to ASTM D412 using a universal testing machine (UTM, INSTRON/5565) with a load cell of 5 kN, a crosshead speed of 500 mm/min and a gauge length of 33 cm. To determine specific modulus or specific tensile strength of NR and NR composite, the modulus and tensile strength were divided by the specific gravity of NR and NR composites respectively.

Tear properties of NR and NR composites were tested according to ASTM D624 using a universal testing machine (UTM, INSTRON/5565) with a load cell of 5 kN at a crosshead speed of 500 mm/min.

Hardness of NR and NR composites were determined according to ASTM D2240 using an international rubber hardness degrees tester (IRHD, BAI EISS/DIGI TEST).

3.2.5.3 Morphological properties

Tensile fracture surfaces of NR composites were examined using a scanning electron microscope (SEM, JEOL/JSM-6400) at 20 keV. The samples were coated with gold before examination.

3.2.5.4 Fiber length distribution analysis

Sisal fibers were removed from NR matrix by dissolution 1 g of sisal/NR composites in toluene. The length of fibers were measured based on 200 samples using an optical microscope (OM, NIKON/ECLIPSE E600 POL). The number average fiber length ($\overline{L}_n$) and the weight average fiber length ($\overline{L}_w$) were calculated using equation 4.1 and 4.2 respectively (Jacob, Thomas, and Varughese, 2004).

$$\overline{L}_n = \frac{\sum N_i L_i}{\sum N_i} \tag{3.3}$$

$$\overline{L}_w = \frac{\sum N_i L_i^2}{\sum N_i L_i} \tag{3.4}$$

where N_i is the number of fibers having length L_i.

3.2.5.5 Crosslink density

Crosslink density (V_e) of the NR and NR composites were estimated according to ASTM D6814. The composites were swollen in toluene at room temperature for 72 hrs until equilibrium swelling was reached. The Flory-Rehner equation was used for calculation of crosslinking density as follows (Flory, 1953):

$$V_e = \frac{-[\ln(1-V_r)+V_r+\chi_1 V_r^2]}{V_1[V_r^{1/3}-(V_r/2)]} \tag{3.5}$$

where V_e is effective number of chains in a real network per unit volume. χ_1 is polymer-solvent interaction parameter (χ_1 is 0.391 for toluene). V_1 is molecular volume of solvent (V_1 is 106.2 for toluene). V_r is volume fraction of polymer in swollen network in equilibrium with pure solvent and calculated as follows:

$$V_r = \frac{\text{Weight of dry rubber/ density of dry rubber}}{\dfrac{\text{Weight of dry rubber}}{\text{Density of dry rubber}} + \dfrac{\text{Weight of solvent absorbed by sample}}{\text{Density of solvent}}} \tag{3.6}$$

3.2.5.6 Specific gravity

Specific gravity of crosslinked NR and NR composites were determined according to JIS K 6350 on Electronic Densimeter (MIRAGE, MD-200S).

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of initiator content on grafting level of NR-g-MA

In this study, FTIR spectroscopy was used to identify the grafted anhydride on NR backbone. FTIR spectra of NR and NR-g-MA at 1 phr of DCP are shown in Figure 4.1. The unreacted MA may show absorption peak in the same region as the NR-g-MA therefore the removal of the unreacted MA was necessary (Nakason, C. et al., 2004). The NR's spectrum shows the characteristic peaks of C=C at 1662 cm^{-1} and 835 cm^{-1} while that of NR-g-MA shows the two new peaks at 1867 cm^{-1} and 1790 cm^{-1}. Lin-Vien, Colthup, Fateley, and Grasselli (1991) reported that the cyclic-five-membered ring, a part of anhydride, gave rise to two peaks of C=O at 1870-1845 cm^{-1} (weaker) and 1800-1775 cm^{-1} (stronger). So, the two new peaks at 1867 cm^{-1} and 1790 cm^{-1} can be used to confirm the MA grafted onto NR backbone. The similar results were also observed by Nakason, C. et al. (2004); Saelao, J. and Phinyocheep, P. (2005). The NR-g-MA's spectrum also shows the disappearance of peak at 698 cm^{-1} (C=C bond of MA) indicating the absence of the unreacted MA. In addition, there was an absorption peak around 1736 cm^{-1} assigned to carbonyl group of carboxylic acid. This indicated that a ring opening reaction of the anhydride group of succinic anhydride was occurred (Nakason, C., Kaesman, A., Homsin, S., and Kiatkamjornwong, S., 2001). The succinic anhydride unit grafted onto NR was sensitive to moisture so the anhydride ring may open and form carboxylic acid during the grafting reaction. The possible reaction of ring opening reaction of anhydride group is shown in Figure 4.2 (Saelao, J. and Phinyocheep, P., 2005).

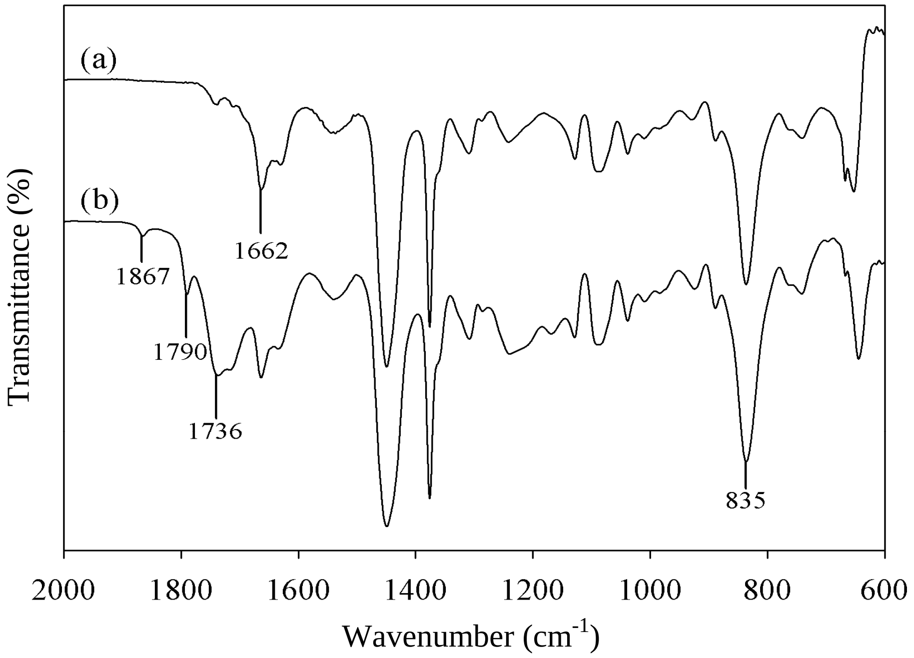


Figure 4.1 FTIR spectrum of NR (a) and NR-g-MA at 1.0_DCP (b).

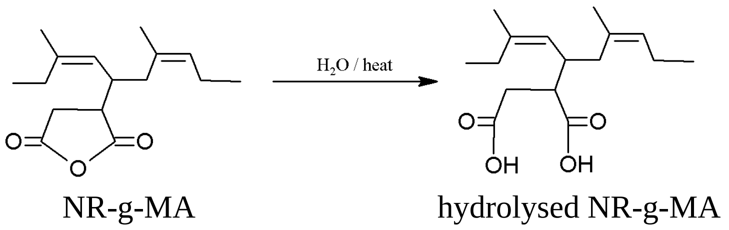


Figure 4.2 Possible reaction of ring opening reaction of anhydride unit.

FTIR spectra of NR-g-MA prepared at various initiator contents are shown in Figure 4.3. The level of grafted MA can be estimated by the absorbance ratio of peaks at 1867 cm^{-1} and 1790 cm^{-1} to 835 cm^{-1} (Nakason, C. et al., 2004). With increasing initiator (DCP) content up to 1 phr, the absorbance ratio of the NR-g-MA increased as shown in Figure 4.4. This was because an increase in initiator content resulted in more free radicals generation. The reaction mechanisms of grafted MA onto NR backbone without and with initiator are shown in Figure 4.5 and Figure 4.6 respectively. For the grafting reaction without an initiator, the free radicals were generated from shearing and heating NR by an internal mixer. After that, NR backbone with free radicals were reacted with MA and a succinic anhydride unit attached to NR backbone was formed. Then, the radical chain transfer reaction with another NR backbone was generated to terminate the radical on grafted NR backbone consequently, as a result NR-g-MA was achieved. In a case of the grafting reaction with initiator (DCP), the free radicals were generated from the decomposition of DCP under heat. Then, the free radicals were transferred to NR backbone. After that, the grafting reaction was occurred resulting in NR-g-MA. At a initiator content of 1.5 phr, the absorbance ratio dropped off due to the high crosslinking density of NR molecules when DCP content was increased as shown in Figure 4.4.

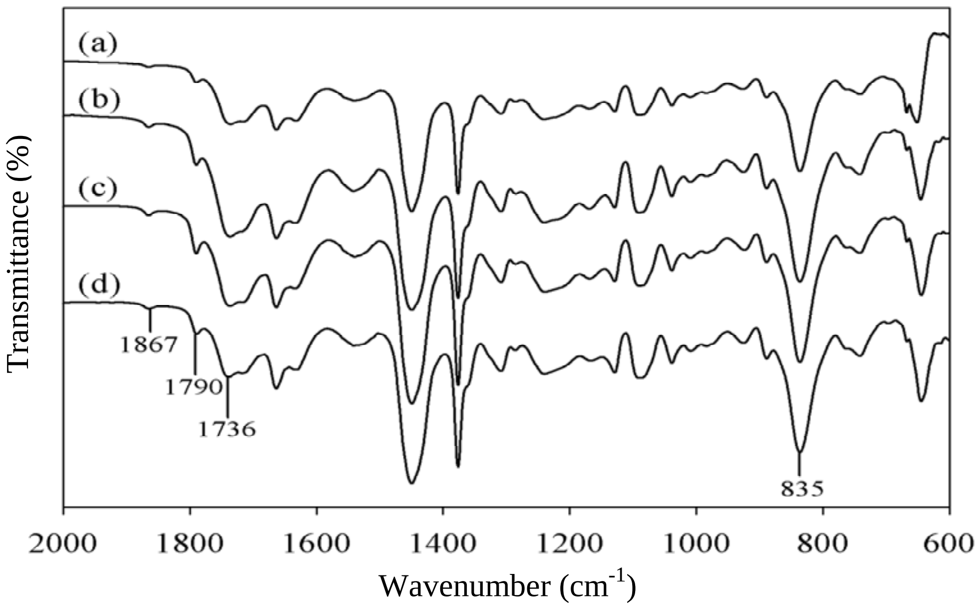


Figure 4.3 FTIR spectra of NR-g-MA; (a) 0_DCP, (b) 0.5_DCP, (c) 1.0_DCP, and (d) 1.5_DCP.

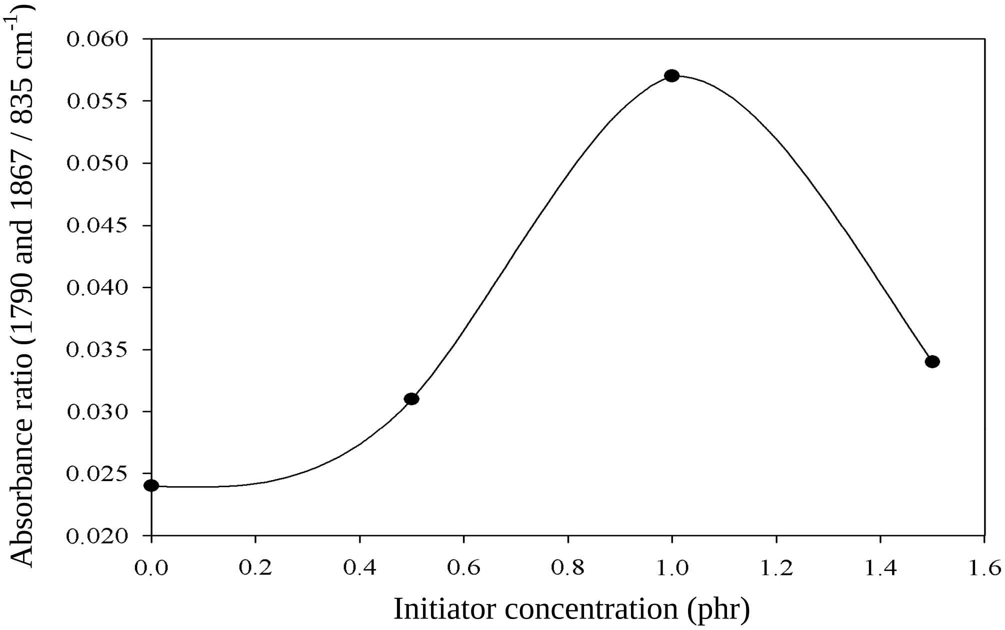


Figure 4.4 Effect of initiator content on absorbance ratio of NR-g-MA.

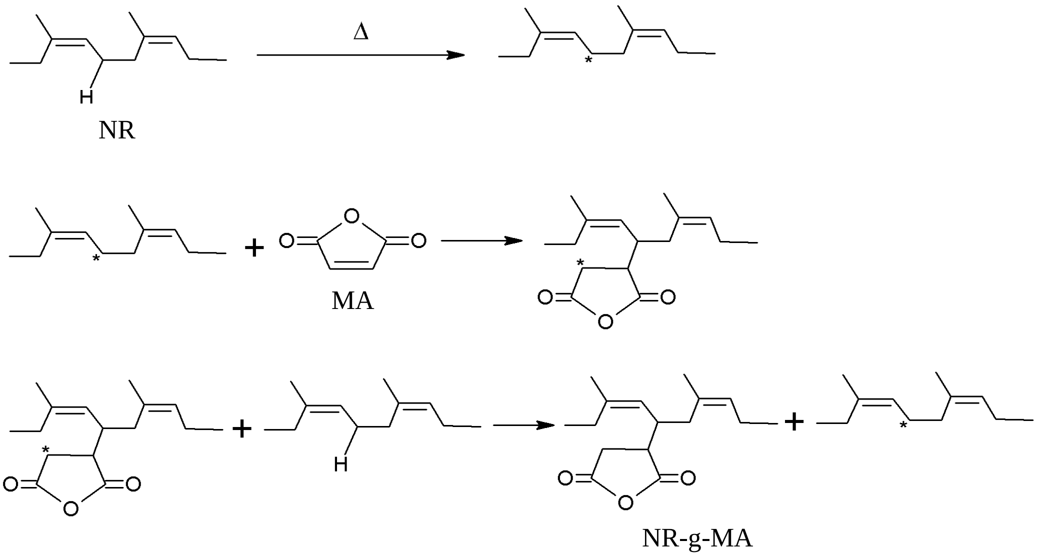


Figure 4.5 Possible reaction mechanism of grafting MA onto NR backbone without initiator.

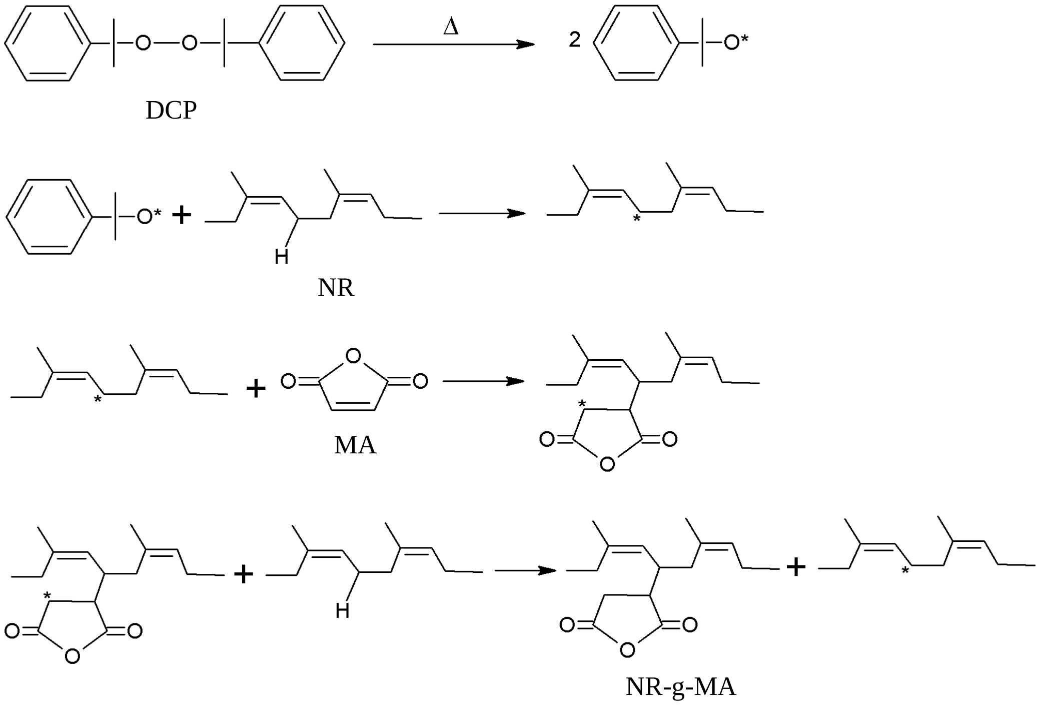


Figure 4.6 Possible reaction mechanism of grafting MA onto NR backbone with initiator (Saelao, J., and Phinyocheep, P., 2005).

The quantity of MA grafted onto NR molecules can be verified by the titration method. The quantity of MA grafted onto NR molecules and gel fraction of NR-g-MA at various initiator contents are listed in Table 4.1. At the DCP content of 1.5 phr, the determination of quantity of MA grafted onto NR molecules cannot be performed due to a high gel fraction (31.38 wt%) as shown in Table 4.1. This NR-g-MA sample only swelled and did not completely dissolve in toluene due to crosslinking of NR molecules. FTIR spectra of the NR-g-MA at 1.5 phr of DCP was obtained by casting film of NR-g-MA onto KBr disc. The grafted MA content increased with increasing initiator concentration as shown in Figure 4.7. The highest maleic anhydride grafted onto NR molecule was 1.38 wt% and was obtained by the addition of 1 phr of DCP. Therefore, NR-g-MA containing 1 phr of DCP and 6 phr of MA was used throughout this study. In the grafting reaction with the presence of DCP, the gel fraction was observed. This may be due to three possible reasons. The first possible reason is due to the formation of crosslinking between succinic anhydride attached onto NR and NR macroradical as shown in Figure 4.8 (a). On the other hand, the second mechanism reason is probably due to the formation of crosslinking of the NR macroradical and other NR macroradical as shown in Figure 4.8 (b). The third possible reason is the reaction of acid groups from ring opening reaction interact with NR-g-MA as shown in Figure 4.8 (c).

Table 4.1 Quantity of MA grafted onto NR molecules and gel fraction of NR-g-MA at various initiator contents.

DCP content (phr)	**Grafted MA content (wt%)**	**Gel fraction (wt%)**
0.0	0.19±0.0400	0.00±0.0000
0.5	0.37±0.0458	3.27±0.2468
1.0	1.38±0.0971	7.83±0.4430
1.5	-	31.38±1.4327

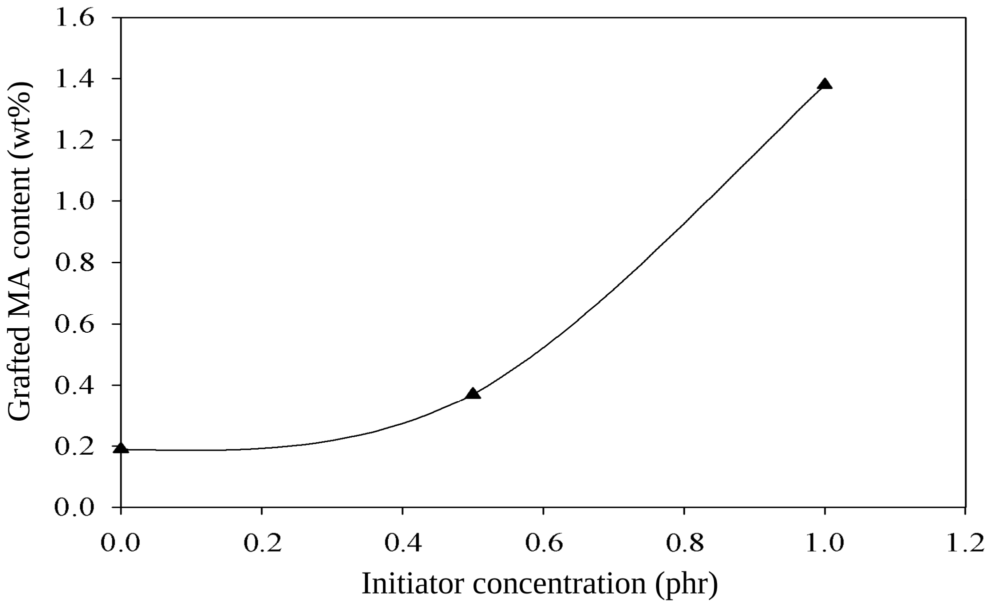


Figure 4.7 Effect of initiator content on grafted MA content of NR-g-MA.

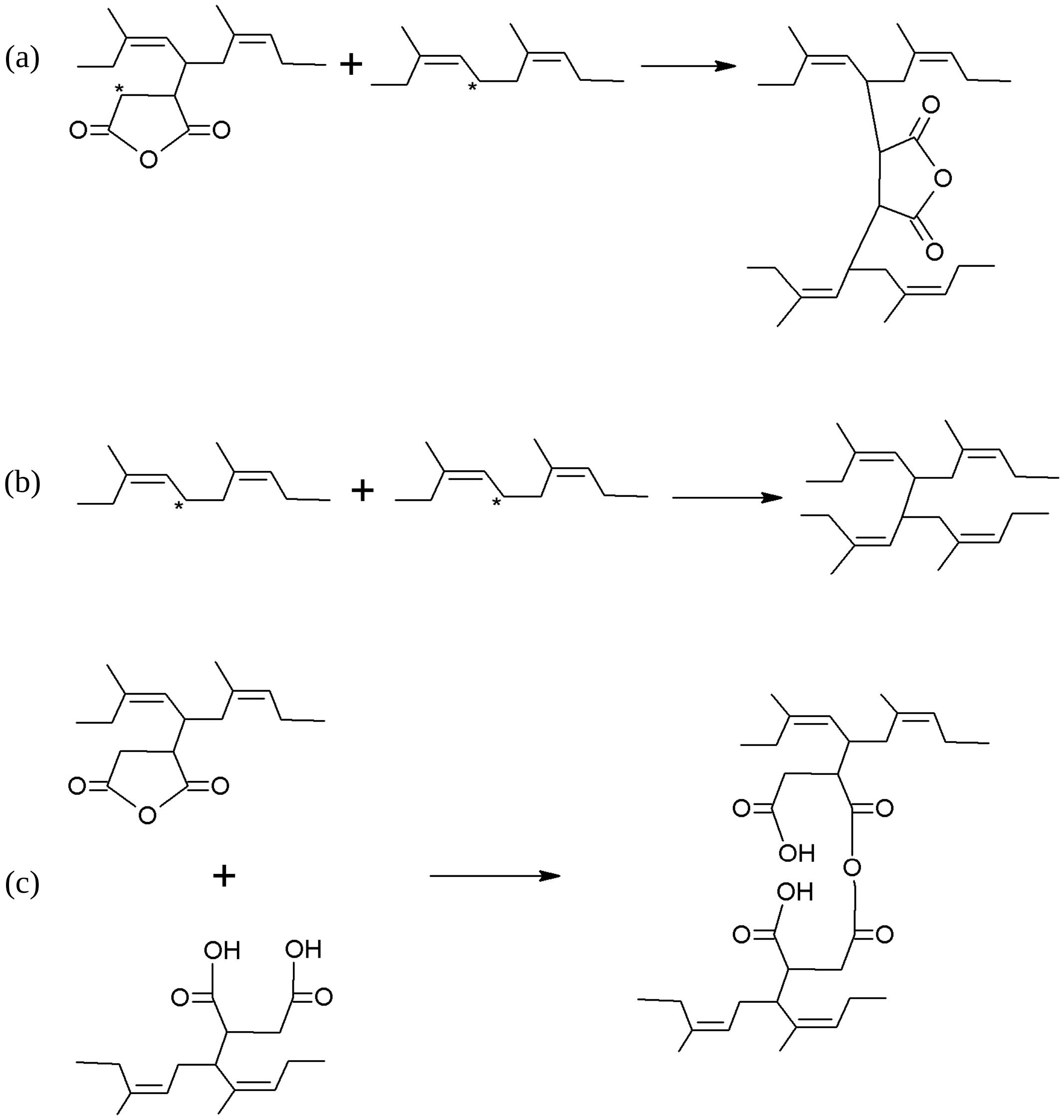


Figure 4.8 Possible crosslinking reactions during the grafting of MA onto NR (Saelao, J., and Phinyocheep, P., 2005).

4.2 Effect of interfacial modification and fiber loading on properties of sisal fiber/NR composites

4.2.1 Cure characteristics

From MDR result, maximum torque (MH) value measures stiffness in the rubber while minimum torque (ML) value indicates the initial viscosity of rubber compounds. MH, ML, scorch time (t_{s1}), and cure time (t_{90}) of NR, NR composites filled with UT and AT fiber, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites are listed in Table 4.2. With increasing UT fiber loading, MH and ML values increased as shown in Figure 4.9 and 4.10 respectively, due to an increase in stiffness of the composites and a reduction of the deformation of NR molecules. Mathew and Joseph (2007) also reported that increasing fiber loading resulted in increased MH of isora fiber/NR composites.

From Figure 4.11, it can be seen that scorch time was not much affected by UT fiber loading. Ismail et al. (2002) and Lopattananon, N. et al. (2006) also observed the similar results with bamboo fiber/NR composites and pineapple leaf fiber/NR composites respectively. Cure time of NR composites decreased with increasing UT fiber loading as shown in Figure 4.12. As the UT fiber loading was increased, more heat was generated due to the additional friction. In general, the cure characteristics of rubber composites also depend on properties of fillers such as surface area, surface activity, particle size, moisture content, and metal oxide content (Ismail, Rosnah, and Rozman, 1997).

Similarly, In a case of AT fiber/NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites, MH and ML increased while scorch time and cure time decreased with increasing fiber loading.

At the same sisal fiber loading, it can be seen that AT fiber filled NR composites exhibited higher MH and ML values than the NR composites filled with UT fiber as shown in Figure 4.9 and 4.10 respectively. When fibers were treated with alkali solution, hemicellulose, wax, and other impurities covering the external surface of fibers were removed resulting in increased surface roughness of the fibers. So, the adhesion between fiber and NR matrix was improved through the mechanical interlocking mechanism. The similar observation was reported by Mathew and Joseph (2007) in isora fiber/NR composites. The alkalization had no significant effect on the scorch time and cure time of the composites as shown in Figure 4.11 and 4.12 respectively. On the other hand, De et al. (2006) found that cure time of alkali treated grass fiber filled NR composites was lower than that of untreated grass fiber filled composites. This was attributed to the influence of pH on the fiber (8.1). The vulcanization reaction became faster in alkaline pH. In our study, the fibers were treated with NaOH solution then the fibers were washed in distrilled water until pH of the fiber reached 7. Therefore, the alkalization did not affect on the cure time of the composites.

Table 4.2 Cure characteristics of NR, NR composites filled with UT and AT fiber, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

Formulation	**MH (dN-m)**	**ML (dN-m)**	**Time (min)**	
			t_{s1}	**t_{90}**
NR	16.662	2.310	4.27	7.54
NR/10 UT	19.741	2.620	3.35	7.16
NR/20 UT	21.170	3.373	3.29	6.33
NR/30 UT	22.790	3.722	3.20	6.02
NR/10 AT	23.650	3.757	3.33	7.08
NR/20 AT	26.641	3.919	3.23	6.21
NR/30 AT	28.410	4.022	3.18	5.93
NR/5 ENR/10 UT	26.016	4.416	3.16	7.39
NR/5 ENR/20 UT	27.938	4.666	3.01	7.04
NR/5 ENR/30 UT	29.821	4.922	2.96	6.38
NR/5 NR-g-MA/10 UT	26.348	4.376	4.22	8.43
NR/5 NR-g-MA/20 UT	28.612	4.847	4.06	8.05
NR/5 NR-g-MA/30 UT	29.734	5.446	4.03	7.72

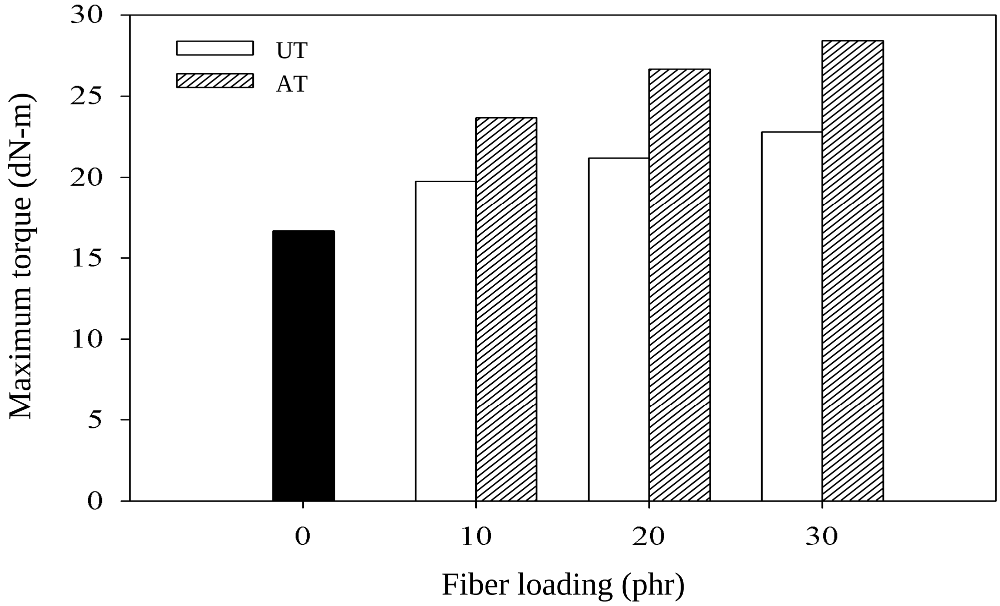


Figure 4.9 Effect of fiber loading on maximum torque of NR and NR composites filled with UT and AT fiber.

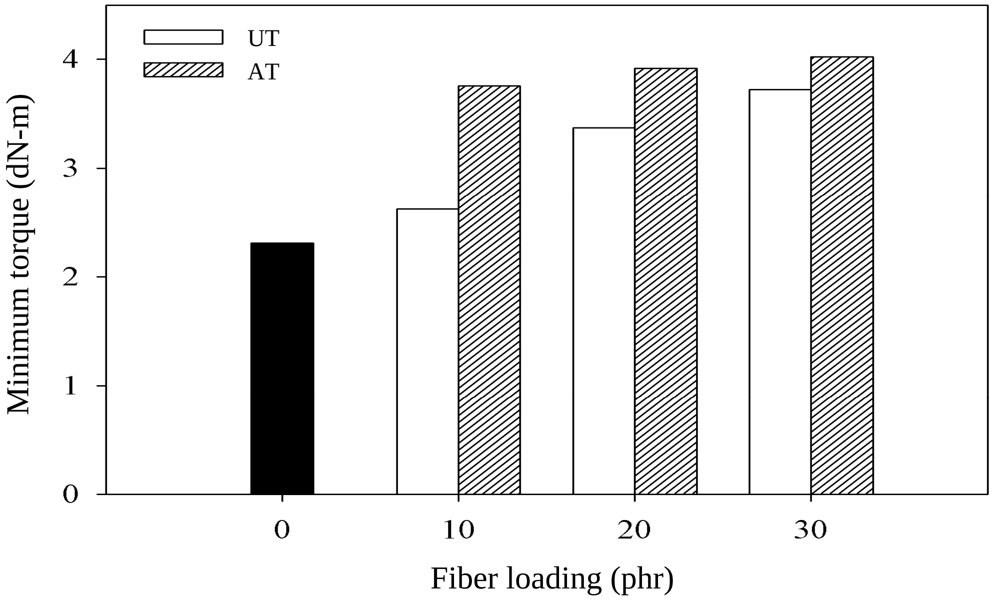


Figure 4.10 Effect of fiber loading on minimum torque of NR and NR composites filled with UT and AT fiber.

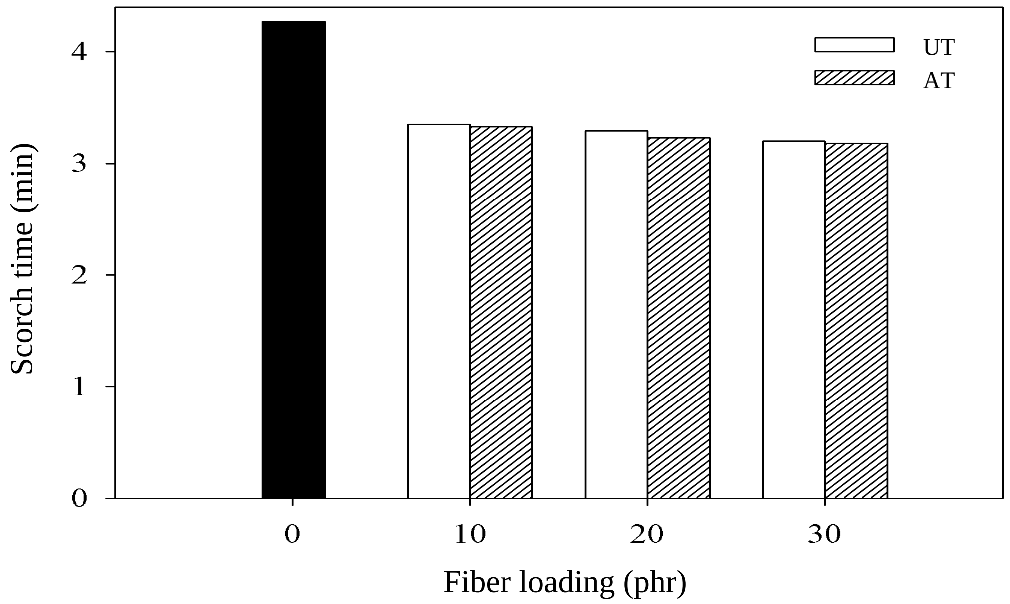


Figure 4.11 Effect of fiber loading on scorch time of NR and NR composites filled with UT and AT fiber.

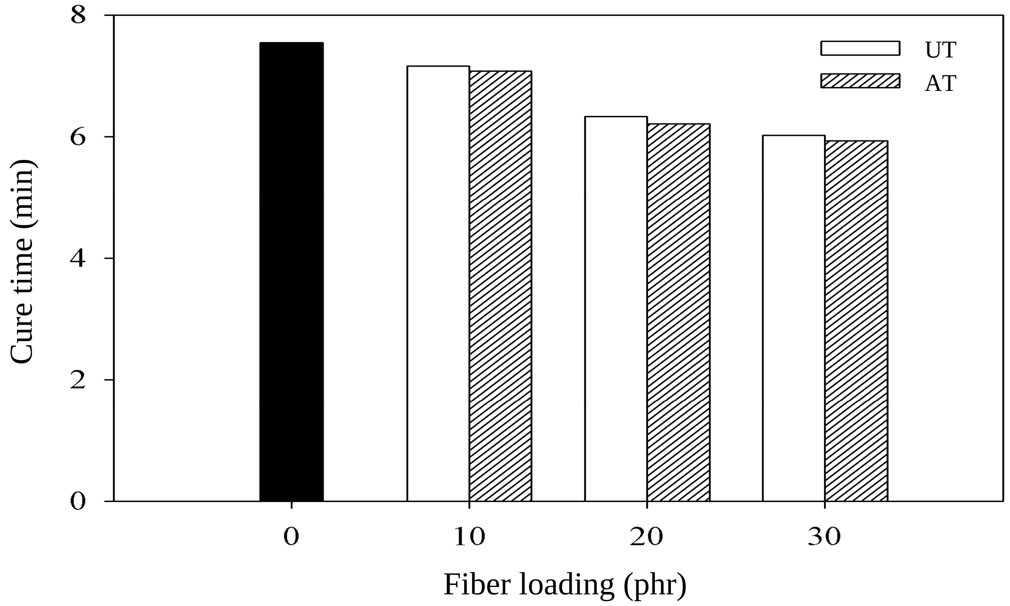


Figure 4.12 Effect of fiber loading on cure time of NR and NR composites filled with UT and AT fiber.

MH and ML values increased with adding 5 phr of compatibilizers (ENR and NR-g-MA) into UT fiber/NR composites as shown in Figure 4.13 and 4.14 respectively. This was due to improved interfacial adhesion between the fiber and NR matrix. Ismail and Haw (2008) found that the incorporation of NR-g-MA resulted in increase of MH values of palm ash/NR composites. However, MH and ML values of ENR compatibilized NR composites were not much different when compared to those of NR-g-MA compatibilized NR composites. In addition, both ENR compatibilized NR composites and NR-g-MA compatibilized NR composites showed higher MH and ML values than uncompatibilized NR composites (NR composites filled with UT fiber). This might be due to the formation of a good interaction between fiber and NR matrix in the presence of compatibilizers. Scorch time and cure time of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites are shown in Figure 4.15 and 4.16 respectively. Scorch time and cure time of the NR-g-MA compatibilized NR composites were longer than those of the NR, uncompatibilized NR composites, and ENR compatibilized NR composites. This may be due to the acidity of maleic acid and the interaction between maleic anhydride and the accelerator (Teh et al., 2004). Among NR, uncompatibilized NR composites, NR-g-MA compatibilized NR composites, and ENR compatibilized NR composites, the ENR compatibilized NR composites showed the shortest scorch time due to the activation of adjacent double bonds in the rubber by epoxide group resulting in free radicals generation.

Among AT fiber filled NR composite, ENR compatibilized NR composite, and NR-g-MA compatibilized NR composite, the AT fiber filled NR composite had the lowest MH and ML values while ENR compatibilized NR composite showed the shortest scorch time. This suggested that the addition of compatibilizers (NR-g-MA and ENR) into NR composite improves interfacial adhesion between fiber and NR matrix much better than the addition of alkali treated fiber into NR composite.

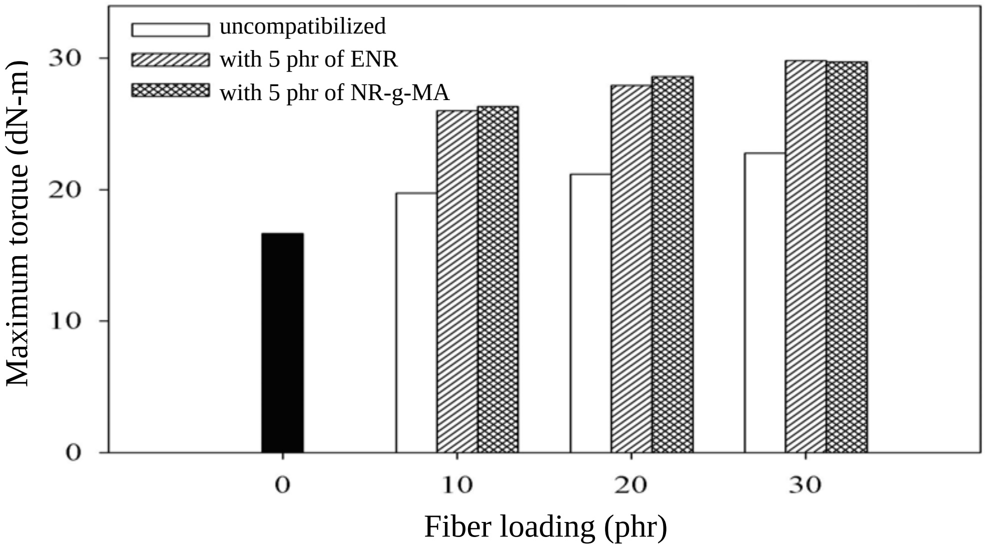


Figure 4.13 Effect of fiber loading on maximum torque of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

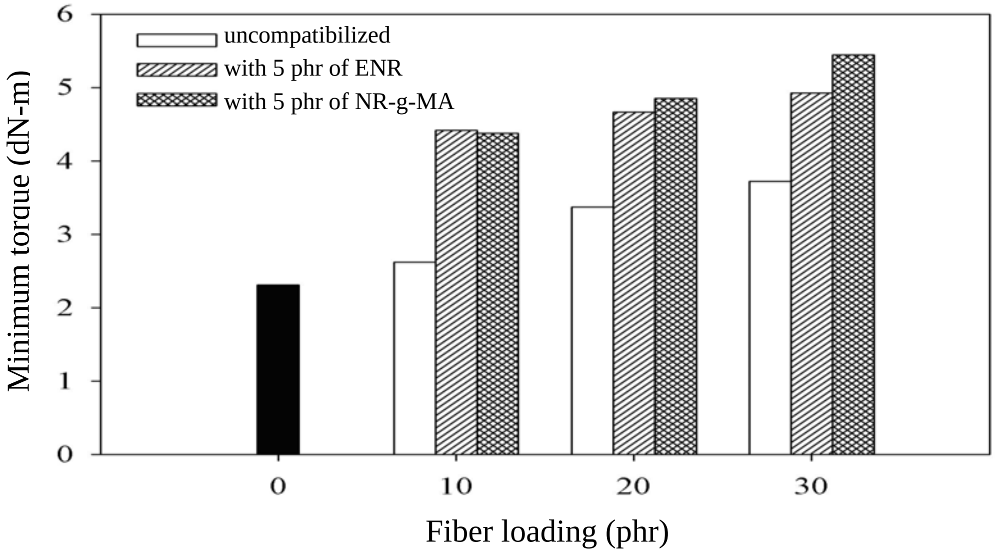


Figure 4.14 Effect of fiber loading on minimum torque of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and, NR-g-MA compatibilized NR composites.

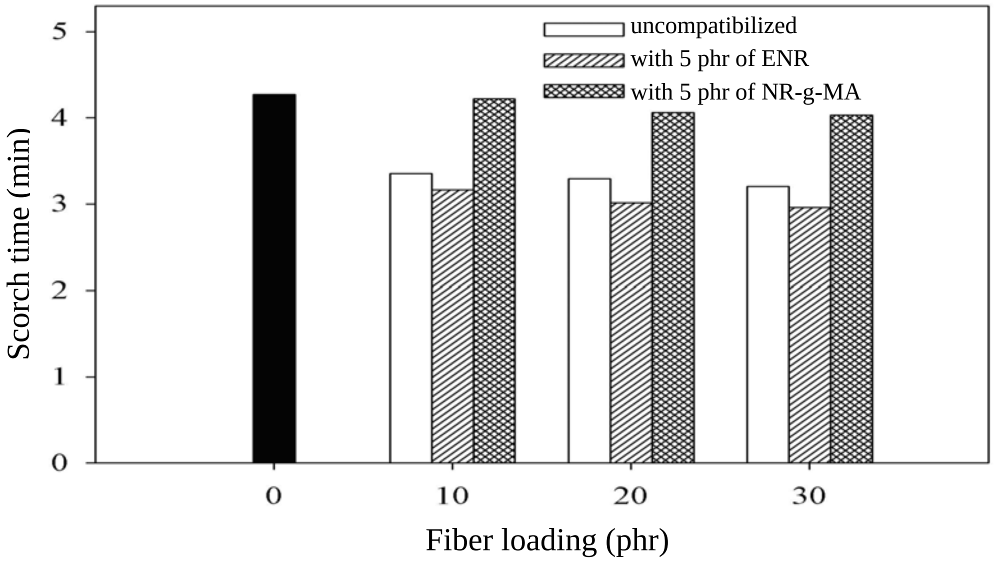


Figure 4.15 Effect of fiber loading on scorch time of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

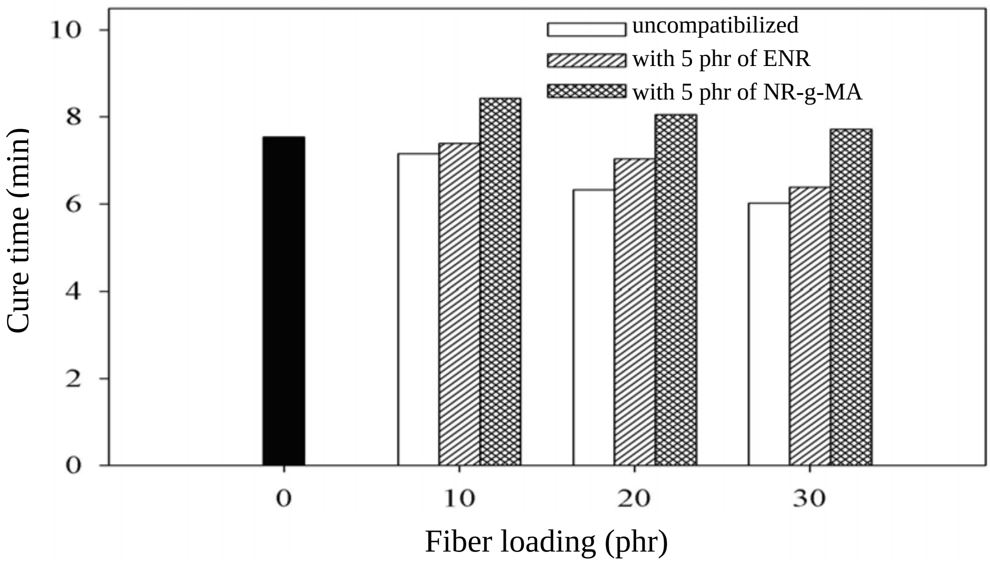


Figure 4.16 Effect of fiber loading on cure time of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

4.2.2 Mechanical properties

Mechanical properties of NR, NR composites filled with UT and AT fiber, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites are listed in Table 4.3.

4.2.2.1 Tensile properties

Modulus at 100% strain (M100) and modulus at 300% strain (M300) of NR and NR composites filled with UT fiber are shown in Figure 4.17 and 4.18 respectively. As fiber loading was increased, M100 and M300 of the composites also increased. This was due to reduced elasticity of the rubber chain resulting in more rigid NR composites. Figure 4.19 shows tensile strength of NR and NR composites filled UT fiber. Tensile strength of NR was higher than those of all NR composites. NR inherently has high tensile strength owing to strain-induced crystallization. With incorporating the fibers into NR, the regular arrangement of rubber molecules was disrupted; thus, the efficiency of strain-induced crystallization was lost. So, the fiber reinforced NR composites have lower tensile strength than NR. In addition, tensile strength of UT fiber/NR composites decreased with increasing fiber loading. High population of fiber led to fiber agglomeration resulting in difficult stress transmission from matrix to fiber and disturbance of the continuity of the matrix phase (De et al., 2006). This led to a reduction of the tensile strength of the composites. The incorporation of UT fiber into NR resulted in reduction of elongation at break as shown in Figure 4.20. Moreover, when fiber loading was increased the composites became stiffer and harder leading to a reduction of resistance to break and resilience of the composites. With increasing AT fiber loading, M100, M300, tensile strength, and elongation at break of AT fiber/NR composites also showed the same trend as the UT fiber/NR composites as shown in Figure 4.17 – 4.20. Mathew and Joseph (2007) reported the similar results on isora fiber/NR composites. However, from Figure 4.17 – 4.20, it can be seen that all of the composites filled with AT fiber exhibited higher M100, M300, tensile strength, and elongation at break in comparison to the composites filled with UT fiber. It has been previously addressed that when fibers were treated with alkali solution, the hemicellulose, wax, and other impurities were removed from the fiber resulting in an increase of surface roughness of fiber. This led to the enhancement in the interfacial adhesion between the fiber and NR matrix through mechanical interlocking. The stress transfer ability at fiber-matrix interface of the composites subjected to given tensile loading was efficiently improved. Lopattananon, N. et al. (2006) also observed the similar results on alkali treated pineapple leaf fiber/NR composites.

In a case of ENR compatibilized NR composites and NR-g-MA compatibilized NR composites, M100, M300, tensile strength, and elongation at break of both compatibilized NR composites drop off after fiber loading of 10 phr as shown in Table 4.3. This was probably because the compatibilizer content was insufficient to improve the interfacial adhesion between the fiber and NR matrix.

Table 4.3 Mechanical properties of NR and NR composites.

Formulation	M100 (MPa)	M300 (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (IRHD)	Tear strength (kN/m)
NR	0.82±0.068	1.65±0.138	20.13±0.113	1350±17.67	39.34±0.195	21.38±0.471
NR/10 UT	1.09±0.081	1.75±0.132	11.05±0.121	1090±21.22	45.96±0.955	22.43±1.220
NR/20 UT	1.13±0.032	1.78±0.112	9.67±0.092	1050±19.03	49.14±0.776	24.91±0.560
NR/30 UT	1.22±0.046	1.92±0.171	8.70±0.146	920±23.49	55.18±0.756	27.34±0.770
NR/10 AT	1.36±0.022	1.83±0.075	13.09±0.082	1111±19.21	50.74±1.775	26.54±1.450
NR/20 AT	1.48±0.051	2.02±0.061	11.04±0.104	1070±24.60	52.82±0.726	28.60±1.200
NR/30 AT	1.59±0.044	2.26±0.052	9.42±0.093	950±18.44	59.16±0.896	30.24±0.890
NR/5 ENR/10 UT	1.48±0.055	2.32±0.090	14.12±0.129	1100±19.90	52.34±0.770	29.90±1.440
NR/5 ENR/20 UT	1.30±0.052	2.15±0.071	10.20±0.089	1090±14.43	54.24±0.508	31.14±0.670
NR/5 ENR/30 UT	1.22±0.048	2.11±0.070	8.82±0.120	942±29.65	60.96±0.879	32.24±0.880
NR/5 NR-g-MA/10 UT	1.67±0.033	2.52±0.035	15.75±0.087	1139±18.34	52.38±0.925	31.87±1.548
NR/5 NR-g-MA/20 UT	1.35±0.082	2.03±0.100	11.01±0.184	1107±17.67	56.89±0.939	33.41±1.777
NR/5 NR-g-MA/30 UT	1.43±0.007	2.04±0.056	9.44±0.219	961±19.29	61.12±0.676	34.67±0.588

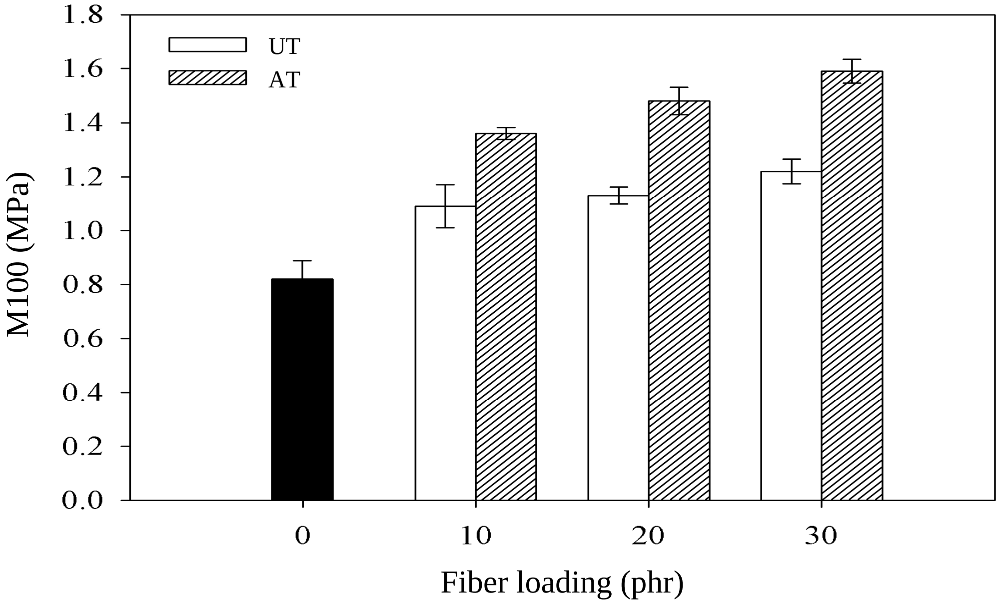


Figure 4.17 Effect of fiber loading on modulus at 100% strain of NR and NR composites filled with UT and AT fiber.

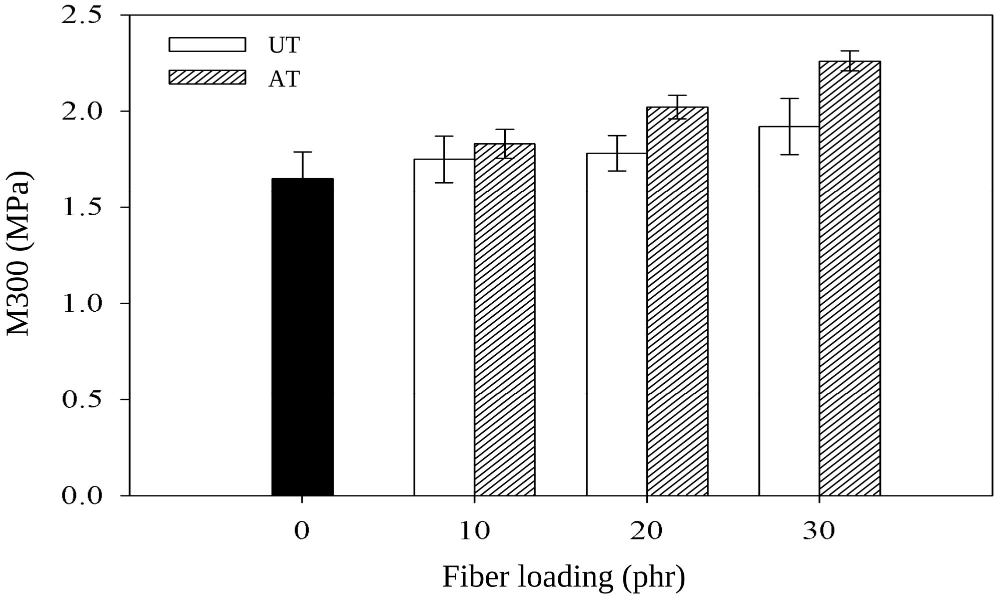


Figure 4.18 Effect of fiber loading on modulus at 300% strain of NR and NR composites filled with UT and AT fiber.

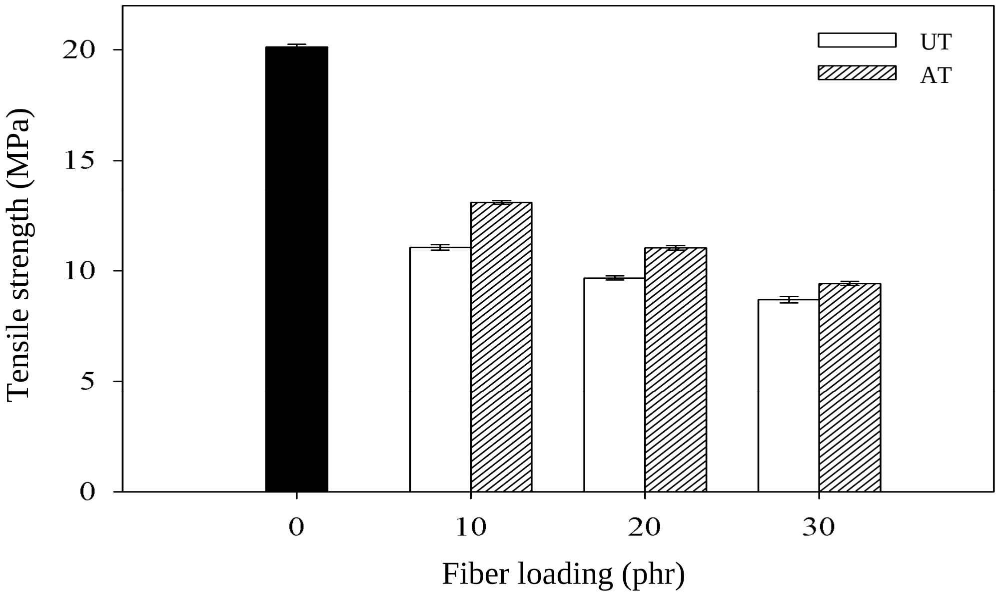


Figure 4.19 Effect of fiber loading on tensile strength of NR and NR composites filled with UT and AT fiber.

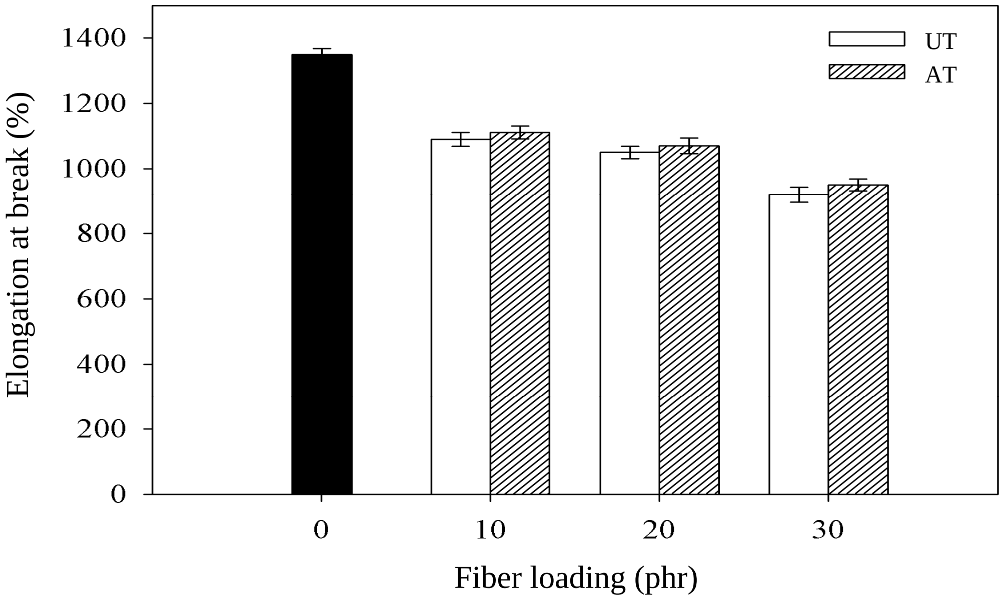


Figure 4.20 Effect of fiber loading on elongation at break of NR and NR composites filled with UT and AT fiber.

The addition of compatibilizers i.e. ENR and NR-g-MA into UT fiber/NR composites gave a positive impact on M100, M300, tensile strength, and elongation at break of the composites as shown in Figure 4.21, 4.22, 4.23, and 4.24 respectively. This was attributed to the improvement in interfacial adhesion between the fiber and NR matrix by the presence of compatibilizers. As the NR is epoxidized, its chemical and physical properties change according to the extent to which the mol% of modification is introduced. When the degree of epoxidation is increased the rubber becomes more polar. This may make ENR become more compatible to sisal fiber than NR. When the ENR was added into the composites, the polar part of ENR may form interaction with sisal fiber while the NR part of ENR may form miscible blend with NR. So, the interfacial interaction between sisal fiber and NR matrix was improved. In case of NR-g-MA, the improved interfacial adhesion between the fiber and NR matrix may occur via the formation of miscible blends between the NR segments of NR-g-MA and the bulk NR and the formation of hydrogen bonds between the polar part of NR-g-MA and the hydroxyl group of fibers in the interfacial region (Ismail and Haw, 2008). Both ENR and NR-g-MA attend at the interface during blending and play the roles of reducing the interfacial tension and strengthening interfacial adhesion resulting in improvement of the mechanical properties of the composites.

Among AT fiber filled NR composite, ENR compatibilized NR composite, and NR-g-MA compatibilized NR composite, AT fiber filled NR composite had the lowest M100, M300, and tensile strength while elongation at break was not much different to those of compatibilized NR composites. This suggested that adding compatibilizers into NR composite may have more efficiency to improve interfacial adhesion between fiber and NR matrix than the fiber alkalization.

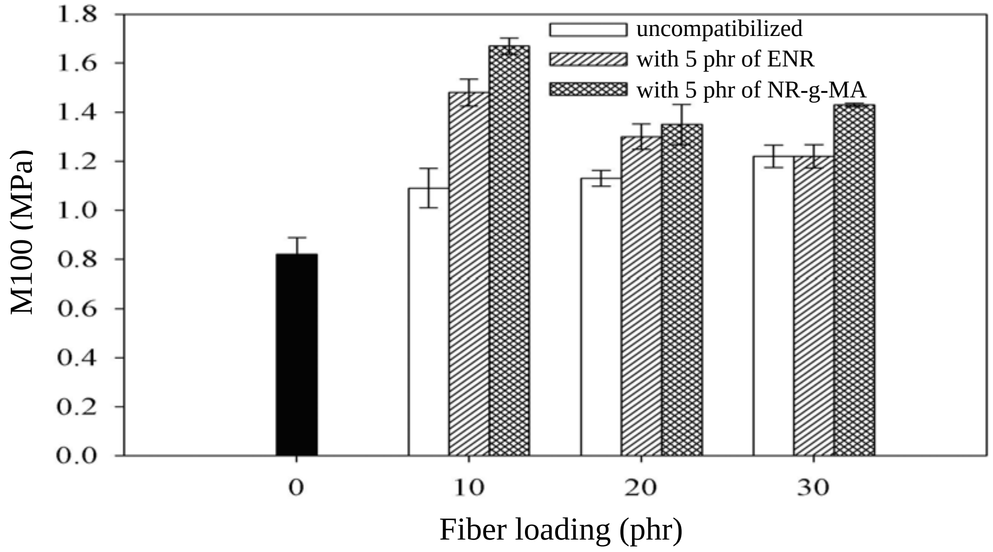


Figure 4.21 Effect of fiber loading on modulus at 100% strain of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

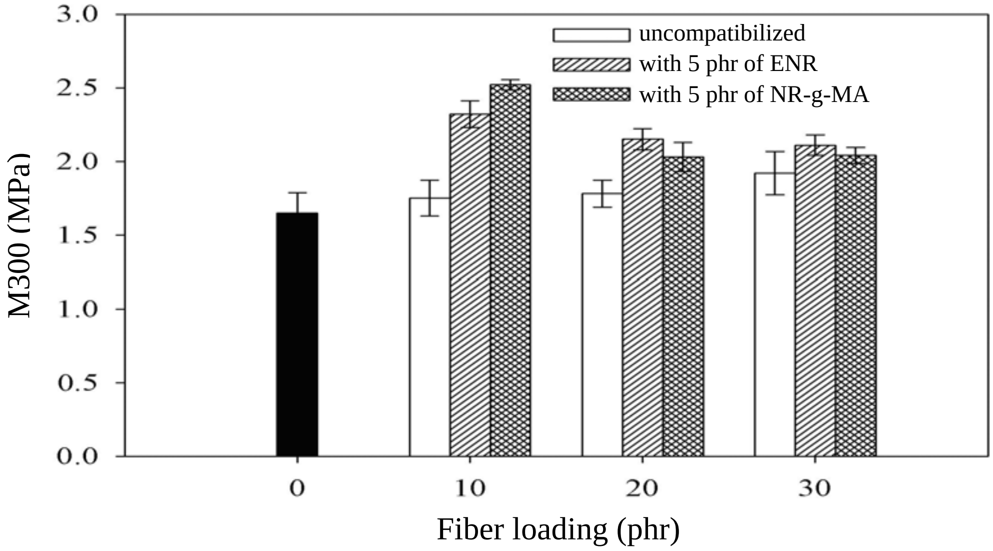


Figure 4.22 Effect of fiber loading on modulus at 300% strain of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

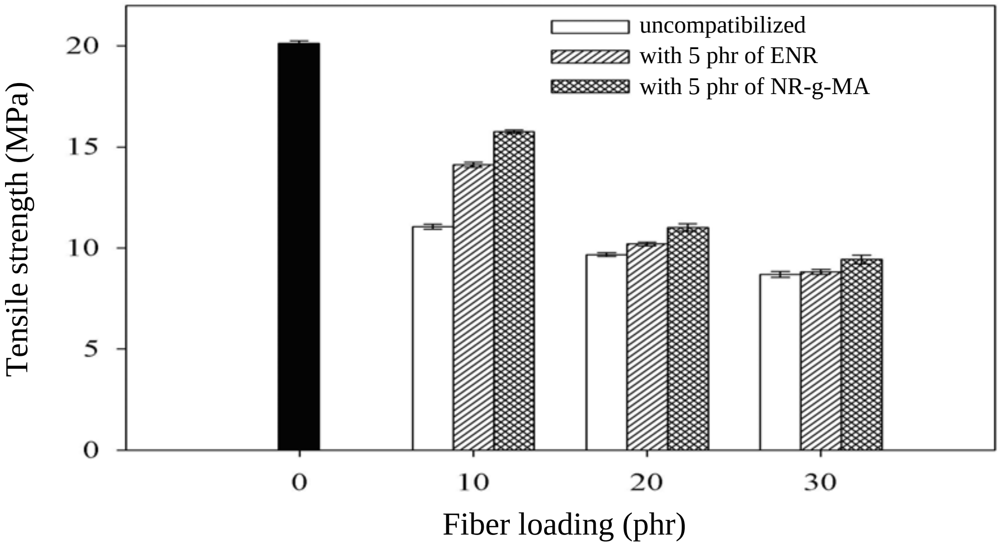


Figure 4.23 Effect of fiber loading on tensile strength of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

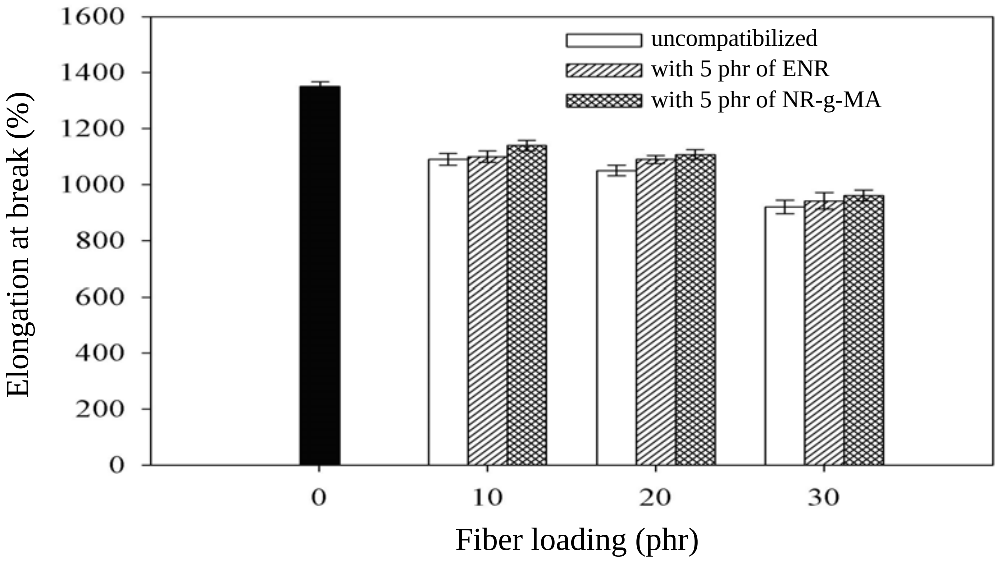


Figure 4.24 Effect of fiber loading on elongation at break of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

4.2.2.2 Tear properties

Tear strength of NR and NR composites filled with UT fiber are shown in Figure 4.25. With increasing UT fiber loading, tear strength of the composites increased. This may be attributed to the obstruction of fiber to the tear paths resulted in more difficult of crack propagation (Ismail, Rozman, Jaffri, and Mohd Ishak, 1997). The similar trend was found with AT fiber/NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites when fiber loading was increased. The composites filled with AT fiber showed better tear strength than the composites filled with UT fiber due to the better adhesion between fiber and NR matrix. Mathew and Joseph (2007) reported the similar observation in isora fiber/NR composites.

Figure 4.26 shows the tear strength of NR, NR composites, and compatibilized NR composites. NR-g-MA compatibilized NR composites gave higher tear strength than the ENR compatibilized NR composites at all fiber loading. This may be because the NR-g-MA provided better interfacial adhesion between fiber and NR matrix than the ENR.

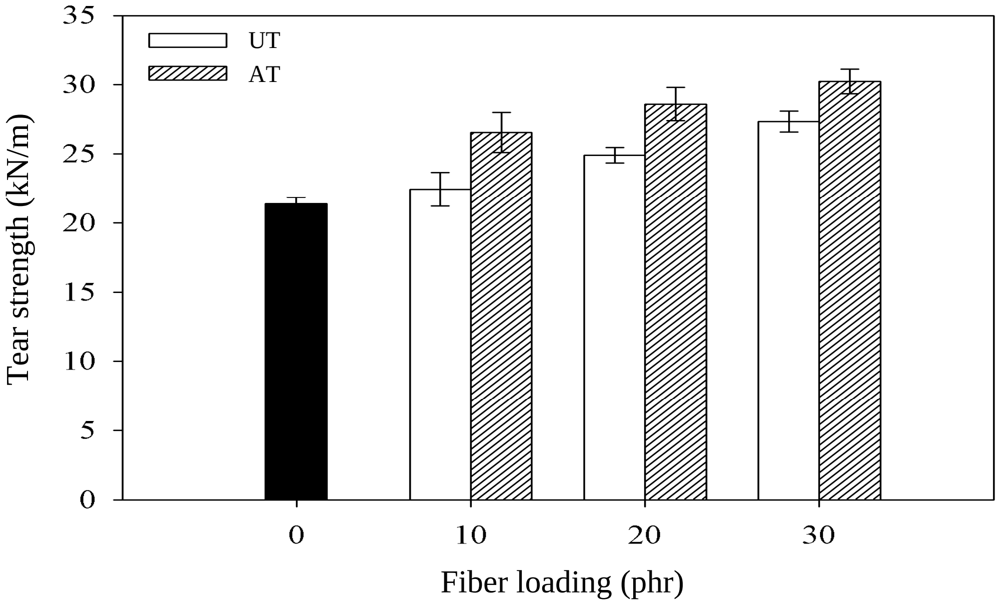


Figure 4.25 Effect of fiber loading on tear strength of NR and NR composites filled with UT and AT fiber.

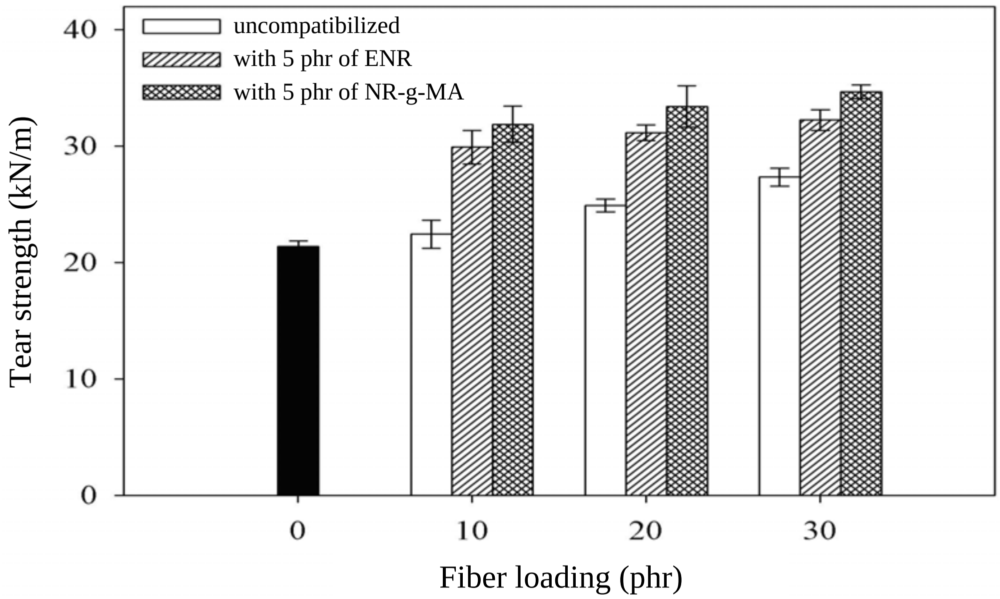


Figure 4.26 Effect of fiber loading on tear strength of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

4.2.2.3 Hardness

Hardness of the composites increased with increasing UT fiber loading as shown in Figure 4.27. As fiber loading was increased, the composites became stiffer and harder resulted in increased hardness of the composites. Moreover, from Figure 4.27, the hardness of the composites filled with AT fiber were better than that of the composites filled with UT fiber since the alkali treatment improved the adhesion between the fiber and rubber. The similar observation was reported by De et al. (2006).

With adding compatibilizer into NR matrix, hardness of the composites also increased as shown in Figure 4.28. This can be attributed to the improvement of interaction between fiber and NR matrix by the compatibilizer.

There was no significant difference in hardness value of ENR compatibilized NR composites and that of NR-g-MA compatibilized NR composites.

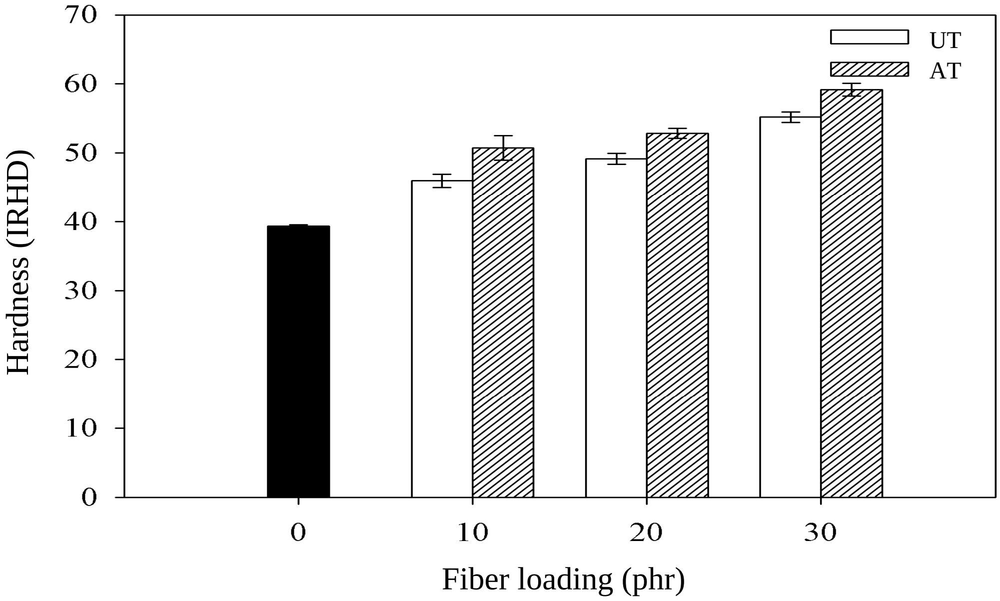


Figure 4.27 Effect of fiber loading on hardness of NR and NR composites filled with UT and AT fiber.

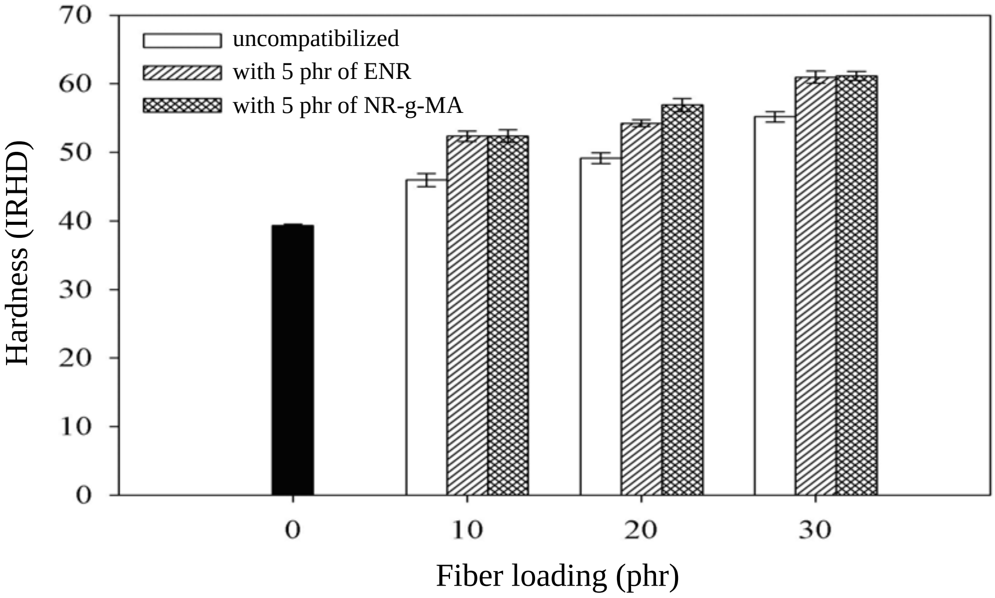


Figure 4.28 Effect of fiber loading on hardness of NR, uncompatibilized NR composites, ENR compatibilized NR composites, and NR-g-MA compatibilized NR composites.

4.2.3 Fiber length distribution analysis

The fiber length distribution index before and after mixing of NR/10UT, NR/10AT, NR/5ENR/10UT, and NR/5NR-g-MA/10UT composites are listed in Table 4.4. No significant difference in the number average fiber length ($\overline{L}_n$) and the weight average fiber length ($\overline{L}_w$) values, diameter of fiber, and length to diameter ratio before and after mixing of the composites was found. The value of $\overline{L}_w / \overline{L}_n$, the polydispersity index, can be taken as a measure of fiber length distribution. The polydispersity index of the composites did not change before and after mixing. This may suggest that the change in mechanical properties of the composites was not influenced by the fiber breakage.

Table 4.4 Fiber length distribution index, diameter, and length to diameter of NR/10UT, NR/10AT, NR/5ENR/10UT, and NR/5NR-g-MA/10UT composites before and after mixing.

Formulation	**Distribution index**						**Diameter (μm)**		**Length/Diameter**	
	$\overline{\mathbf{L}}_{\mathbf{n}}$		$\overline{\mathbf{L}}_{\mathbf{w}}$		$\overline{\mathbf{L}}_{\mathbf{w}}/\overline{\mathbf{L}}_{\mathbf{n}}$					
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
NR/10 UT	2.1523	2.1300	2.2271	2.2182	1.0456	1.0306	317.23	316.54	7.20	7.40
NR/10 AT	2.1432	2.1360	2.2432	2.2398	1.0466	1.0486	317.20	316.05	7.28	7.27
NR/5 ENR/10 UT	2.1475	2.1380	2.2455	2.2361	1.0457	1.0459	316.82	315.77	7.25	7.22
NR/5 NR-g-MA/10 UT	2.1551	2.1417	2.2533	2.2428	1.0456	1.0472	317.41	315.93	7.29	7.24

4.2.4 Crosslink density

Crosslink density of NR, NR composites, and compatibilized NR composites are listed in Table 4.5 and shown in Figure 4.29. There was no significant difference in the crosslink density of the composites after addition of NR-g-MA. This implied that addition of NR-g-MA insignificantly affected the crosslink density of the composites. However, Jacob, Francis, Thomas, and Varughese (2006) determined crosslink density of sisal/oil palm hybrid fiber filled NR composites by dynamic mechanical analysis method and found that NR composites with alkali treated sisal/oil palm hybrid fiber provided higher crosslink density than NR composite filled with untreated fiber. Moreover, Zeng et al. (2010) reported that crosslink density which was determined using equilibrium swelling method of cotton fiber/NR composite filled with NR-g-MA was higher than that of NR composite without NR-g-MA.

Table 4.5 Crosslink density of NR, NR composites, and compatibilized NR composites.

Formulation	**Crosslink density x 10^4 (mole/cm^3)**
NR	1.0382±0.021
NR/10 UT	1.0319±0.015
NR/20 UT	1.0226±0.012
NR/30 UT	0.9829±0.011
NR/10 AT	1.0665±0.017
NR/20 AT	1.0583±0.020
NR/30 AT	1.0438±0.018
NR/5 ENR/10 UT	1.0663±0.014
NR/5 ENR/20 UT	1.0571±0.018
NR/5 ENR/30 UT	1.0447±0.015
NR/5 NR-g-MA/10 UT	1.0832±0.015
NR/5 NR-g-MA/20 UT	1.0753±0.222
NR/5 NR-g-MA/30 UT	1.0612±0.019

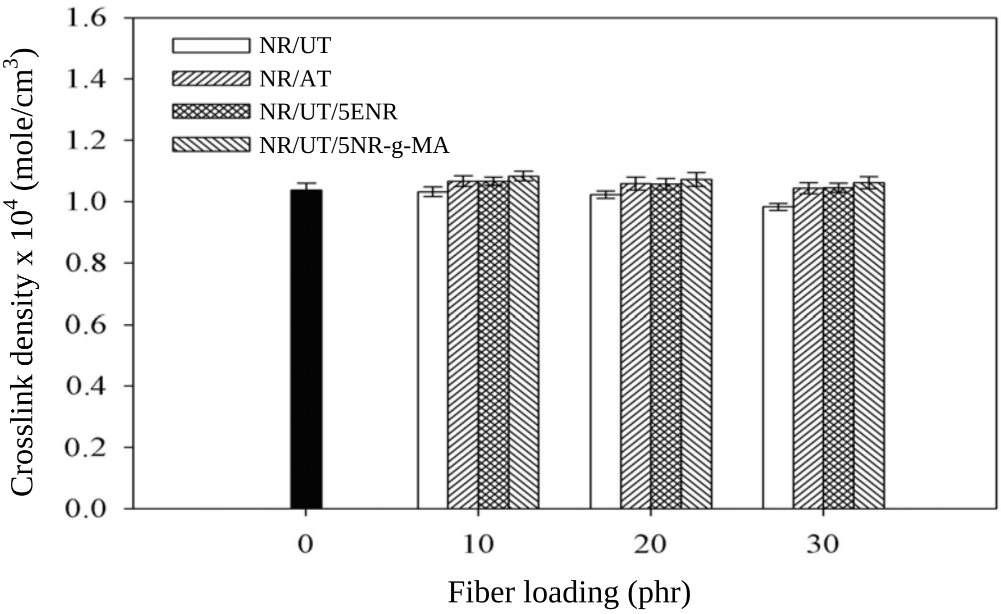
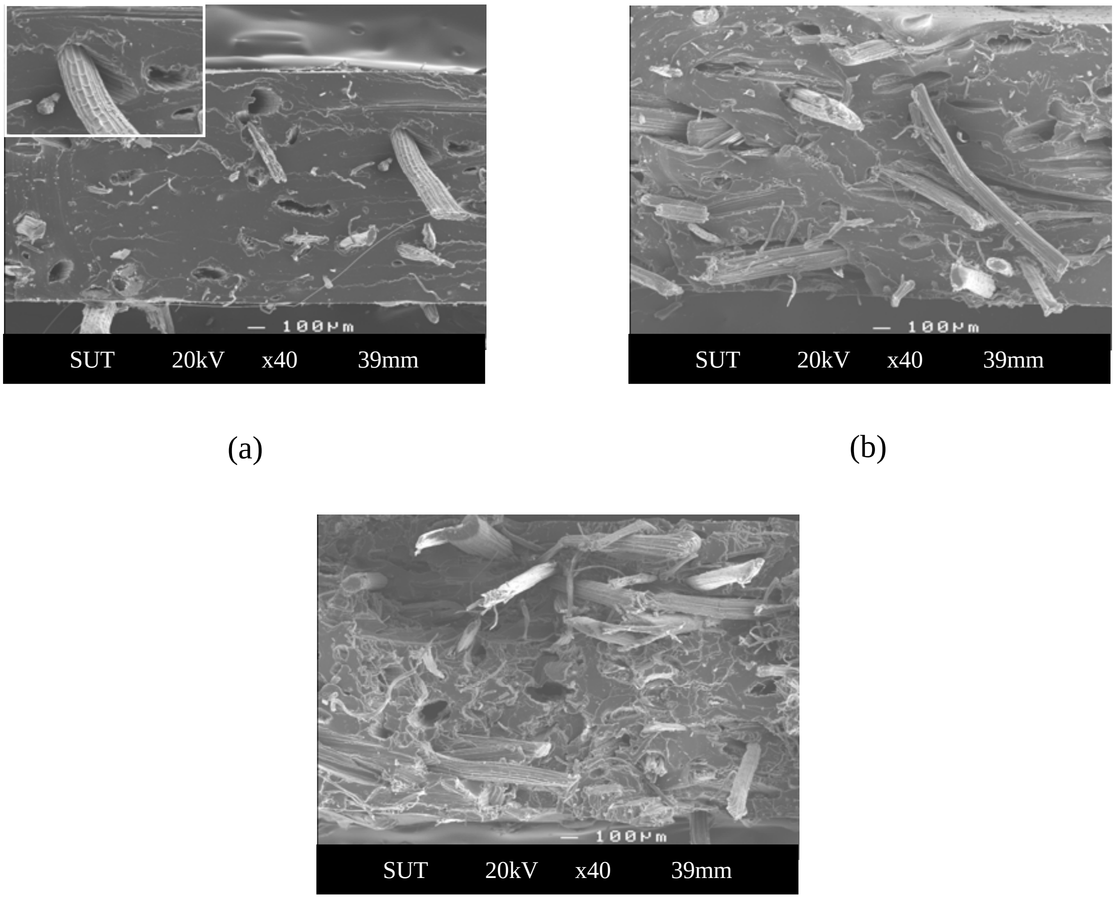


Figure 4.29 Crosslink density of NR, NR composites, and compatibilized NR composites at various fiber loading.

4.2.5 Morphological properties

SEM micrographs of tensile fracture surfaces of NR/UT composites with various fiber loading (Figure 4.30) revealed a few holes after the fibers were pull out from NR matrix due to weak adhesion between hydrophilic sisal fiber and hydrophobic NR. Moreover, with increasing fiber loading, the agglomeration of fibers in NR matrix was observed as shown in Figure 4.30 (b) and (c). This caused a reduction in tensile strength of the composites.

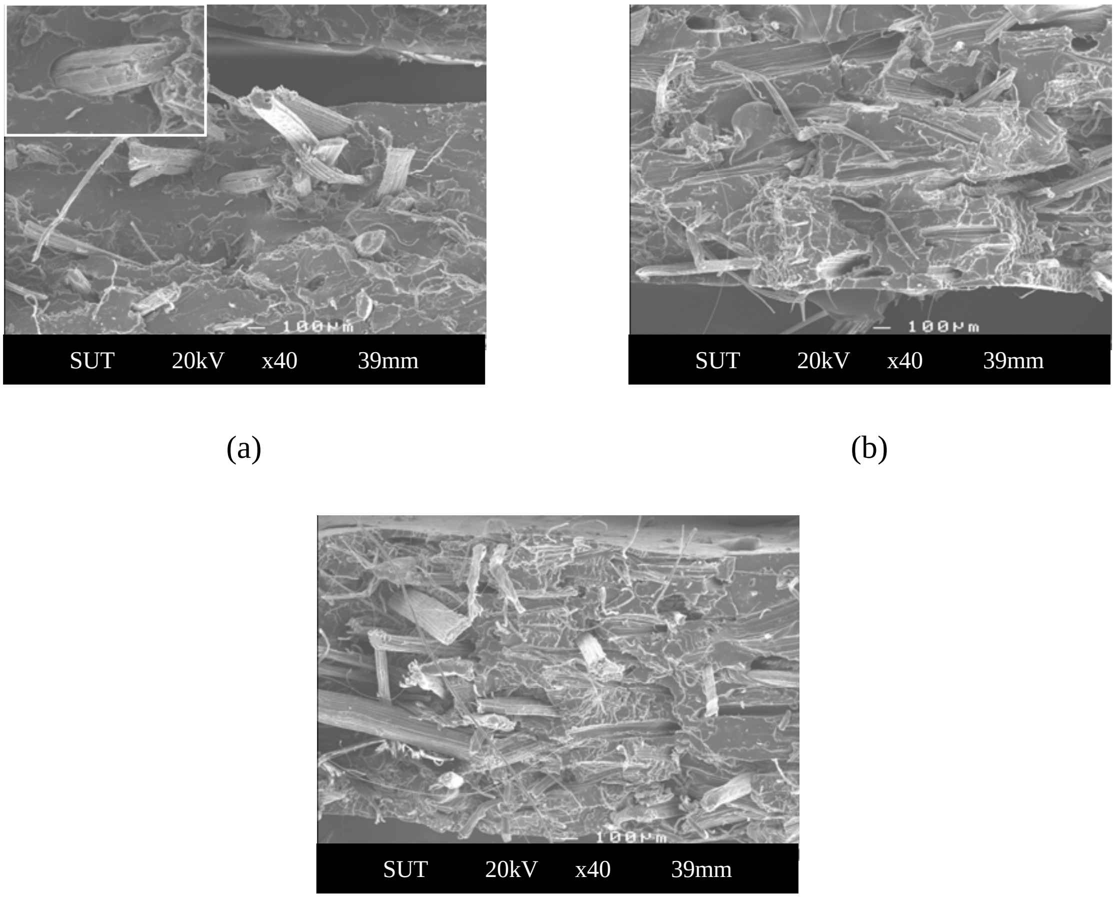
SEM micrographs of NR/AT composites showed the reduction in fiber pull out from NR matrix and small gap between fiber and NR matrix when compared with NR/UT composites as shown in Figure 4.31. This indicated an improved adhesion between the fiber and NR matrix. With increasing AT fiber loading, agglomeration of fiber was observed. The similar observation was found in ENR compatibilized NR composites and NR-g-MA compatibilized NR composites as shown in Figure 4.32 and 4.33 respectively. However, from SEM micrographs, it could not make the distinction between alkali treated sisal fiber/NR composites and the compatibilized NR composites.



(a) (b)

(c)

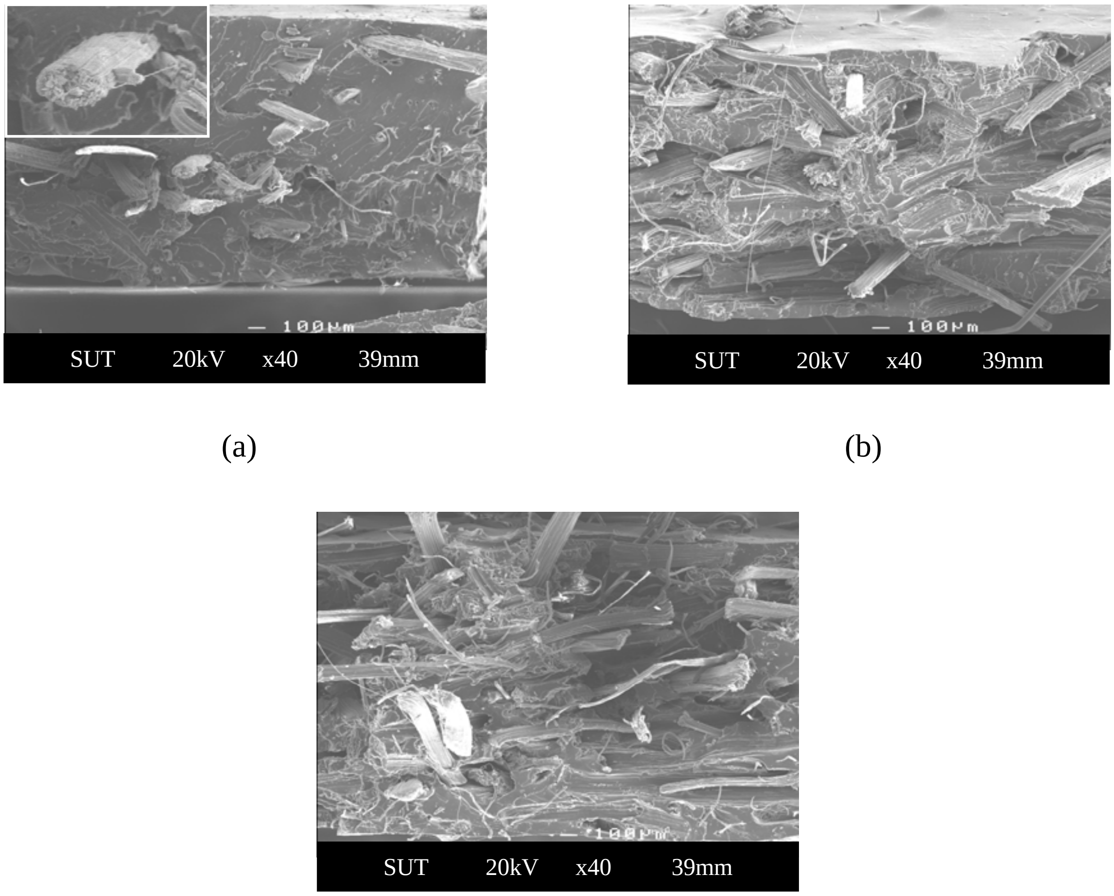
Figure 4.30 SEM micrographs at 40x magnification of (a) NR/10UT, (b) NR/20UT, and (c) NR/30UT composites.



(a) (b)

(c)

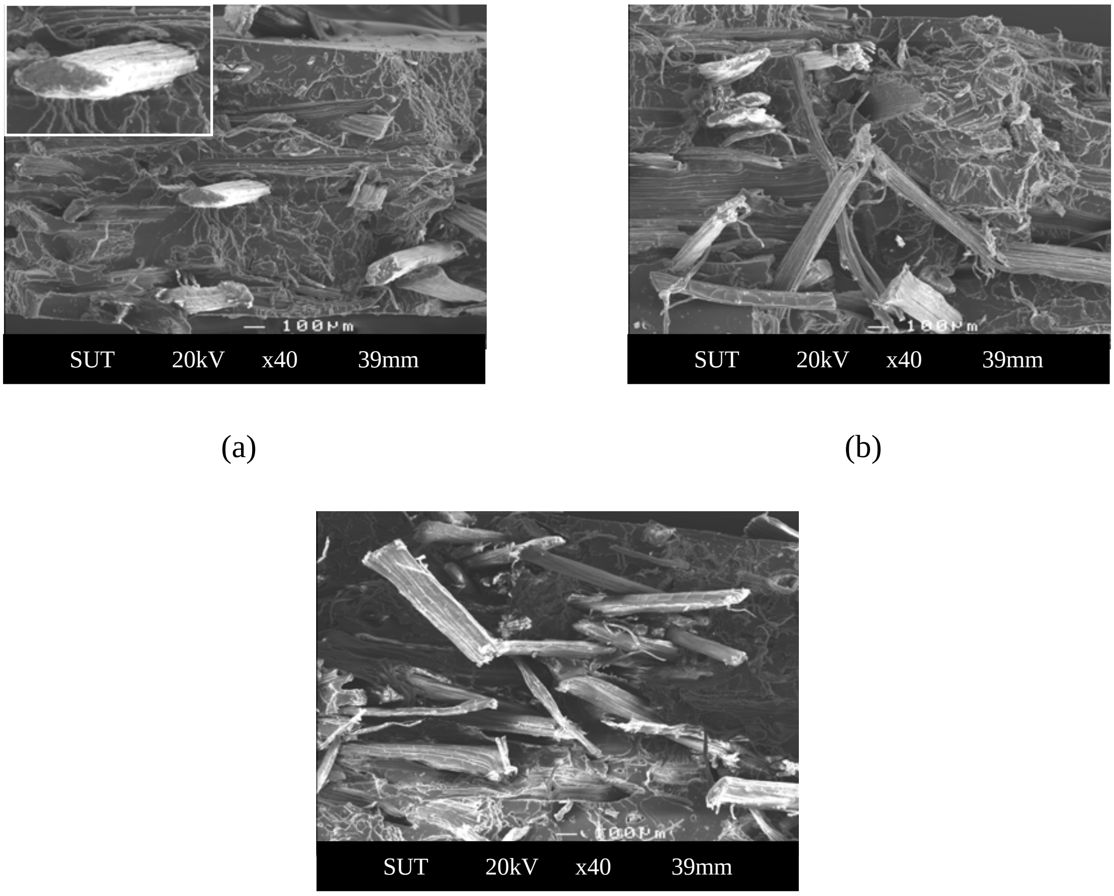
Figure 4.31 SEM micrographs at 40x magnification of (a) NR/10AT, (b) NR/20AT, and (c) NR/30AT composites.



(a) (b)

(c)

Figure 4.32 SEM micrographs at 40x magnification of (a) NR/10UT/5ENR, (b) NR/20UT/5ENR, and (c) NR/30UT/5ENR composites.



(a) (b)

(c)

Figure 4.33 SEM micrographs at 40x magnification of (a) NR/10UT/5NR-g-MA, (b) NR/20UT/5NR-g-MA, and (c) NR/30UT/5NR-g-MA composites.

From cure characteristics and mechanical properties results, the NR-g-MA compatibilized NR composite with 10 phr of UT fiber was selected to study effect of compatibilizer contents on the properties of the NR composites.

4.3 Effect of NR-g-MA loading on properties of sisal fiber/NR composites

4.3.1 Cure characteristics

Increasing NR-g-MA loading resulted in increased MH and ML of the NR composites as shown in Table 4.6 and Figure 4.34. This was due to strong bonding at the fiber-rubber interface resulting in stronger and stiffer composites. Ismail and Haw (2008) suggested that an increase in MH and ML by increasing NR-g-MA loading showed the advantage of using NR-g-MA as the damping characteristics reducer in oil palm ash/NR composites. Figure 4.35 shows scorch time and cure time of the composites. Scorch time and cure time of the compatibilized NR composites were longer than that of uncompatibilized NR composite. Moreover, with increasing NR-g-MA loading, scorch time and cure time of NR-g-MA compatibilized NR composites also increased. This may be attributed to the increase of acidity of maleic acid and the interation between maleic anhydride and the accelerator (Pattamaprom, C. et al., 2008).

Table 4.6 Cure characteristics of uncompatibilized NR composite and NR-g-MA compatibilized NR composites at various NR-g-MA loading.

Formulation	**MH (dN-m)**	**ML (dN-m)**	**Time (min)**	
			t_{s1}	**t_{90}**
NR/10 UT	19.741	2.620	3.35	7.16
NR/10 UT/2.5 NR-g-MA	21.552	3.651	4.04	8.16
NR/10 UT/5.0 NR-g-MA	26.348	4.376	4.32	8.43
NR/10 UT/7.5 NR-g-MA	26.970	4.480	6.44	9.42
NR/10 UT/10.0 NR-g-MA	27.881	4.633	7.19	9.46

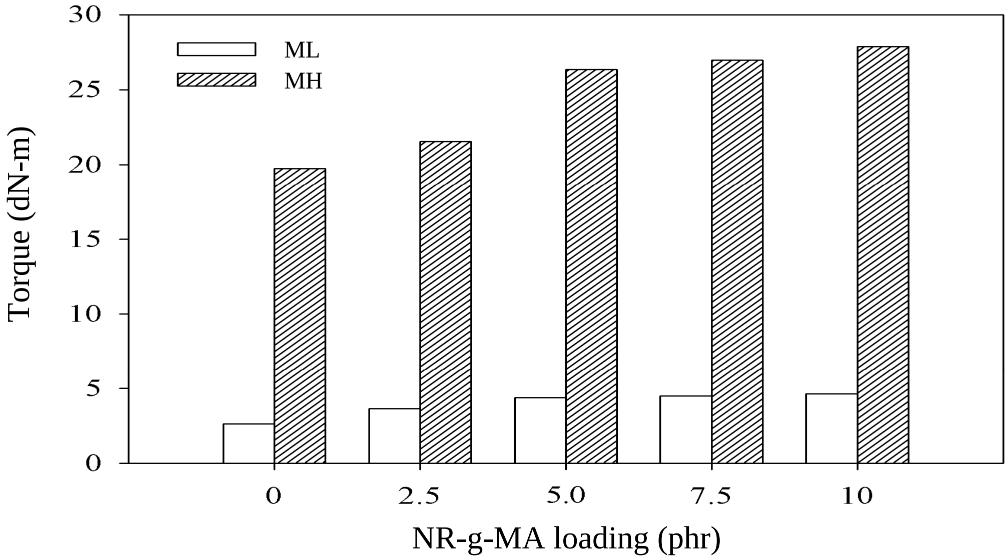


Figure 4.34 Effect of NR-g-MA loading on maximum torque and minimum torque of uncompatibilized NR composite and NR-g-MA compatibilized NR composites.

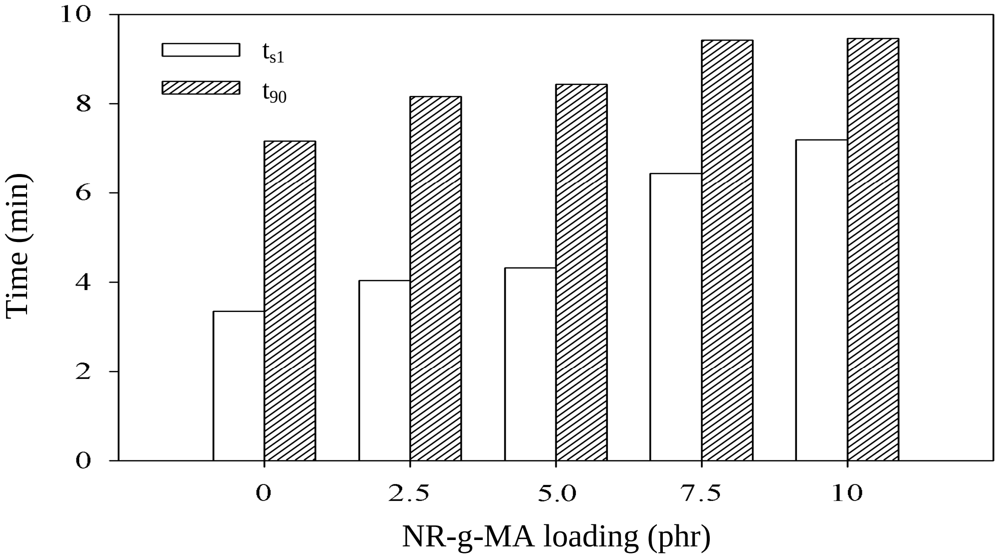


Figure 4.35 Effect of NR-g-MA loading on scorch time and cure time of uncompatibilized NR composite and NR-g-MA compatibilized NR composites.

4.3.2 Mechanical properties

The mechanical properties of uncompatibilized NR composite and NR-g-MA compatibilized NR composites at various NR-g-MA loading are listed in Table 4.7.

4.3.2.1 Tensile properties

The increment in the modulus at 100% strain (M100) and modulus at 300% strain (M300) with increasing NR-g-MA loading indicated the increase in interfacial adhesion between the fiber and NR matrix by NR-g-MA as shown in Figure 4.36. In addition, Figure 4.37 and 4.38 show the effect of NR-g-MA loading on the tensile strength and elongation at break of uncompatibilized NR composite and NR-g-MA compatibilized NR composites respectively. Tensile strength and elongation at break of the compatibilized NR composites also increased with increasing NR-g-MA loading due to better adhesion between fiber and NR matrix. This led to better stress transfer from fiber and NR matrix resulting in higher tensile strength and elongation at break of the composites (Ismail and Haw, 2008).

Table 4.7 Mechanical properties of uncompatibilized NR composite and NR-g-MA compatibilized NR composites at various NR-g-MA loading.

Formulation	M100 (MPa)	M300 (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (IRHD)	Tear strength (kN/m)
NR/10 UT	1.09±0.081	1.75±0.132	11.05±0.121	1090±21.22	45.96±0.955	22.43±1.220
NR/10 UT/2.5 NR-g-MA	1.28±0.072	1.91±0.128	12.66±0.162	1115±20.65	49.44±1.031	27.21±1.492
NR/10 UT/5.0 NR-g-MA	1.67±0.033	2.52±0.035	15.75±0.087	1139±18.34	52.38±0.925	31.87±1.548
NR/10 UT/7.5 NR-g-MA	1.71±0.051	2.66±0.079	16.90±0.085	1150±18.49	54.82±1.090	33.75±1.075
NR/10 UT/10.0 NR-g-MA	1.78±0.077	2.72±0.130	18.21±0.099	1210±25.80	56.66±1.070	34.13±1.490

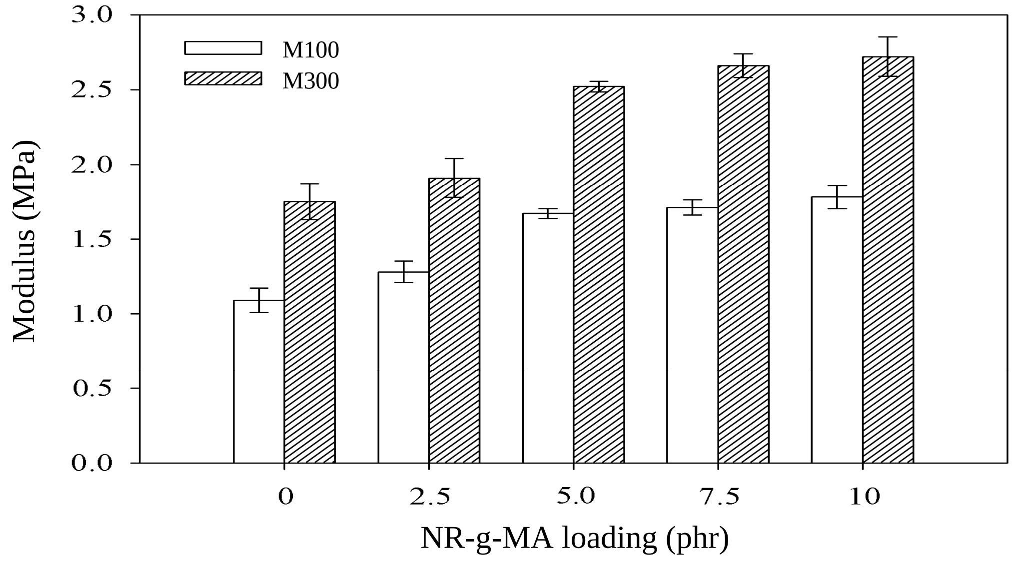


Figure 4.36 Effect of NR-g-MA loading on modulus at 100% strain and modulus at 300% strain of uncompatibilized NR composite and NR-g-MA compatibilized NR composites.

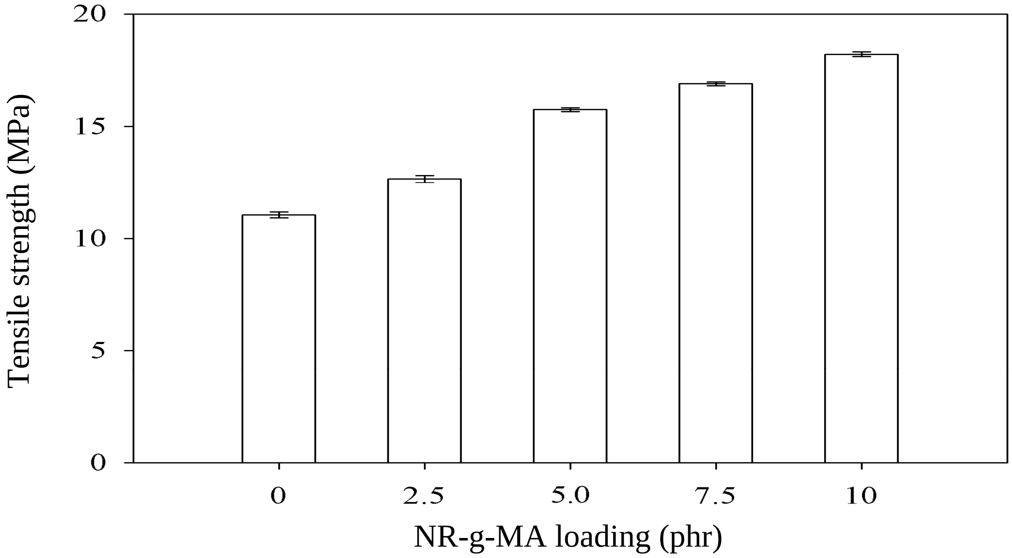


Figure 4.37 Effect of NR-g-MA loading on tensile strength of uncompatibilized NR composite and NR-g-MA compatibilized NR composites.

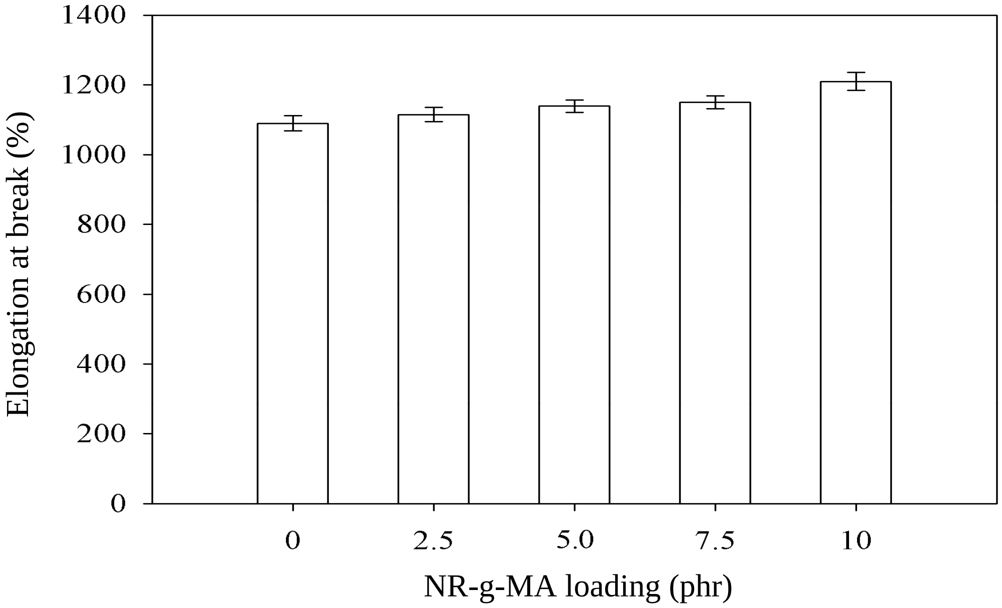


Figure 4.38 Effect of NR-g-MA loading on elongation at break of uncompatibilized NR composite and NR-g-MA compatibilized NR composites.

4.3.2.2 Tear properties

Tear strength like tensile strength was affected by filler-rubber adhesion, particle size, and surface area of the filler (Mohd Ishak and Bakar, 1995). Tear strength of NR-g-MA compatibilized NR composites were higher than that of uncompatibilized NR composite. Moreover, as NR-g-MA loading was increased tear strength of the compatibilized NR composites increased as shown in Figure 4.39. The improvement of tear strength was attributed to the better interfacial adhesion between fiber and NR matrix with the presence of NR-g-MA.

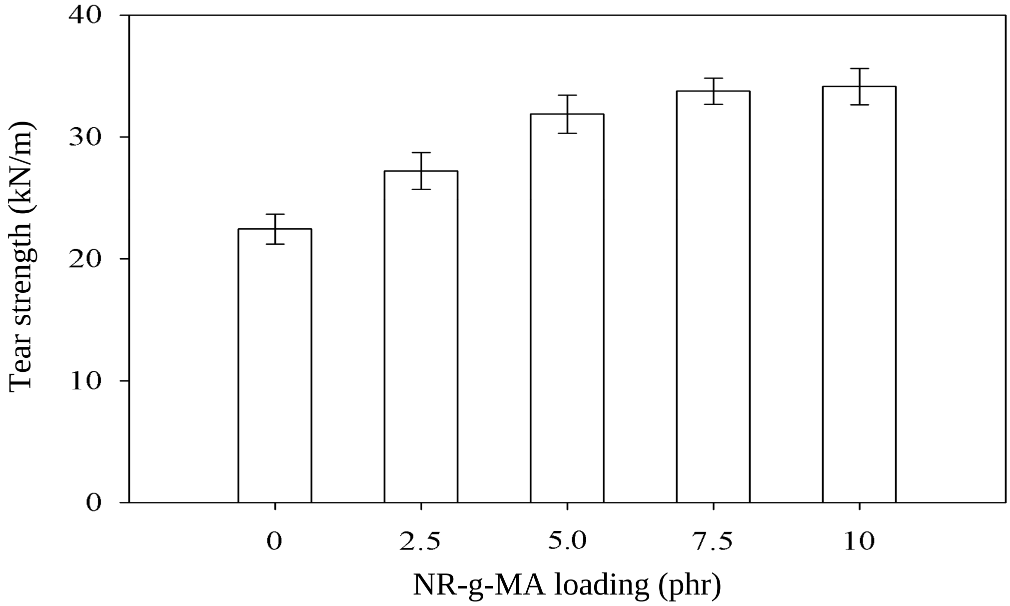


Figure 4.39 Effect of NR-g-MA loading on tear strength of uncompatibilized NR composite and NR-g-MA compatibilized NR composites.

4.3.2.3 Hardness

Adding NR-g-MA into NR composite resulted in improved hardness of the composite. In addition, with increasing NR-g-MA loading, hardness of the composites increased as shown in Figure 4.40. This was due to the improvement of interfacial interaction between fiber and NR matrix by NR-g-MA. In addition, the increase in hardness was correlative to the high modulus of rubber matrix (Brown and Soulagnet, 2001)

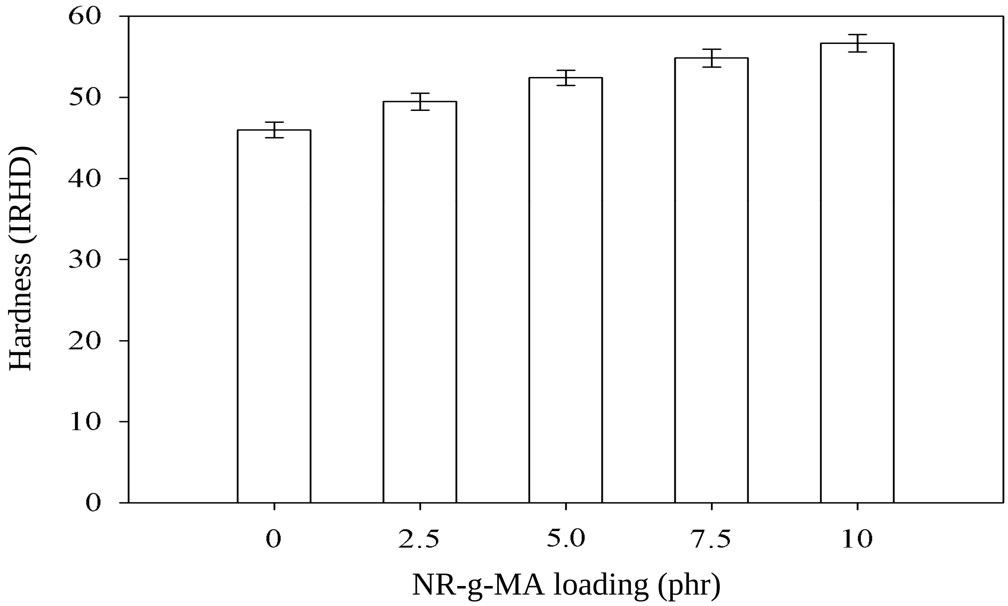


Figure 4.40 Effect of NR-g-MA loading on hardness of uncompatibilized NR composite and NR-g-MA compatibilized NR composites.

4.3.3 Crosslink density

Crosslink density of uncompatibilized NR composites and NR-g-MA compatibilized NR composites with various NR-g-MA loading are listed in Table 4.8 and shown in Figure 4.41. No significant difference in the crosslink density of the composites was found. So, the increase in torque and the improved mechanical properties of the composites after addition of NR-g-MA may cause from the improved interfacial interaction between fiber and NR matrix.

Table 4.8 Crosslink density of uncompatibilized NR composite and NR-g-MA compatibilized NR composites.

Formulation	**Crosslink density x 10^4 (mole/cm^3)**
NR/10 UT	1.0319±0.015
NR/10 UT/2.5 NR-g-MA	1.0597±0.011
NR/10 UT/5.0 NR-g-MA	1.0832±0.014
NR/10 UT/7.5 NR-g-MA	1.0966±0.013
NR/10 UT/10.0 NR-g-MA	1.0991±0.013

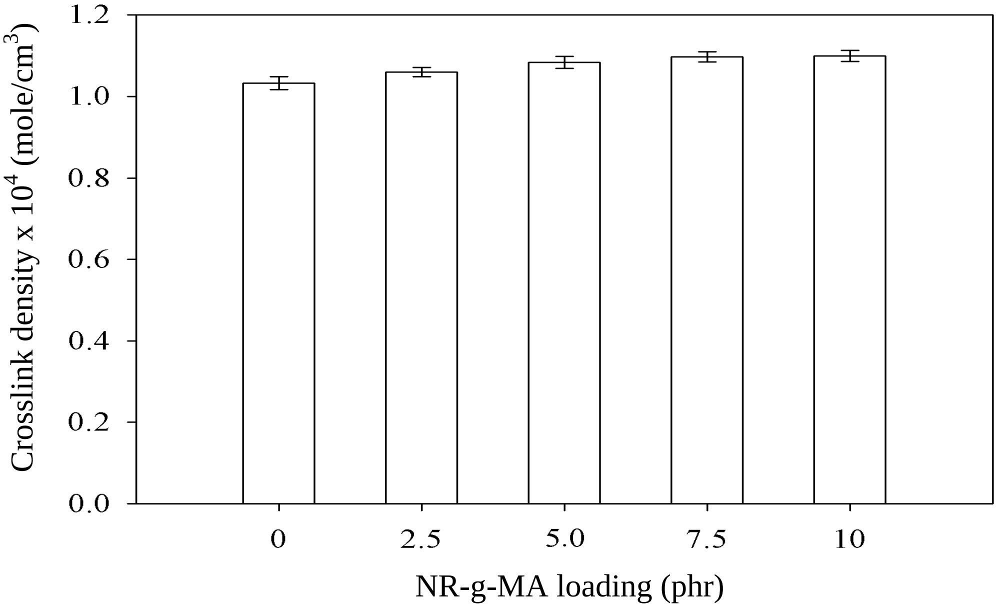
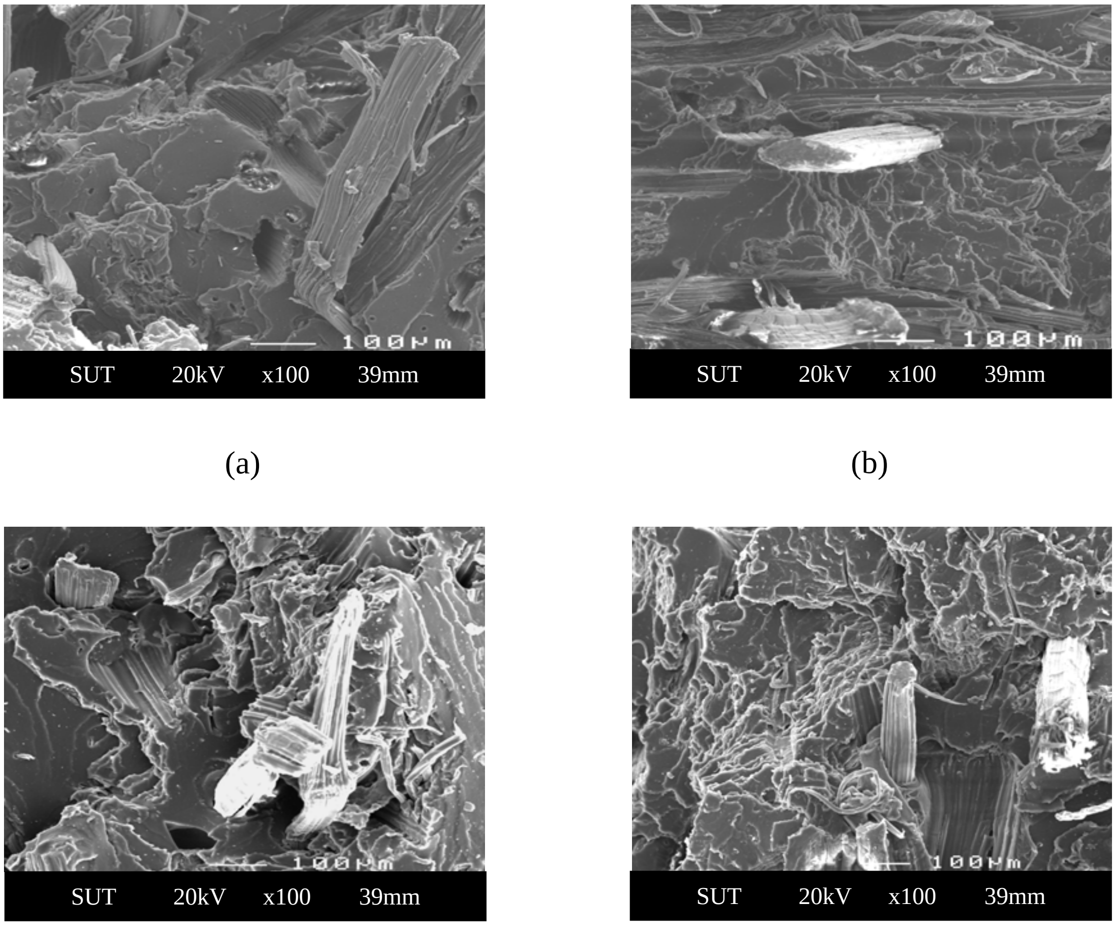


Figure 4.41 Crosslink density of uncompatibilized NR composite and NR-g-MA compatibilized NR composites at various NR-g-MA loading.

4.3.4 Morphological properties

SEM micrographs of tensile fracture surface of uncompatibilized NR composite and NR-g-MA compatibilized NR composites with various NR-g-MA contents are shown in Figure 4.42. When compared to uncompatibilized NR composite, NR-g-MA compatibilized NR composites showed less fiber pull out indicating strong interaction between the fiber and rubber matrix as shown in Figure 4.42 (b) – (d).



(a) (b)

(c) (d)

Figure 4.42 SEM micrographs at 100x magnification of (a) NR/10UT, (b) NR/10UT/5.0NR-g-MA, (c) NR/10UT/7.5NR-g-MA, and (d) NR/10UT/10.0NR-g-MA composites.

From cure characteristics and mechanical properties results, the properties of sisal fiber/NR composite containing 10 phr of NR-g-MA were compared with those of silica/NR and carbon black/NR composites at equal filler loading (10 phr).

4.4 Cure characteristics and tensile properties comparison of NR-g-MA compatibilized NR composite filled with sisal fiber, NR composite filled with carbon black, and NR composite filled with silica

4.4.1 Cure characteristics

Cure characteristics of NR, NR/10UT/10NR-g-MA, NR/10silica, and NR/10carbon black composites are listed in Table 4.9. The difference in cure characteristics of the composites may be because each filler type has different properties e.g. surface area, surface activity, particle size, moisture content, and metal oxide content (Ismail et al., 1997). Figure 4.43 shows the maximum torque (MH) and minimum torque (ML) of NR, NR/10UT/10NR-g-MA, NR/10silica, and NR/10carbon black composites. MH and ML of NR were lower than those of NR/10UT/10NR-g-MA, NR/10silica, and NR/10carbon black composites. This was because the incorporation of more rigid filler into rubber reduced elasticity of the rubber chains leading to more rigid vulcanizates. When compared between NR/10silica and NR/10carbon black composites, NR/10silica composite showed lower MH and ML than NR/10carbon black composite. This may be attributed to larger particle size of silica (80 µm) than carbon black (28 nm). The smaller surface area of silica implied the poorer interaction between filler and rubber matrix. So, a lower restriction to molecular motion of the silica-macromolecules was obtained. Mohd Ishak and Bakar (1995) suggested that the addition of smaller fillers size tended to impose extra resistance to flow. However, NR/10UT/10NR-g-MA and NR/10carbon black composites provided insignificant difference in MH and ML.

NR/10UT/10NR-g-MA composite showed the longest scorch time and cure time as shown in Figure 4.44. This may be attributed to the acidity of maleic acid and the interaction between maleic anhydride and the accelerator (Pattamaprom, C. et al., 2008). NR/10silica composite exhibited longer scorch time and cure time than NR/10carbon black composite due to the silica-activator interaction. The silica reacted with zinc oxide and subsequently reduced the zinc reactivity, therefore the sulfur reaction was slow down (Nasir, Poh, and Ng, 1988). Patterman (1973) studied the effect of silica on cure behaviour of rubber and suggested that cure retardation was dependent on the surface area of silica and total content of silica. Sae-Oui, P., Rakdee, C., and Thanmathorn, P. (2002) also observed the similar result that cure time of silica/NR composite was higher than carbon black/NR composite due to the reduction of zinc complex in the rubber matrix, as it was trapped on the silica surface.

Table 4.9 Cure characteristics of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

Formulation	**MH (dN-m)**	**ML (dN-m)**	**Time (min)**	
			t_{s1}	**t_{90}**
NR	16.662	2.310	4.27	7.54
NR/10 UT/10 NR-g-MA	27.881	4.633	7.19	9.46
NR/10 Silica	21.266	3.511	3.15	8.03
NR/10 Carbon black	28.005	5.328	2.48	6.22

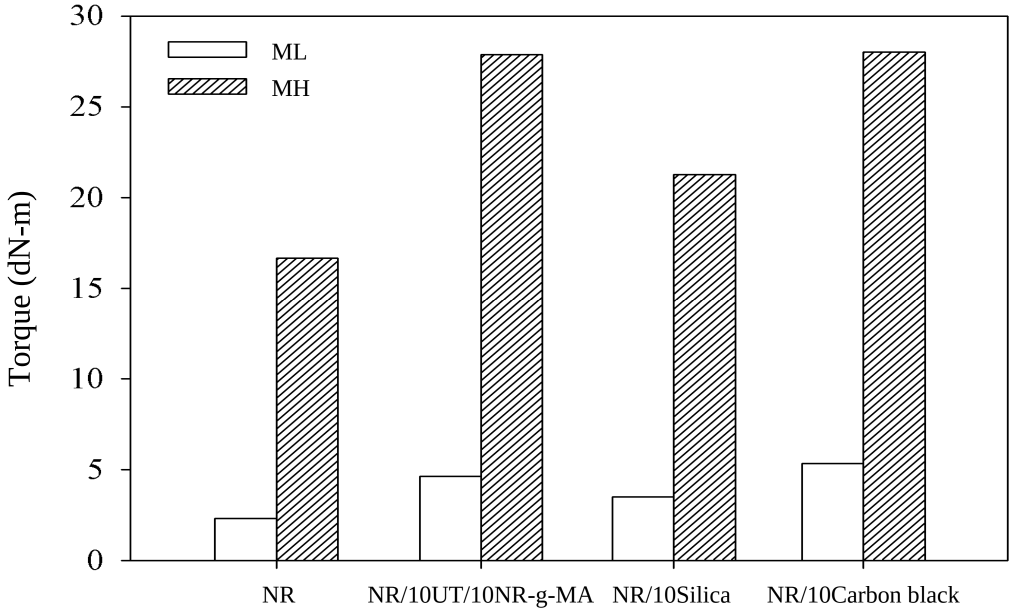


Figure 4.43 Maximum and minimum torque of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

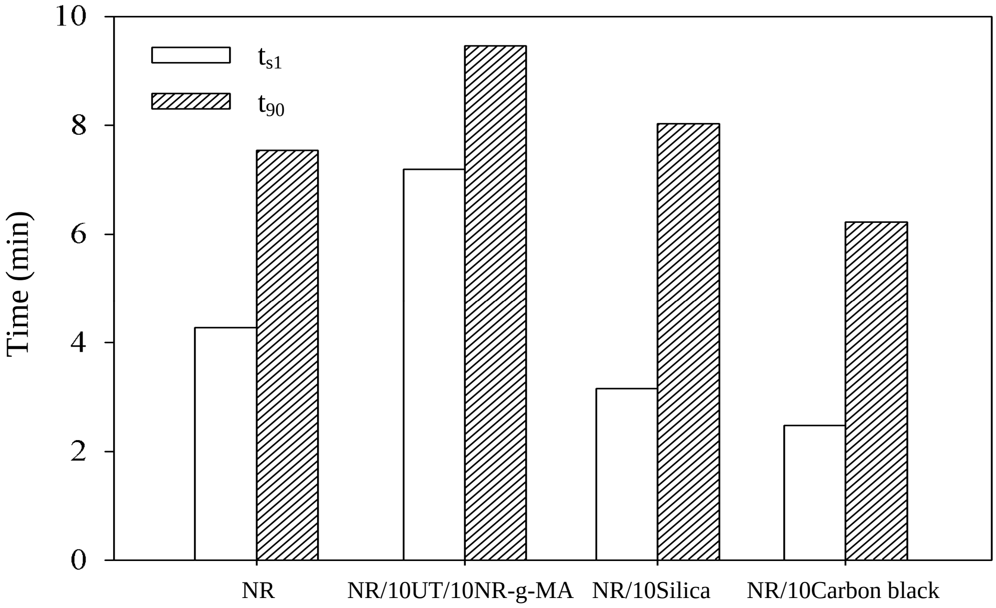


Figure 4.44 Scorch time and cure time of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

4.4.2 Tensile properties

The tensile properties of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black are listed in Table 4.10. Specific modulus (tensile strength) is a ratio between the modulus (tensile strength) and the density of composites. With adding fillers into NR, modulus at 100% (M100) and 300% strain (M300) of the composites increased while tensile strength and elongation at break decreased as shown in Figure 4.45, 4.46, and 4.47 respectively. Among three types of filler, carbon black gave the most effective reinforcement on NR. This may be explained in terms of particle size and surface area of fillers. Carbon black has the smallest particle size hence it has the largest surface area leading to the greatest interaction between filler and rubber matrix (Mohd Ishak and Bakar, 1995; Egwaikhise et al., 2007). In addition, according to reinforcement concept, the factors affecting the reinforcement of elastomer include filler shape, filler structure, specific surface area, and volume fraction of filler. Parkinson (1957) reported that decreasing the particle size of carbon black filler generally improved the tensile properties of the rubber composites. Wagner (1976) suggested that the stiffness or modulus of the filler filled NR composite can be enhanced by improving the surface area and surface reactivity of fillers, filler dispersion, and filler-rubber interaction. In case of silica filled NR composite, it is well known that silica is more difficult to disperse in NR matrix than carbon black due to its polar surface resulting in poor dispersion and agglomeration in non-polar NR matrix (Buathong, S., Pongprayoon, T., and Suwanmala, P., 2005; Sahakaro and Beraheng, 2008). This caused reduced filler-rubber interactions and consequently decreased the ability of the fillers to restrain gross deformation of the rubber matrix. This led to worst tensile properties of silica/NR composite. NR-g-MA compatibilized NR composite showed higher elongation at break than carbon black filled NR and silica filled NR. This was due to the fiber-rubber matrix adherence resulting from fiber-rubber interactions, which led to an increase in the strain under stress. Osabohien and Egboh (2008) also observed the similar result in hemp fiber filled NR and carbon black filled NR. The NR/10UT/10NR-g-MA composite gave better specific modulus and specific tensile strength when compared with the composites filled with carbon black and silica as shown in Figure 4.48 and 4.49. This suggested that NR-g-MA compatibilized NR composite would be beneficial for applications requiring weight reduction.

Table 4.10 Mechanical properties of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

Test		**Formulation**			
		NR	**NR/10 UT/10 NR-g-MA**	**NR/10 Silica**	**NR/10 Carbon black**
Modulus (MPa)	M100	0.82±0.068	1.78±0.077	1.41±0.059	1.84±0.099
	Specific M100	0.89	1.91	1.40	1.80
	M300	1.65±0.138	2.72±0.130	2.02±0.140	2.76±0.203
	Specific M300	1.80	2.92	2.01	2.71
Tensile strength (MPa)	Tensile strength	20.13±0.113	18.21±0.099	11.09±1.312	19.36±0.530
	Specific tensile strength	21.97	19.58	11.02	18.99
Elongation at break (%)		1350±17.67	1210±25.80	984±25.11	1049±20.79

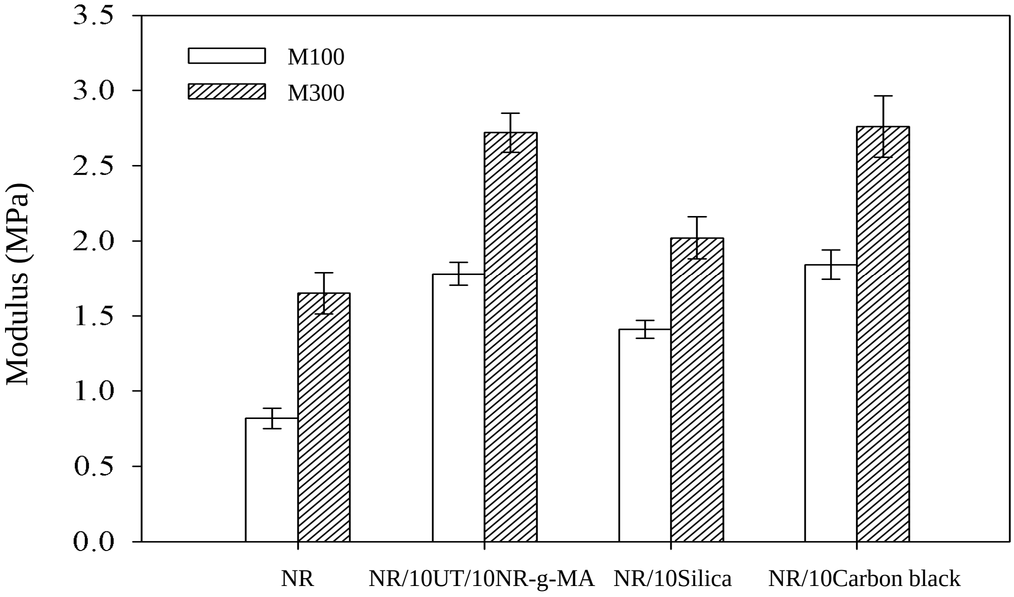


Figure 4.45 Modulus at 100% strain and 300% strain of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

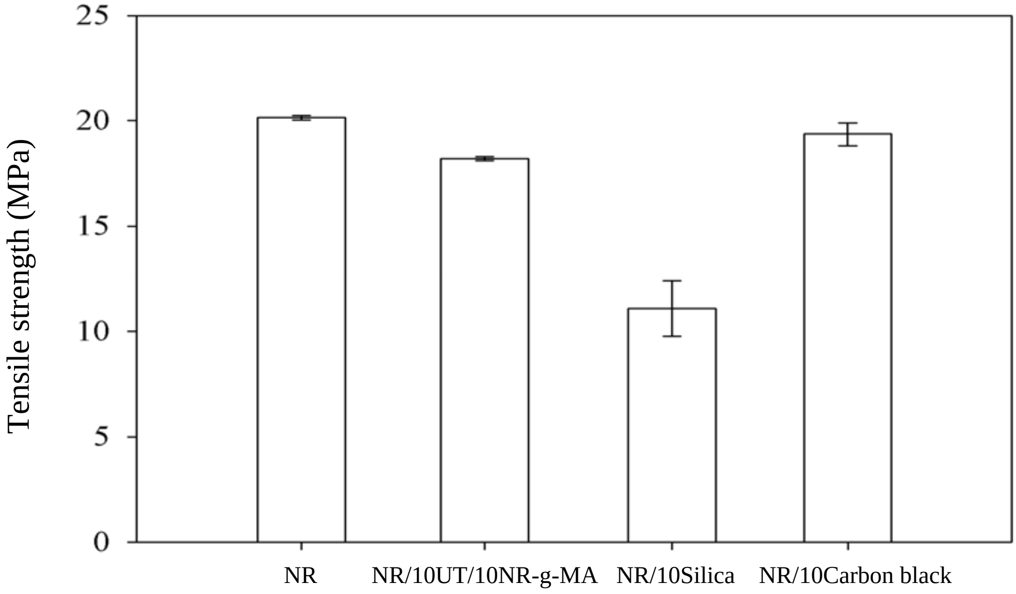


Figure 4.46 Tensile strength of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

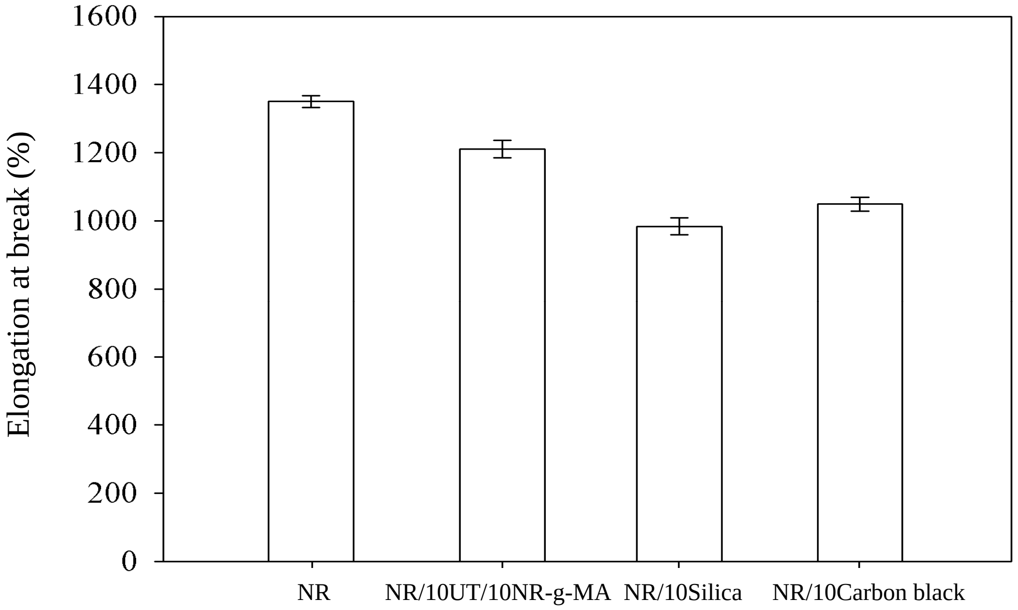


Figure 4.47 Elongation at break of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

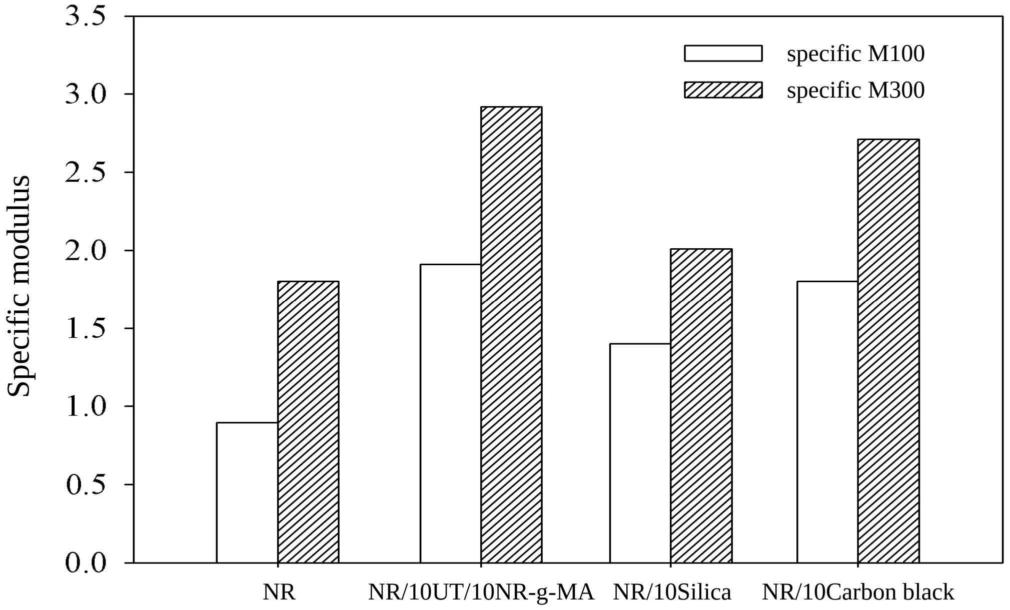


Figure 4.48 Specific modulus of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

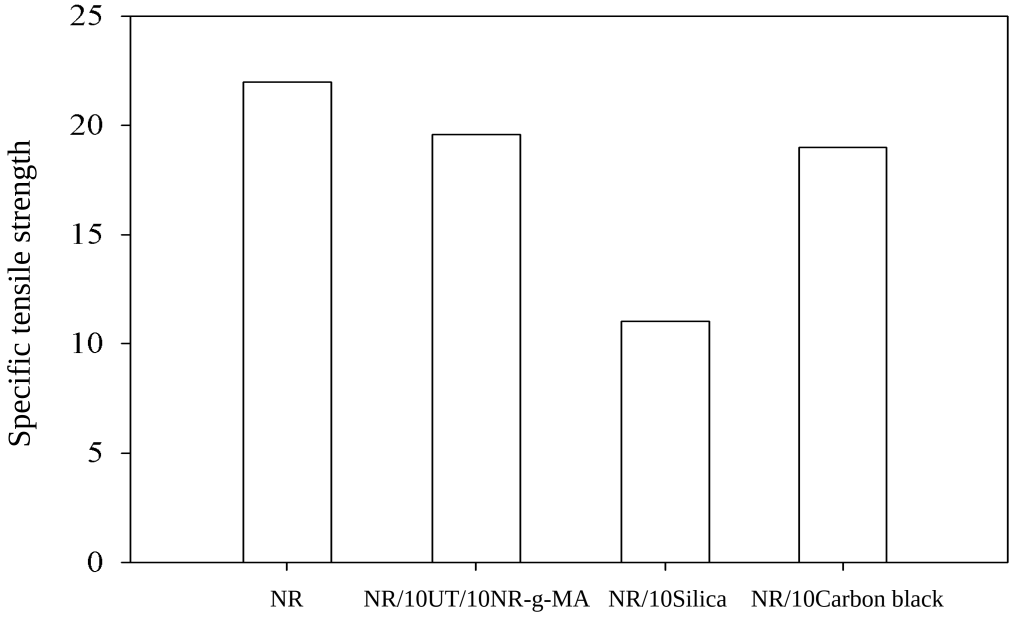


Figure 4.49 Specific tensile strength of NR, NR-g-MA compatibilized NR composite, NR filled with silica, and NR filled with carbon black.

CHAPTER V

CONCLUSIONS

The effect of initiator content on level of MA grafted onto NR molecule was studied. Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the MA grafted onto NR molecule. FTIR spectrum of NR-g-MA showed two new peaks at 1867 cm^{-1} and 1790 cm^{-1} assigned to the MA grafted onto NR molecule. The highest level of MA grafted onto NR molecule determined from the titration method was 1.38 wt% with the addition of 1 phr of DCP and 6 phr of maleic anhydride.

As fiber loading was increased, modulus at 100% strain (M100), modulus at 300% strain (M300), tear strength, and hardness of the composites filled with untreated and alkali treated fibers increased while tensile strength and elongation at break decreased. This was due to reduced elasticity of the rubber chain resulting in more rigid NR composites. Moreover, high population of fiber led to fiber agglomeration resulting in difficult stress transmission from matrix to fiber and disturbance of the continuity of the matrix phase. With increasing fiber loading, cure time of sisal fiber/NR composites decreased because more heat was generated due to the additional friction. On the other hand, scorch time was not much affected by fiber loading.

Alkali treated sisal fiber/NR composites showed better mechanical properties than untreated sisal fiber/NR composites at all fiber loadings. When fibers were treated with alkali solution, hemicellulose, wax, and other impurities covering the external surface of fibers were removed resulting in increased surface roughness of the fibers. This led to an improvement of adhesion between fiber and NR matrix through the mechanical interlocking mechanism. There was no significant effect of alkalization on cure time and scorch time of the composites.

Incorporating NR-g-MA into sisal fiber/NR composite gave the most effective improvement of the mechanical properties of the composites due to better adhesion between the sisal fiber and NR matrix. The longer scorch time and cure time of the composites were observed with presence of NR-g-MA due to the acidity of maleic acid and the interation between maleic anhydride and the accelerator. Furthermore, as NR-g-MA loading was increased the mechanical properties, scorch time, and cure time of the sisal fiber/NR composites were increased.

Among silica/NR composite, carbon black/NR composite, and NR-g-MA compatibilized composite, the NR-g-MA compatibilized composite showed the highest specific tensile modulus and specific tensile strength. This suggested that the compatibilized composite could be useful in light weight products with high strength.

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APPENDIX A

PROCEDURE TO ESTIMATE THE LEVEL OF GRAFTED MALEIC ANHYDRIDE ONTO NATURAL RUBBER

Procedure to estimate the level of grafted maleic anhydride onto natural rubber

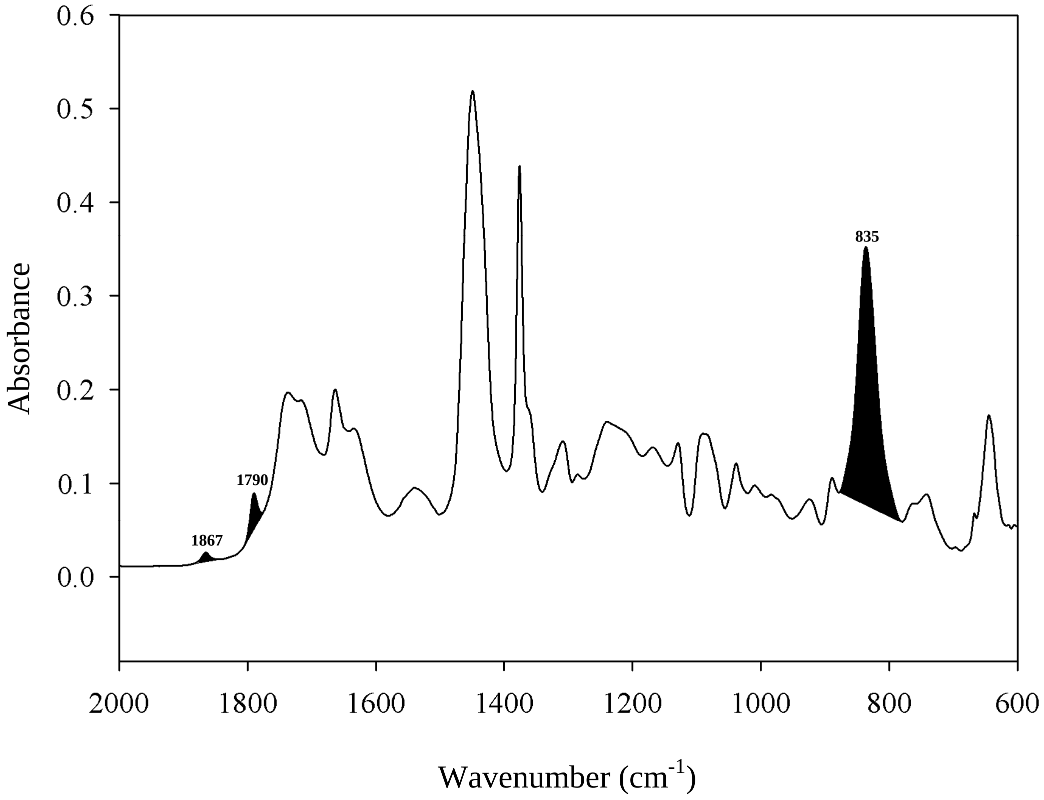

Figure A.1 FITR spectrum of NR-g-MA at 1.0_DCP.

$$\text{Level of grafted MA onto NR} = \frac{\text{Peak area of peaks at 1790 and 1867 cm}^{-1}}{\text{Peak area of peak at 835 cm}^{-1}} \quad \text{(A.1)}$$

APPENDIX B

LIST OF PUBLICATIONS

List of publications

Wongsorat, W., Suppakarn, N., and Jarukumjorn, K. (2009). Sisal fiber reinforced natural rubber composites: Effect of fiber content and fiber treatment. In **Proceeding of Pure and Applied Chemistry International Conference** 2009 (pp 304-306). Phitsanulok, Thailand.

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Wongsorat, W., Suppakarn, N., and Jarukumjorn, K. (2010). Mechanical properties, morphological properties, and cure characteristics of sisal fiber/natural rubber composites: Effect of fiber and compatibilizer content. **Adv. Mater. Res.** 123-125: 1171-1174.

SISAL FIBER REINFORCED NATURAL RUBBER COMPOSITES: EFFECT OF FIBER CONTENT AND FIBER TREATMENT

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Abstract: Natural fiber filled natural rubber composites have gained considerable growth due to their attractive properties and environmental concerns. However, the main problem in natural fiber filled natural rubber composites is the incompatibility between hydrophilic natural fibers and hydrophobic natural rubber leading to poor properties of the composites. In this study, fiber treatment with alkali solution was performed to improve interfacial adhesion between the sisal fiber and natural rubber. In addition, the effect of fiber loading on the mechanical properties and cure characteristics of sisal fiber filled natural rubber composites were investigated. Tensile properties and hardness of the composites filled with treated fibers were higher than those filled with untreated fibers at similar fiber loading. However, scorch time and cure time of the composites were not much affected by alkali treated fiber. As the fiber loading increased, hardness, 100% modulus and 300% modulus also increased while tensile strength and elongation at break decreased.

Introduction

Natural fiber reinforced natural rubber composites have gained more attention because of their low cost, processing advantages, good strength and stiffness. The parameters affecting properties of the fiber reinforced rubber composites are fiber content, fiber-rubber adhesion, fiber length, fiber aspect ratio, fiber dispersion and orientation [1]. The main problem of using natural fiber to reinforce natural rubber is incompatibility between a hydrophilic natural fiber and a hydrophobic natural rubber leading to poor mechanical properties. The surface characteristics of the reinforcing fibers are important in the transfer of stresses from the matrix to the fiber. In cellulose fibers, even though they possess hydroxyl groups on their surface, the lignin and other waxy contents make them a less effective reinforcement. Alkali treatment is one of methods that remove the lignin and other waxy impurities [2]. Other ways to enhance the adhesion between the natural fiber and natural rubber include treatment of the fibers with silane coupling agent [3], use bonding agents [4] or use maleated natural rubber as a coupling agent [5].

Geethamma et al. [6] reported that the treatment of coir fibers with 5% sodium hydroxide (NaOH) significantly increased the mechanical properties of the rubber composites. Lopattananon et al. [7] found that 5% NaOH treated pineapple fiber/natural rubber composites had higher elongation at break than that of untreated fiber/natural rubber composite. This improvement was due to an increase in fiber-rubber bonding through mechanical interlocking between the fiber and rubber. Jacob and Thomas [8] studied mechanical properties of sisal fabric reinforced natural rubber composites. Alkali treatment resulted in a lowering of Young's modulus and tear strength because alkali did not penetrate uniformly within the thick strands of the fabric.

The objective of this study was to investigate the effect of fiber content and fiber treatment (alkalization) on the mechanical properties and cure characteristics of the sisal fiber-natural rubber composites.

Materials and Methods

Materials: Natural Rubber (NR, STR 5L) was supplied from Thai Hua Co., Ltd. Sisal fiber were purchased from Sisal-Handicraft OTOP group, Nakhon Ratchasima, Thailand. The fiber contents were varied at 10, 20, and 30 phr. The other ingredients used to vulcanize natural rubber were stearic acid, zinc oxide, N-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS) and sulfur.

Fiber preparation: The sisal fibers were cut into an approximate length of 2 mm. The short fibers were treated with 2 wt% sodium hydroxide (NaOH) solution for 2 hrs. The fibers were washed with water several times and dried in an oven at 60°C overnight.

Sample preparation: All compounds were mixed under the same conditions on two-roll mill at room temperature. NR formulations used are shown in Table 1. The compounds were compression molded at 150°C. Cure times were determined using a moving die rheometer (MDR).

Properties measurements: Cure characteristics were measured on a moving die rheometer (GOTECH, M2000F) at temperature of 150°C. Tensile properties were tested according to ASTM D 412 on the Instron Universal Testing Machine at the extension rate of 500 mm/min, gauge length of 33 mm, and gap length of 80 mm at room temperature. Hardness was determined according to ASTM D 1415 on Micro hardness (IRHD).

Table 1: NR formulation

Materials	Formulation (phr)
NR	100
Sulfur	2.5
ZnO	5.0
Stearic acid	1.5
CBS	0.5
Sisal fiber	0, 10, 20, 30

Results and Discussion

Cure characteristics: Table 2 shows the maximum torque (MH), minimum torque (ML), scorch time (t_{s1}) and cure time (t_{90}) of NR composites with various fiber loading. The maximum torque increased with increasing fiber loading. This was due to an increase in stiffness of the composites. It can be seen that the composites with alkali treated fiber showed higher maximum torque than composites with untreated fiber. This may be due to strong bonding at the fiber-rubber interface consequently made the composites stronger and stiffer. No significant effect of alkali treated fiber on the minimum torque, scorch time and cure time was found. On the other hand, Stiehler and Wakelin [9] found that cure time of alkali treated fiber filled NR composites decreased when compared to untreated fiber filled composites. This was attributed to the influence of pH on the fiber so the vulcanization reaction became faster in alkaline pH. Ismail et al. [3] also found that scorch time and cure time of bamboo fiber filled NR composites were lower than unfilled composites because the present of fiber into NR composites caused an increase in mixing time.

Table 2: Cure characteristics of NR composites

Fiber loading (phr)	MH (lbf-in)	ML (lbf-in)	Time (min)	
			t_{s1}	t_{90}
0	12.40	2.58	2.59	8.06
10 untreated	14.74	2.92	3.35	5.56
10 treated	18.65	2.57	3.24	6.41
20 untreated	15.17	2.57	3.31	6.13
20 treated	20.86	2.81	3.23	7.46
30 untreated	17.79	2.62	3.30	7.32
30 treated	22.41	3.02	3.05	7.13

Mechanical properties: Tensile properties (100% modulus, 300% modulus, tensile strength and elongation at break) of the composites are shown in Figure 1-4. The tensile properties of the composites filled with treated fibers were higher than those filled with untreated fibers at similar fiber loading. This was suggested that alkali treatment improved the fiber-rubber adhesion. According to Lopattananon et al. [7], alkali treatment can be used to enhance pineapple fiber-natural rubber bonding through the mechanical interlocking mechanism. Gassan and Bledzki [10] reported that when hemicellulose were removed by alkali treatment, the interfibrillar region became less dense and less rigid, so it led the microfibrils to be more able to rearranging themselves along the direction of tensile deformation. As fiber loading was increased, 100% modulus and 300% modulus also increased while tensile strength and elongation at break decreased. When fiber loading increased the composites became more and more stiff. Debasish et al. [4] also observed a similar result. Tensile strength decreased with an increase in fiber loading because stress transmission from matrix to fiber was very difficult. Hardness of the composites is shown in Figure 5. With increasing in fiber loading, the hardness of the composites increased because the composites became stiffer. Hardness of the composites with alkali treated fiber was also higher than those of untreated composites.

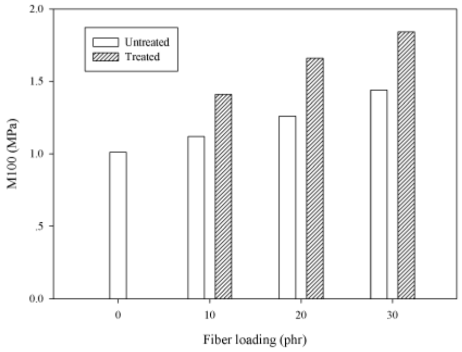

Figure 1. Variation of 100% modulus with fiber loading

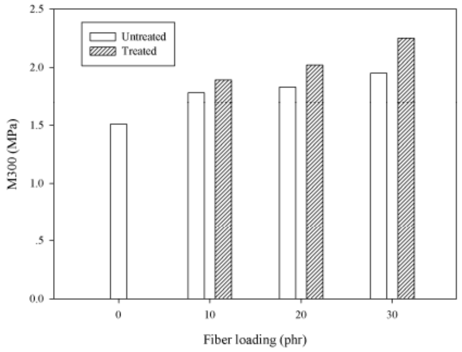

Figure 2. Variation of 300% modulus with fiber loading

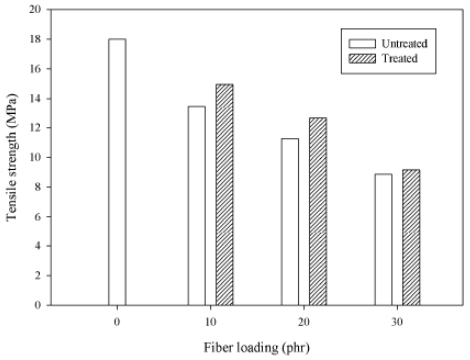

Figure 3. Variation of tensile strength with fiber loading

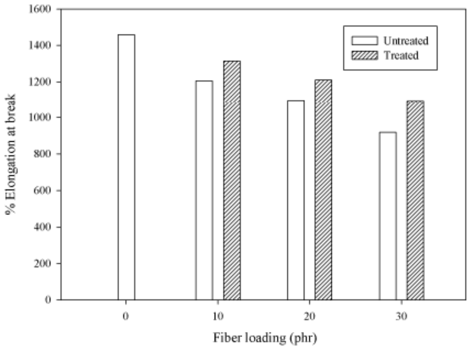

Figure 4. Variation of elongation at break with fiber loading

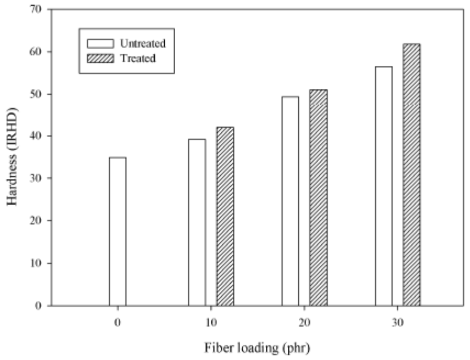

Figure 5. Variation of hardness with fiber loading

Conclusions

The addition of alkali treated fiber to rubber matrix increased maximum torque with mechanical properties such as 100% modulus, 300% modulus, tensile strength, elongation at break and hardness compared to composites filled with untreated fiber and unfilled. Maximum torque, 100% modulus, 300% modulus and hardness increased with an increase in fiber loading while tensile strength and elongation at break decreased. Minimum torque, scorch time and cure time were not much affected by alkali treated fiber.

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INFLUENCE OF FILLER TYPES ON MECHANICAL PROPERTIES AND CURE CHARACTERISTICS OF NATURAL RUBBER COMPOSITES

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ABSTRACT

Nowadays, materials from natural/renewal resources gain more attention in several applications due to environmental concerns. Among those kinds of materials, natural fibers can be alternative fillers for reinforcing natural rubber (NR). In this study, NR was reinforced with three types of fillers: carbon black, calcium carbonate, and sisal fiber. The filler content was 20 phr. Effect of sisal fiber and conventional fillers: carbon black and calcium carbonate on mechanical properties and cure characteristics of the NR composite was compared. In addition, influence of fiber treatment (alkalization) on mechanical properties and cure characteristics of sisal fiber-NR composites was investigated. All filler filled NR showed higher maximum torque than that of unfilled NR. Maximum torque of the composite filled with carbon black was higher than those filled with calcium carbonate, sisal fibers, and alkali treated sisal fibers. However, scorch time and cure time of the composites were not much affected by filler types. Alkali treated sisal fiber-NR composites provided higher tensile strength, modulus, elongation at break, and hardness in comparison to untreated sisal fiber-NR composite.

KEYWORDS: (natural rubber, sisal fiber, alkalization, carbon black)

Sisal Fiber Reinforced Natural Rubber Composites: Effect of Fiber Length and Fiber Treatment

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Introduction

Natural fiber reinforced natural rubber (NR) composites have gained more attention because of their low cost, processing advantages, good strength and stiffness. The parameters affecting properties of the fiber reinforced rubber composites are fiber content, fiber-rubber adhesion, fiber length, fiber aspect ratio, fiber dispersion and orientation.[1] The main problem of using natural fiber to reinforce NR is incompatibility between a hydrophilic natural fiber and a hydrophobic NR leading to poor mechanical properties of the composite. The surface characteristics of the reinforcing fibers are important in the transfer of stresses from the matrix to the fiber. In cellulose fibers, even though they possess hydroxyl groups on their surface, the lignin and other waxy contents make them a less effective reinforcement. Alkali treatment is one of methods that remove the lignin and other waxy impurities.[2] Lopattananon et al.[3] found that alkali treated pineapple fiber-NR composites had higher elongation at break than that of untreated pineapple fiber-NR composite. The improvement of tensile strength of the alkali treated pineapple fiber-NR composites was not found when the concentration of NaOH was less than 5% (w/v). This improvement was due to an increase in interfacial bond strength through mechanical interlocking between the fiber and the NR. The objective of this study was to investigate the effect of fiber length and fiber treatment (alkalization) on the mechanical properties and cure characteristics of the sisal fiber-NR composites.

Experimental

NR (STR 5L) was supplied from Thai Hua Co., Ltd. Sisal fiber was used as filler. The other ingredients used to vulcanize NR were stearic acid, zinc oxide, N-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS) and sulfur. Sisal fiber with an approximate length of 370 µm, 2 mm, and 4 mm were dried in an oven at 60°C overnight. This fiber was called untreated fiber (UT). In order to prepare alkali treated fiber (AT), the UT fiber was treated with 2 wt% sodium hydroxide solution (NaOH) for 2 hrs. Then, the fiber was washed with water and dried at 60°C overnight. All compounds were mixed under the same conditions on two-roll mill at room temperature. Fiber content used in this study was 20 phr. Test specimens were prepared by compression molding. Cure characteristics were measured on a Moving Die Rheometer at a temperature of 150°C. Tensile properties were tested on a Universal Testing Machine at an extension rate of 500 mm/min. Hardness was determined on Micro hardness.

Results and discussion

Table 1 shows the maximum torque (MH), minimum torque (ML), scorch time (t_{s1}) and cure time (t_{90}) of NR composites with various fiber lengths. Maximum torque values increased with the addition of sisal fiber. This indicated an increase in stiffness of the composites. The presence of fiber imparted limitation to the deformation of NR molecules so the composites became stronger, harder, and stiffer. The composites with alkali treated fiber showed higher maximum torque than the composites with untreated fiber. This may be because of good fiber-rubber adhesion at the fiber-rubber interface.[1] No significant effect of fiber lengths on minimum torque of the composites was observed. Scorch time and cure time of the composites filled with various fiber lengths were different and lower than gum. Untreated 4 mm sisal fiber-NR composite showed the fastest scorch time and cure. In general, a faster cure rate is obtained with fillers having a low surface area, high moisture content and high metal oxide content.[4]

Table 1: Cure characteristic of NR composites.

Formulation	**MH (dN-m)**	**ML (dN-m)**	**t_{s1} (min)**	**t_{90} (min)**
Gum	13.54	2.76	4.07	8.23
UT 370 μm-NR	18.96	3.71	3.20	5.36
AT 370 μm-NR	20.33	3.87	3.30	5.45
UT 2 mm-NR	15.37	3.64	3.02	5.13
AT 2 mm-NR	19.86	3.71	3.13	5.23
UT 4 mm-NR	14.50	3.27	3.00	5.11
AT 4 mm-NR	18.93	3.52	3.06	5.17

Table 2: Mechanical properties of NR composites.

Formulation	**Test**				
	M100 (MPa)	**M300 (MPa)**	**Tensile strength (MPa)**	**Elongation at break (%)**	**Hardness (IRHD)**
Gum	0.77±0.034	1.57±0.017	19.78±0.256	1280.74±29.270	37.90±0.550
UT 370 μm-NR	1.07±0.032	2.15±0.026	13.89±0.085	1153.20±14.580	48.46±0.650
AT 370 μm-NR	1.25±0.007	2.56±0.042	17.98±0.714	1165.78±17.850	56.22±0.480
UT 2 mm-NR	0.90±0.023	1.85±0.012	12.03±0.224	1090.92±18.231	47.31±0.514
AT 2 mm-NR	1.10±0.015	1.90±0.022	14.20±0.323	1142.30±20.030	53.46±0.483
UT 4 mm-NR	0.83±0.019	1.63±0.031	11.46±0.636	1068.61±19.024	46.80±0.441
AT 4 mm-NR	1.01±0.024	1.79±0.034	13.33±0.434	1110.63±22.011	53.10±0.534

Mechanical properties of the composites are shown in Table 2. Modulus at 100% elongation (M100), 300% elongation (M300), and hardness increased while elongation at break decreased with the addition of sisal fiber into NR due to the improvement of stiffness of NR composites by fillers.[5] The strength, modulus, elongation at break, and hardness of the composites decreased with the increase of fiber length because of poor fibers dispersion in the NR matrix of longer fiber length.[5] The composites with alkali treated fiber provided higher modulus and tensile strength than the composites with untreated fiber. This may be due to an enhanced fiber-NR bonding through the mechanical interlocking mechanism.[1]

Conclusions

The composites containing alkali treated sisal fiber exhibited improved the modulus, tensile strength, elongation at break and hardness. The composite with shorter length of fiber gave better mechanical properties than that with the longer fiber length.

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Mechanical Properties, Morphological Properties, and Cure Characteristics of Sisal Fiber/Natural Rubber Composites: Effects of Fiber and Compatibilizer Content

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Keywords: Sisal fiber, Natural rubber, Natural rubber grafted with maleic anhydride

Abstract. Sisal fiber/natural rubber (NR) composites were prepared by the incorporation of sisal fiber into NR at various content (10, 20, 30 phr) using a two-roll mill. Natural rubber grafted with maleic anhydride (NR-g-MA) prepared in house was used to improve interfacial adhesion between sisal fiber and NR matrix. NR-g-MA contents were varied. Mechanical properties, morphologies, and cure characteristics of the composites were studied. Maximum torque, modulus at 100% strain (M100), modulus at 300% strain (M300), and hardness of the composites increased with increasing fiber content while scorch time, cure time, tensile strength, and elongation at break decreased. The addition of NR-g-MA into the composites gave a positive impact on M100, M300, tensile strength, and hardness. Moreover, increasing NR-g-MA content resulted in increased scorch time, cure time, maximum torque, M100, M300, tensile strength, and hardness of the composites. SEM micrographs of the composites revealed that the addition of NR-g-MA into the composites improved the interfacial interaction between sisal fiber and NR matrix. In addition, the compatibilized NR composites exhibited higher specific tensile strength and modulus than the carbon black/NR composites.

Introduction

Natural rubber (NR) is one of the versatile materials widely used in many applications. The advantages of NR include low cost, low hysteresis, high resilience, excellent dynamic properties, and fatigue resistance. However, raw NR has poor mechanical properties. To improve mechanical properties of NR, ingredients such as accelerators, activators, crosslinking agents, and fillers are commonly mixed into rubber to obtain suitable properties. In particular, the incorporation of fillers in NR matrix leads to significant improvement in mechanical properties of the NR composites. Reinforcement of NR with natural fiber has gained more interest due to many advantages of the natural fiber such as low cost, biodegradability, renewable nature, and reduced tool wear. Sisal fiber is one of the interesting candidates for reinforcing natural rubber due to its high specific strength and modulus, low density, and no health risk. In addition, sisal fiber is a tropical plant grown in a wide range of area in Thailand. However, the main problem of using natural fiber to reinforce NR is the incompatibility of hydrophilic natural fiber and hydrophobic NR matrix leading to poor mechanical properties of the composites. The compatibility between the natural fiber and NR matrix can be enhanced by fiber treatments, matrix modification, and addition of compatibilizers. Basically, natural rubber grafted with maleic anhydride (NR-g-MA) has been used as a compatibilizer in natural fiber/NR composites [1, 2]. The objective of this study was to investigate the effect of fiber and compatibilizer (NR-g-MA) content on mechanical properties, morphologies, and cure characteristics of sisal fiber/NR composites. In addition, specific tensile properties of sisal fiber/NR composite were compared with carbon black/NR composite.

Materials and Method

Materials. Natural Rubber (NR, STR 5L) was supplied from Thai Hua Co., Ltd. Sisal fiber (SF) was purchased from Sisal-Handicraft OTOP group, Nakhon Ratchasima, Thailand. The fiber contents were varied at 10, 20, and 30 phr. The average length of sisal fiber was 2 mm. Natural rubber grafted with maleic anhydride (NR-g-MA) prepared in house was used as a compatibilizer at various content of 2.5, 5.0, 7.5, and 10.0 phr. The other ingredients used to vulcanize natural rubber were stearic acid, zinc oxide, N-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS) and sulfur.

Sample Preparation. All compounds were mixed under the same conditions on a two-roll mill at room temperature. NR formulations used are shown in Table 1. Test specimens were prepared by a compression molding at 150°C. According to the tensile properties, NR composite giving better tensile properties was chosen to investigate the effect of NR-g-MA content on cure characteristics and mechanical properties of sisal fiber/NR composites.

Properties Measurement. Cure characteristics were measured on a moving die rheometer (MDR, GOTECH: M2000F) at temperature of 150°C. Tensile properties were tested according to ASTM D412 on an universal testing machine (UTM, INSTRON: 5565). Hardness was determined according to ASTM D2240 on an international rubber hardness degrees tester (IRHD, BAI EISS: DIGI TEST). Morphologies of the composites were examined using a scanning electron microscope (SEM, JEOL: JSM-6400). The samples were coated with gold before analysis.

Table 1: NR formulations

Materials	Contents [phr]
Natural rubber	100
Zinc oxide	5.0
Stearic acid	1.5
CBS	0.5
Sulfur	2.5
Sisal fiber	0, 10, 20, 30
NR-g-MA	0, 2.5, 5.0, 7.5, 10.0

Results and Discussion

Effect of fiber content on cure characteristics and mechanical properties of NR composites.

Cure characteristics. Maximum torque (MH), minimum torque (ML), scorch time (t_{s1}), and cure time (t_{90}) of the composites were listed in Table 2. MH and ML values increased with increasing fiber content. The presence of fibers limited the deformation of NR molecules so, the composites became stronger, harder, and stiffer. Scorch time and cure time of the composites decreased with increasing fiber content. As the fiber content increased, more heat was generated due to the additional friction. Lopattananon et al. [3] and Ismail et al. [4] also observed the similar results with pineapple leaf fiber/NR composites and bamboo fiber/NR composites, respectively.

Mechanical properties. Modulus at 100% strain (M100), modulus at 300% strain (M300), tensile strength, elongation at break, and hardness of the composites are shown in Table 3. As fiber content was increased, M100, M300, and hardness also increased while tensile strength and elongation at break decreased. This was due to reduced elasticity of the rubber chain resulting in more rigid NR composites. From the tensile properties results, the NR composite with 10 phr of sisal fiber was selected to study the effect of NR-g-MA content on cure characteristics and mechanical properties of sisal fiber/NR composites.

Effect of NR-g-MA content on cure characteristics and mechanical properties of NR composites.

Cure characteristics. Adding NR-g-MA resulted in increased MH and ML of the NR composites as shown in Table 2. This was due to strong bonding at the fiber-rubber interface so, the composites became stronger and stiffer. Ismail et al. [2] reported that an increase in MH and ML by increasing NR-g-MA content showed the advantage of using NR-g-MA as the damping characteristics reducer in oil palm ash/NR composites. Scorch time and cure time of the compatibilized composites were longer than that of uncompatibilized composite. This may be attributed to the acidity of maleic acid and the interation between maleic anhydride and the accelerator [5]. In general, the scorch time and cure time of rubber composites also depend on properties of fillers such as surface area, surface activity, particle size, moisture content, and metal oxide content [6].

Mechanical properties. M100, M300, tensile strength, elongation at break, and hardness of the composites increased with an increase in NR-g-MA content due to the improved interfacial adhesion between the fiber and NR matrix through the formation of miscible blends between NR parts of NR-g-MA and NR, and the formation of chemical interaction between NR-g-MA and sisal fiber.

Morphological Properties. Tensile fracture surfaces of NR composites without and with NR-g-MA at 10 phr of sisal fiber are shown in Fig. 1. From Fig. 1(a), there were many holes from fiber pull out after the tension was applied. This indicated the weak interfacial adhesion between the sisal fiber and NR matrix. However, for NR composite with the addition of 10 phr of NR-g-MA, the better adhesion between the sisal fiber and NR matrix was observed as shown in Fig. 1(b).

The comparison between tensile properties of compatibilized NR composite and NR composite filled with carbon black. In this study, specific tensile properties of the NR composite containing 10 phr of NR-g-MA were compared with NR composite filled carbon black at 10 phr of filler. Specific tensile properties is a ratio between the tensile properties and the density of the composite. Specific tensile properties of compatibilized NR composite and NR composite filled with carbon black are shown in Fig. 2. The compatibilized NR composite gave better specific strength and specific modulus when compared with the composite filled with carbon black. This suggested that compatibilized NR composite would be beneficial for applications requiring weight reduction.

Conclusions

Maximum torque, minimum torque, modulus at 100% strain, modulus at 300% modulus, and hardness of the sisal fiber/NR composites increased with an increase in fiber content while scorch time, cure time, tensile strength, and elongation at break decreased. The presence of NR-g-MA improved the tensile properties, hardness, and prolonged scorch time and cure time of the composites. SEM micrographs of tensile fracture surface of NR composites showed that the addition of NR-g-MA resulted in better adhesion between the sisal fiber and NR matrix. Specific tensile strength and specific modulus of the compatibilized NR composite were higher than that of NR filled with carbon black. So, the compatibilized NR composite could be useful in light weight products with high strength.

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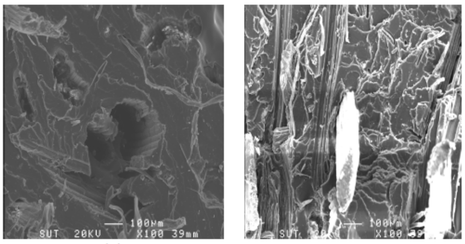
Table 2: Cure characteristic of NR composites

Designation	MH [dN-m]	ML [dN-m]	t_{s1} [min]	t_{90} [min]
NR	16.662	2.310	4.27	7.54
NR/10SF	19.741	2.620	3.35	7.16
NR/20SF	21.170	3.373	3.29	6.33
NR/30SF	22.790	3.722	3.20	6.02
NR/10SF/2.5NR-g-MA	21.552	3.651	4.04	8.16
NR/10SF/5.0NR-g-MA	26.348	4.376	4.32	8.43
NR/10SF/7.5NR-g-MA	26.970	4.480	6.44	9.42
NR/10SF/10.0NR-g-MA	27.881	4.633	7.19	9.46

Table 3: Mechanical properties of NR composites

Designation	M100 [MPa]	M300 [MPa]	Tensile strength [MPa]	Elongation at break [%]	Hardness [IRHD]
NR	0.82±0.068	1.65±0.138	20.13±0.113	1350±17.67	39.34±0.195
NR/10SF	1.09±0.081	1.75±0.121	11.05±0.124	1090±21.22	45.96±0.955
NR/20SF	1.13±0.032	1.78±0.092	9.67±0.081	1050±19.03	49.14±0.776
NR/30SF	1.22±0.046	1.92±0.146	8.70±0.185	920±23.49	55.18±0.756
NR/10SF/2.5NR-g-MA	1.28±0.072	1.91±0.132	12.66±0.162	1115±20.65	49.44±1.031
NR/10SF/5.0NR-g-MA	1.67±0.033	2.52±0.035	15.75±0.087	1139±18.34	52.38±0.925
NR/10SF/7.5NR-g-MA	1.71±0.051	2.66±0.079	16.90±0.085	1150±18.49	54.82±1.090
NR/10SF/10.0NR-g-MA	1.78±0.077	2.72±0.132	18.21±0.099	1210±25.80	56.66±1.070



(a) (b)

Figure 1. Tensile fracture surfaces of NR composites filled with 10 phr of sisal fiber: (a) without NR-g-MA and (b) with 10 phr of NR-g-MA (magnification 100X).

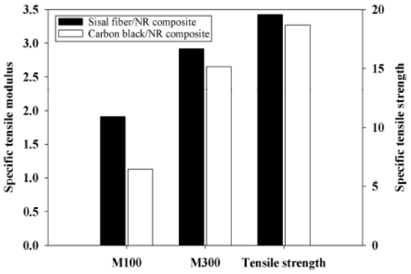


Figure 2. Specific tensile properties of sisal fiber/NR composite containing 10 phr of NR-g-MA and carbon black/NR composite.

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BIOGRAPHY

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