# EFFECT OF INTERFACIAL MODIFICATIONS ON PHYSICAL PROPERTIES OF SISAL FIBER/ POLYPROPYLENE COMPOSITES

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# ผลของการปรับปรุงอินเทอร์เฟสต่อสมบัติทางกายภาพของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน

นางสาวสุลาวัลย์ แก้วกุก

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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# EFFECT OF INTERFACIAL MODIFICATIONS ON PHYSICAL PROPERTIES OF SISAL FIBER/POLYPROPYLENE COMPOSITES

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

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สุลาวัลย์ แก้วกุก : ผลของการปรับปรุงอินเทอร์เฟสต่อสมบัติทางกายภาพของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน (EFFECT OF INTERFACIAL MODIFICATIONS ON PHYSICAL PROPERTIES OF SISAL FIBER/POLYPROPYLENE COMPOSITES) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.กษมา จารุกำจร, 144 หน้า

วิทยานิพนธ์นี้เป็นการศึกษาผลของการปรับปรุงอินเทอร์เฟสต่อสมบัติกายภาพของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน พอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีนถูกเตรียมโดยเครื่องบดผสมภายใน และชิ้นงานทดสอบถูกขึ้นรูปโดยเครื่องฉีดขึ้นรูป ปริมาณเส้นใยคือ 10 20 และ 30 เปอร์เซ็นต์โดยน้ำหนัก การดัดแปรเส้นใยโดยการอัลคาไลน์เซชั่นและการดัดแปรด้วยความร้อน และการเติมสารช่วยให้เข้ากัน (พอลิโพรพิลีนกร๊าฟด้วยมาเลอิกแอนไฮไดรด์) ถูกใช้ในการปรับปรุงความเข้ากันได้ระหว่างเส้นใยป่านศรนารายณ์และพอลิโพรพิลีนเมทริกซ์

การดัดแปรด้วยความร้อนทำที่อุณหภูมิ 150 170 และ 200 องศาเซลเซียส ที่เวลา 5 10 15 30 45 60 90 และ 120 นาที สำหรับการดัดแปรที่อุณหภูมิ 150 และ 170 องศาเซลเซียส ค่าการทนแรงดึงของเส้นใยสูงสุดได้เมื่อเวลาในการดัดแปรเท่ากับ 30 นาที ส่วนการดัดแปรที่ 200 องศาเซลเซียสได้ที่เวลาการดัดแปร 5 นาที ความเสถียรต่อความร้อนของเส้นใยที่ผ่านการดัดแปรด้วยความร้อนดีกว่าเส้นใยที่ไม่ผ่านการดัดแปร การเพิ่มขึ้นของอุณหภูมิและเวลาในการดัดแปรแสดงให้เห็นถึงการเพิ่มขึ้นอย่างมีนัยสำคัญของการเสื่อมสลายของส่วนประกอบที่มีน้ำหนักโมเลกุลต่ำ ขี้ผึ้ง และบางส่วนของเฮมิเซลลูโลสที่อยู่บนพื้นผิวของเส้นใย ภาพจากกล้องจุลทรรศอิเล็กตรอนแบบส่องกราดแสดงให้เห็นถึงการหลุดออกของวัสดุเชื่อมติด และลักษณภายนอกของพื้นผิวของเส้นใยที่ผ่านการดัดแปรด้วยความร้อน ผลที่ได้สอดคล้องกับการลดลงของความสูงของพีคของเฮมิเซลลูโลสและลิกนินจากการวิเคราะห์ด้วยเทคนิคอินฟราเรดสเปคโตรสโคปีและการลดลงของปริมาณเฮมิเซลลูโลสและลิกนินจากการวิเคราะห์องค์ประกอบของเส้นใย

อุณหภูมิการเสื่อมสลายของเซลลูโลสและพอลิโพรพิลีนของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์ที่มีการทำอัลคาไลเซชั่นและการดัดแปรด้วยความร้อนกับพอลิโพรพิลีนสูงกว่าของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์ที่ไม่ผ่านการดัดแปรกับพอลิโพรพิลีน อย่างไรก็ตาม การเติมพอลิโพรพิลีนกร๊าฟด้วยมาเลอิกแอนไฮไดรด์ไม่มีผลกระทบต่ออุณหภูมิการเสื่อมสลายของเซลลูโลส และพอลิโพรพิลีนของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน การเพิ่มขึ้นของปริมาณเส้นใยส่งผลต่อการลดลงของอุณหภูมิการ

เสื่อมสลายของเซลลูโลสและการเปลี่ยนอย่างไม่มีนัยสำคัญของอุณหภูมิการเสื่อมสลายของพอลิโพรพิลีนของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน การปรับปรุงอินเทอร์เฟสไม่ส่งผลอย่างมีนัยสำคัญต่ออุณหภูมิการตกผลึก และปริมาณผลึกของพอลิโพรพิลีน เมื่อปริมาณเส้นใยเพิ่มขึ้นอุณหภูมิการหลอมเหลวของพอลิโพรพิลีนไม่เปลี่ยนแปลงอย่างมีนัยสำคัญในขณะที่อุณหภูมิการตกผลึก และปริมาณผลึกของพอลิโพรพิลีนเพิ่มขึ้น การดัดแปรเส้นใยและการเติมสารช่วยให้เข้ากันส่งผลในการปรับปรุงความต้านทานต่อการดูดน้ำและการเปลี่ยนแปลงอย่างไม่มีนัยสำคัญของอุณหภูมิการบิดงอและความหนืดของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน นอกจากนี้การดัดแปรเส้นใยและการเติมสารช่วยให้เข้ากันปรับปรุงสมบัติทางกลของพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน พอลิโพรพิลีนคอมโพสิทที่มีการปรับปรุงความเข้ากันได้ด้วยพอลิโพรพิลีนกร๊าฟด้วยมาเลอิกแอนไฮไดรด์แสดงให้เห็นการเพิ่มขึ้นอย่างมีนัยสำคัญของค่าการทนแรงดึง และค่าการทนแรงกระแทก

การใส่เส้นใยแก้วเข้าไปในพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน นอกจากส่งผลต่อการเพิ่มขึ้นอย่างมากของความเสถียรต่อความร้อนและอุณหภูมิการบิดงอของพอลิเมอร์คอมโพสิทลูกผสมแล้ว ยังปรับปรุงสมบัติทางกลและความต้านทานต่อการดูดน้ำ แต่อย่างไรก็ตาม การเติมเส้นใยแก้วลงในพอลิเมอร์คอมโพสิทระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีนที่อัตราส่วนเส้นใยป่านศรนารายณ์ต่อเส้นใยแก้ว 15 ต่อ 15 เปอร์เซ็นต์โดยน้ำหนักไม่ส่งผลอย่างมีนัยสำคัญต่อความหนืดของพอลิเมอร์คอมโพสิท

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ลายมือชื่อนักศึกษา ____________________
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SULAWAN KAEWKUK : EFFECT OF INTERFACIAL MODIFICATIONS ON PHYSICAL PROPERTIES OF SISAL FIBER/POLYPROPYLENE COMPOSITES. THESIS ADVISOR : ASST. PROF. KASAMA JARUKUMJORN, Ph.D., 144 PP.

SISAL FIBER/ POLYPROPYLENE/ ALKALIZATION/ HEAT TREATMENT/ COMPATIBILIZER

In this thesis, the effect of interfacial modifications on physical properties of sisal fiber/polypropylene (PP) composites was studied. The sisal/PP composites were prepared using an internal mixer and test specimens were molded using an injection molding machine. The fiber contents were 10, 20, and 30 wt%. Fiber treatments (alkalization and heat treatment) and adding the compatibilizer (maleic anhydride grafted polypropylene, MAPP) were used to enhance the compatibility between the sisal fiber and PP matrix.

Heat treatment was performed at 150, 170, and 200°C for 5, 10, 15, 30, 45, 60, 90, and 120 min. For the treatment at 150 and 170°C, the maximum tensile strength of the treated fiber was obtained at the treatment time of 30 min whereas for the treatment at 200°C, it was obtained at 5 min treatment. Thermal stability of the heat treated fibers was better than that of untreated fiber. Increasing treatment temperature and treatment time showed significant increase in degradation of the low molecular weight composition, wax, and some hemicellulose covering the fiber surface. SEM micrograph showed some removal of binding materials and showed surface topology of heat treated fiber. The result corresponded to the decrease in hemicellulose and lignin peak height from FTIR analysis and decrease in hemicellulose and lignin content from fiber composition analysis.

The decomposition temperature of cellulose and PP of alkali and heat treated sisal/PP composites were higher than that of untreated sisal/PP composite. However, adding MAPP did not affect the decomposition temperature of cellulose and PP of sisal/PP composites. Increasing fiber content led to a decrease in decomposition temperature of cellulose and an insignificant change of decomposition temperature of PP of sisal/PP composites. The interfacial modifications did not significantly affect crystallization temperature and crystallinity of PP. With increasing fiber content, melting temperature of PP insignificantly changed while crystallization temperature and crystallinity of PP increased. The fiber treatments and adding compatibilizer resulted in improved resistance of water absorption and insignificant change in HDT and viscosity of sisal/PP composites. In addition, fiber treatments and adding compatibilizer enhanced mechanical properties of sisal/PP composites. The PP composites compatibilized with MAPP showed a remarkable increase in tensile and impact strength.

The incorporation of glass fiber into sisal/PP composites not only resulted in considerable increase in the thermal stability and HDT of the hybrid composite but also improved mechanical properties and resistance of water absorption. However, adding glass fiber into the sisal/PP composites at a ratio of sisal:glass fiber 15:15 wt% had no remarkable effect on the viscosity of the composites.

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Finally, I thank my parents and teachers who support and encourage me throughout the course of this study at the Suranaree University of Technology.

Sulawan Kaewkuk

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# SYMBOLS AND ABBREVIATIONS

% = Percent

ºC = Degree Celsius

µm = Micrometer

cm = Centimeter

g = Gram

GPa = Gigapascal

hrs = Hours

J = Joule

keV = Kilo electron volt

kg = Kilogram

kJ = Kilojoule

kN = Kilo Newton

kPa = Kilopascal

$m^2$ = Square meter

min = Minute

ml = Milliliter

mm = Millimeter

MPa = Megapascal

phr = Part per hundred resin

wt% = Percent by weight

# SYMBOLS AND ABBREVIATIONS (Continued)

rpm = Revolution per minute

Deriv. = Derivative

# CHAPTER I

# INTRODUCTION

## 1.1 General introduction

Environmental friendly materials are of great interest in the field of automotive, construction, textile, etc. (Sanjay, Smita, and Sushanta, 2009). Natural fibers based polymer composites are interest as an alternative biodegradable material (Vera and Analĭa, 2006). Therefore, more attention has been drawn to natural plant fibers such as sisal, flax or jute fiber. These natural fibers have been paid as alternative fibers by many scientists. The developing environmental friendly materials and partly replacing currently used glass or carbon fibers in fiber reinforced composites were regarded (Deshpande, Rao, and Rao, 2000). The advantages of the natural fibers over glass fiber, carbon fiber, and other synthetic fibers are low density, acceptable specific strength, less tool wear, biodegradability, and renewability (Ali, Iannace, and Nicolais, 2003).

Natural fibers are hydrophilic in nature therefore they are not well compatible with hydrophobic polymer matrices such as polyethylene and polypropylene leading to weak fiber-matrix interfacial adhesion. The weak interfacial adhesion lowers mechanical properties of the composites. The compatibility between the fibers and polymer matrix can be improved by fiber modification, matrix modification or adding compatibilizers. The studies of fiber and/or polymer modification have been focused on both physical and chemical methods. Physical methods include heat treatment

(Robin and Breton, 2001), plasma treatment (Tu, Young, and Denes, 1994), corona treatment (Gassan and Voytek, 2000), etc. Chemical methods involve modification of matrix and/or fiber by grafting with different monomers (Doan, Gao, and Mäder, 2006), silanization (Gonzalez, Uc, Olayo, and Franco, 1999), alkalization (Gassan and Bledzki, 1999), acetylation (Albano, Gonzalez, Ichazo, and Kaiser, 1999), and functionalization with maleic anhydride (Cantero, Arbelaiz, Ponte, and Mondragon, 2003), etc.

Sisal fibers, natural fiber, are popularly used to reinforce thermoplastic composites. They are available in Amphur Dan Khun Thod, Nakhon Ratchasima, and Amphur Pran Buri, Prajuab Kirikhan, Thailand. In addition, the sisal fibers are easy to prepare. They have high specific strength and modulus and low density. They compose of α-cellulose, hemicellulose, lignin, pectin, waxes, and water soluble substances. The cellulose, hemicellulose, and lignin are the basic components involving on the physical properties of fibers (Bledzki and Gassan, 1999). Hemicellulose is responsible for the biodegradation, moisture absorption, and least of thermal resistance while lignin is thermally stable and bounds cellulose microfibrills of fibers together.

Polypropylene (PP) is one of the most popular thermoplastic matrix used in short fiber reinforced composites. PP is not expensive and has high heat stability. It is also easily molded at low processing temperature. However, the problem of using natural fibers to reinforce PP is poor interfacial adhesion. In order to enhance the interfacial adhesion, fiber modification and addition of compatibilizer have been carried out as a result mechanical properties of the PP composites improved.

Among the chemical treatments undertaken, the most economically available one is the alkali treatment. It is a purifying treatment process that removes impurities such as waxes, pectin, and mineral salts (Vera and Analĭa, 2006). These impurities contribute to ineffective fiber-matrix interaction and poor surface wet-out (Mohanty, Wibowo, Misra, and Drzal, 2004). Removal of impurities also results in a formation of a rougher surface leading to an increase of surface area (Arbelaiz, Fernandez, Ramos, and Retegi, 2005). Therefore, alkalization results in improvement of mechanical interlocking between the resin and fiber. This resulted in better mechanical properties (Sharifah, Aziz, and Ansell, 2004).

Heat treatment is an environmental friendly method used to improve compatibility between natural fiber and polymer matrix (Robin and Breton, 2001). Heating cellulose at high temperature make change in its physical and chemical properties. Thermal modification of cellulose fiber results in changes of lignin and hemicellulose that mean less hydroxyl group and more carbon-carbon double bonds (Robin and Breton, 2001). Hemicelluloses and less ordered cellulose deteriorate and as a consequence, the degree of cellulose crystallinity increases. Changes in the aromatic structures involve cleavage of the aryl-ether linkages between the lignin phenylpropane units as well as lignin demethoxylation at high temperatures (Hanne and Sirkka, 2004). This affects an improvement of adhesion between the fiber and polymer matrix (Robin and Breton, 2001).

Maleic anhydride grafted polypropylene (MAPP) is known to be an effective compatibilizer for natural fibers/PP composites (Arbelaiz et al., 2005). It is suggested that both chemical (ester bond) and physical interaction (hydrogen bond) should be formed between the hydroxyl groups of fiber and the MAPP. On the other hand, the

PP chain of MAPP diffuses into the PP matrix forming the physical interaction (entanglement). Therefore, the interfacial adhesion between the fibers and matrix can be improved by use of MAPP compatibilizer (Doan et al., 2006).

## 1.2 Research objectives

The main objectives of this study are:

(i) To investigate the effect of heat treatment on thermal properties, mechanical properties, and morphology of sisal fibers.

(ii) To investigate thermal properties, rheological properties, mechanical properties, morphology and water absorption of sisal/PP composites.

(iii) To evaluate and compare the effect of heat treatment, alkali treatment, and compatibilizer on the properties of sisal/PP composites.

(iv) To evaluate the effect of glass fiber hybridization on the properties of sisal/PP composites.

## 1.3 Scope and limitation of the study

In this study, sisal fibers were prepared as untreated fibers, heat treated fibers at 150, 170, and 200°C for 15, 30, 45, 60, 90, and 120 min and 2 wt% NaOH treated fibers (alkali treated fibers).

Polypropylene and sisal fibers were mixed in an internal mixer. Fiber contents were 10, 20, and 30 wt%. MAPP was used as a compatibilizer of sisal/PP composites. To prepare hybrid PP composites, glass fibers were added into sisal/PP composites. The ratio of sisal to glass fiber was 15/15 wt%. The test specimens were prepared using an injection molding machine.

The fiber compositions of untreated fibers, heated fibers, and alkali treated fibers were analyzed by a detergent method. The structural compositions of untreated and heat treated sisal fibers were studied by Fourier transform infrared spectrometer (FTIR). The thermal properties of untreated fiber, heat treated fibers, and composites were investigated by a thermogravimetric analyzer (TGA) and a differential scanning calorimeter (DSC). The mechanical properties of fibers and composites were studied using a universal testing machine. Surface morphology of the fiber and the fracture surface of composites were investigated using a scanning electron microscope (SEM). The rheological properties of the composites were investigated using a capillary rheometer and a melt flow indexer (MFI). In addition, heat distortion temperature (HDT) and water absorption of composites were determined.

# CHAPTER II

# LITERATURE REVIEW

## 2.1 Characteristics of sisal fiber

All of lignocellulosic materials consist of α-cellulose, lignin, and hemicelluloses, etc. Figure 2.1 shows a structural constitution of a lignocellulosic fiber (Min, Ming, Yuan, Gui, and Han, 2001). The structure is constituted by several layers concentrically arranged. Chains of cellulose, the main reinforcement material, form microfibrils which are held together by amorphous hemicelluloses and lignin. They are aggregated into longer macrofibrils helically wounded along the fiber axis and embedded into an amorphous lignin/hemicelluloses matrix. The fibrils are assembled in several layers to build up the structure of the fiber. Fibers are cemented together in the plant by lignin, pectins, and hemicelluloses.

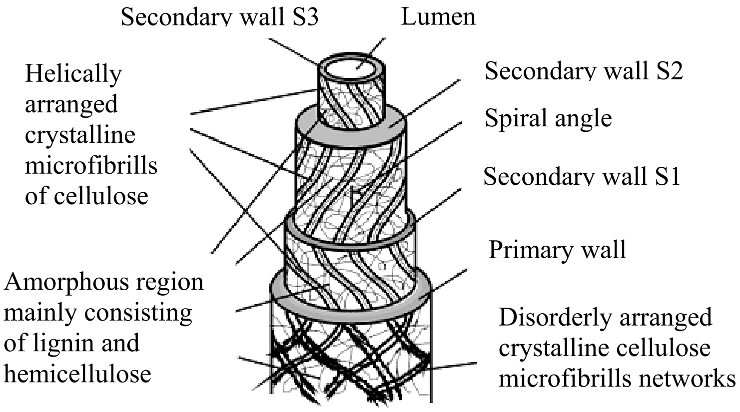


**Figure 2.1** Structural constitution of a lignocellulosic fiber (Min et. al, 2001).

Sisal fiber is a hard fiber extracted from the leaves of sisal plant (*Agave sisalana*). A sketch of a sisal plant is shown in Figure. 2.2. This fiber is composed of α-cellulose, hemicellulose and lignin, as major constituents. This cellulose is a hydrophilic glucan polymer consisting of a linear chain of 1, 4-β-bonded anhydroglucose units (Li, Zadorecki, and Flodin, 1987). The chemical compositions of sisal fibers have been reported by several groups of researchers as shown in Table 2.1. These large variations in the chemical compositions of the sisal fiber are derived from its different source, age, measurement methods, etc. (Yan, Yiu-Wing, and Lin, 2000).

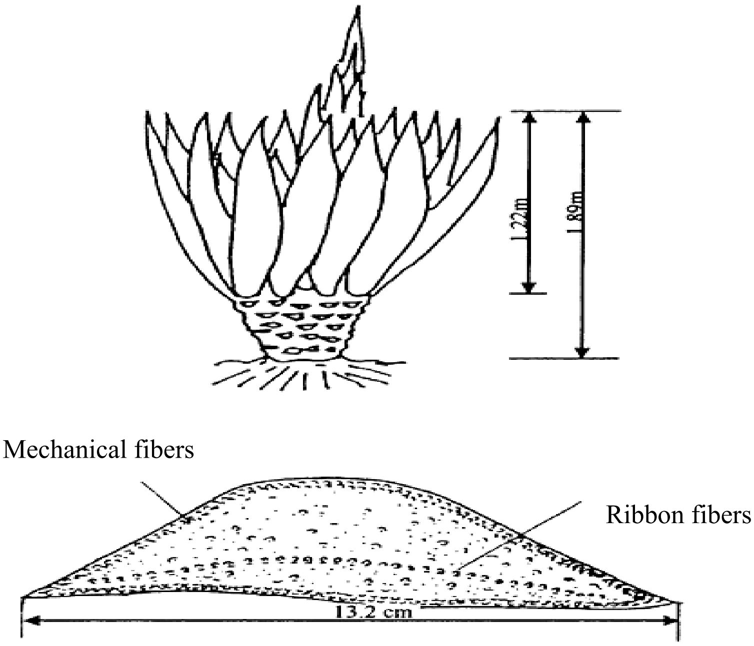


**Figure 2.2** Sketch of sisal plant and the cross-section of a sisal leaf (Bisanda and Ansell, 1992).

**Table 2.1** Chemical compositions of sisal fiber.

| α-Cellulose | Lignin | Hemicellulose | Others | References |
|---|---|---|---|---|
| 78% | 8% | 10% | 2% of wax | Wilson (1971) |
| 66-72 % | 10-14% | 8-12% | - | Chand et. al (1987) |
| 73.0% | 7.6% | 10.1% | 3.1% of ash | Sydenstriker et. al (2003) |
| 56.52% | 10.62% | 16.49% | 16.36% | Ana et. al (2004) |
| 47.6% | 10.6% | 17.8% | 4.5% of ash | Baltazar-y-Jimenez et.al (2007) |

### 2.1.1 Thermal properties

Chand, Sood, Singh, and Rohatgi (1987) studied thermal properties of sisal fiber by using Thermogravimetric analyzer (TGA) in a temperature range from 30 to 500°C and a heating rate of 20°C/min in air. The result showed that there was weight loss about 100°C. This was attributed to removal of water. The main initial weight loss of hemicellulose and lignin began at 200°C to 310°C. The rate of decomposition of cellulose became very high up to 347°C. This degradation was similar to the degradation reaction of cellulose in a case of wood.

Yang, Zeng, and Zhang (1995) studied the thermal properties of sisal fibers by TG analyzer. There was a slight weight loss (~2%) below 200°C probably caused by the evaporation of water absorbed by sisal fibers. However, the large amounts of cellulose, hemicellulose and glucans were not lost. They also found that thermal treatment of sisal fiber could be carried out below 200°C.

Saikia (2008) studied on thermal stability of sisal fiber at elevated temperature. The fibers were heated in a convection oven in an air atmosphere at different temperatures, i.e. 330, 370, 410, 450, 500, 530, and 600K, for 3 hrs. The TG and DTG profiles were recorded at a heating rate of 10K/min under a nitrogen atmosphere in the temperature range from 310K to 760K. There were three districts thermal processes occurred in the fiber under heating. The first thermal process the sample occurred with a sharp mass loss in the temperature range from 310K to 382K and the corresponding mass loss was 7.25%. This corresponded to removal of the water molecules, which were mostly embedded in the amorphous region of the fibers. The second step occurred in the temperature range from 506K to 613K. This consisted of two different closely related processes. The original structure of the cellulosic backbone was not completely lost in this high-temperature range. At the third step, a sharp peak appeared at approximately 710K. The changes attributed to the formation of carbon dioxide and carbon monoxide gases from the carbonized material that was formed during this stage.

Adriana, Maria, Odilon, and Luiz (2010) studied on the thermal properties of sisal fiber and its constituents by using Thermogravimetric analyzer (TGA) in a temperature range from 40 to 600°C and a heating rate of 10°C/min under nitrogen atmosphere. The TG curve of raw sisal showed a weight loss of 2.9% in the temperature range of 32-221°C. This was due to the loss of adsorbed water in the fiber. Sisal fiber degradation started at about 222°C. The first peak is a shoulder on the main degradation peak. This attributed to the hemicellulose degradation which occurred between 220 and 328°C. Thermal degradation of cellulose occurred at higher temperatures compared with hemicellulose. The main degradation peak started at 328°C and was completed at 416°C. At 520°C the char yield was 19.7%. This char yield occurred due to the condensation of the lignin component of fibers and formation of aromatic compounds in nitrogen atmosphere. The thermal degradation behavior of defatted sisal fiber had the same trend as that of the raw sisal fiber. After the weight loss of 2.8% of adsorbed water from the fiber showed in the temperature range from 32 to 230°C, the slope change occurred at around 370°C. This indicated a fast degradation of the cellulose presented in defatted sisal fiber. The degradation of hemicellulose and cellulose of defatted sisal fiber showed at 318 and 380°C, respectively. At 520°C the char yield was 16.5%. Holocellulose showed weight loss of 3.2% up to 185°C. This was due to the loss of adsorbed water in the fiber. Hemicellulose degradation started at 186°C. The cellulose degradation started at around 186-347°C and ended at 401°C. This temperature was lower than the initial degradation temperature of raw and defatted sisal fiber. This was due to delignification of fiber resulting on the higher accessibility of the hemicellulose constituent to thermal degradation. Char yield of 5.5% showed at 600°C. The lignin degradation started at around 174°C and underwent at a slow rate of degradation. Yielding 41.7% of char residue showed at 600°C. The thermal degradation of lignin slowly occurred. This was due to the more complex aromatic structure of lignin as compared to cellulose and hemicellulose structures.

### 2.1.2 Mechanical properties

Chand, Sood, Singh, and Rohatgi (1987) studied tensile behavior of sisal fiber. The tensile properties of sisal samples were determined by using a universal testing machine at a testing speed of 20 mm/min. The average ultimate tensile strength (UTS) and modulus of 100 samples measured by means of a load-elongation curve were 445.0 MPa and 10.0 GPa respectively. Initially, the curve was linearly elastic up to a certain percentage of elongation after that it displayed plastic behavior.

Mukherjee and Satyanarayana (1984) studied the effects of fiber diameter, test length and test speed on the tensile strength, initial modulus and percent elongation at the break of sisal fibers. They concluded that no significant variation of mechanical properties with change in fiber diameter was observed. However, the tensile strength and percent elongation at break decreased while Young's modulus increased with fiber length. With increasing speed of testing, Young's modulus and tensile strength were increased but elongation showed no significant variation. At very slow test speeds, the fiber behaved like a viscous liquid.

Flavio de Andrade, Nikhilesh, and Romildo (2008) studied on tensile behavior of sisal fiber. Tensile tests were conducted in displacement control at a rate of 0.1 mm/min at four different gage lengths (10, 20, 30, and 40 mm). The results showed that the gage length did not influence on the modulus of the fiber. This was due to the variability in the microstructure of the sisal fibers and possible damage that occurred during the extraction process. The tensile strength of the fiber also did not depended on the gage length. The Young's modulus varied between 9 and 19 GPa and the tensile strength from 347 to 577 MPa. This variability depended on test parameters/conditions, plant characteristics, and area measurements.

## 2.2 Interfacial modification of lignocellulosic fiber/polymer composites

The interfacial modification of lignocellulosic fiber/polymer composites included fiber surface modification, matrix modification, and addition of compatibilizer. In this thesis, fiber surface modification and addition of compatibilizer were focused.

### 2.2.1. Physical modification of wood and natural fiber

The physical modifications such as heat treatment, plasma treatment, and corona treatment have been applied to reduce hydrophilicity of fiber and enhance compatibility between fiber and polymer matrix.

#### 2.2.1.1 Heat treatment

Heat treatment of wood has been developed over the last decade. This treatment is an environmental friendly method without impregnating with additional chemicals (Rezayati Charani et al., 2007). Heat treatment of wood is an effective method to improve the dimensional stability, mechanical properties, hygroscopic properties, and durability against biodegradation (Derya et al., 2008). In addition, heat treatment resulted in changes of chemical and physical properties of wood. Besides wood, natural fibers such as sisal or flax fiber have been modified by heat. Mechanical properties, crystallinity of cellulose, and thermal properties of wood and natural fibers were increased by thermal modification.

##### Heat treatment of wood

Akinori, Kiichi, and Hikaru (1984) studied the effect of heat treatment on water absorption of wood flour. Wood flour was heated at 100, 120, 150, 170, 190, and 200°C for 8 hrs under nitrogen atmosphere. Weight loss of wood flour increased with raising treatment temperature. Water absorption of heat treated wood flour decreased with increasing temperature and time due to an increase of hydrophobic nature of heat treated wood flour. Higher hydrophobicity was attributed to a decrease of polarity of fiber.

Tjeerdsma et al. (1998) studied molecular characterization of thermally modified wood. Hygroscopicity of heat treated wood was decreased by an increase of cross-linking network within the lignin. Moreover, hemicelluloses were transformed into a hydrophobic network by esterification which led to more carbon-carbon double bonds.

Robin and Breton (2001) prepared heat treated wood/high density polyethylene (HDPE) composites. Spruce wood fibers with average length of 1 mm were heated at 230°C for overnight. There was an increase in crystallinity of cellulose after fiber treatment. Moreover, when the hemicelluloses were removed the fiber was more hydrophobic. This result led to more compatible between wood fiber and polyethylene matrix.

Weiland and Guyonnet (2003) studied chemical degradation of thermally modified wood using Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. Beech and maritime pine wood were heated at 230-260°C under nitrogen atmosphere. The C=O band (1730 $cm^{-1}$) of acetyl group in hemicelluloses decreased by heat treatment at temperature as high as 240°C. The aromatic skeleton of lignin was also affected by this method due to creating of new ether linkage. This resulted in an increase of hydrophobicity of the fiber.

Pavlo and Peter (2003) investigated the effect of high temperature on changes in dimensional stability and mechanical properties of spruce wood. Wood specimens were subjected to heat treatment at 200°C for 2, 4, 8, 10, and 24 hrs and 100, 150, and 200°C for 24 hrs. The result showed that dimensional stability of wood improved while its mechanical properties reduced. Heat treatment at temperature of 200°C led to a decrease in average bending strength of specimens about 44-50 % while modulus of elasticity was reduced by only 4-9 %. The treatment temperature had stronger effect on the bending strength than on the modulus of elasticity.

Tjeerdsma and Militz (2005) studied the chemical transformation of thermally treated wood using Fourier Transform Infrared Spectroscopy (FTIR). Beech and scots pine wood samples were heat treated to 165-190°C in an oven under nitrogen atmosphere. The 1740 $cm^{-1}$ (ester) peak of FTIR spectra increased due to cleavage of acetyl group of hemicellulose. This result led to a decrease of hydroxyl groups of wood. The reduction of hydroxyl group from esterification consequently reduced the hygroscopicity of wood samples.

Mohammed, Mathieu, André, and Philippe (2005) investigated wettability changes of wood during heat treatment on the basis of chemical analysis. Heat treatments were applied on the test samples at different temperature from ambient to desired operating temperature for 8 hrs under nitrogen atmosphere. The result of contact angle measurement showed value near zero for heat treatment below 120°C. The value changed suddenly to reach 90° for a heat treatment temperature between 120 and 160°C. Shift of the C-4 signal from $^{13}C$ NMR spectra related to conformation change of crystalline and amorphous cellulose component. 36% of weight loss was occurred by increasing temperature to 260°C due to the degradation of hemicellulose. From the results, this indicated that the wood became more hydrophobic.

Vincent and Guyonnet (2005) measured the swelling properties of heat treated wood by differential scanning calorimetry (DSC) in relation to chemical composition. Beech and maritime pine wood were heated at 180, 200, 220, 240, and 260°C for different durations (5, 60, 180, and 600 min). Fiber saturation point (FSP) determined by DSC was used to measure the total swelling of natural and heat treated wood. The result showed that FSP of common beech and maritime pine wood decreased with increasing treatment temperature and duration. The effect of long time exposure at low treatment temperature on FSP values seemed to be equivalent to short time at high temperature.

Sibel, Engin, and Umit (2006) studied the effect of heat treatment on compression strength of spruce wood (*Picea orientalis*). Heat treatment was performed by heating test sample in an oven at four different temperatures (130, 150, 180, and 200°C) and different durations (2, 6, and 10 hrs) under air and nitrogen atmosphere. Compression strength of spruce wood decreased with increasing treatment duration and temperature. Heat treatment of the wood resulted in chemical structure change of wood component. Hemicellulose contents were decreased. Thermal degradation of wood heated in the presence of oxygen was more rapid than oxygen-free atmosphere.

Follrich, Müller, and Gindl (2006) examined the change of wood surface property by heat treatment. Spruce wood samples were heated at 200°C for 5, 30, and 60 min. Contact angle of the samples were measured. The results presented that contact angle increased from 50°C for untreated wood up to 90° for thermally modified wood. Thermal treatment of spruce wood at 200°C remarkably decreased the hydrophilicity of the wood surface.

Boonstra and Tjeerdsma (2006) analyzed chemical component of heat treated wood. The heat treatment was performed by heating wood samples at 165-180°C for 4 hrs. A reduction of the hemicellulose percentage of heated wood was found. Hemicelluloses are amorphous and disorder structure, therefore they were easy to hydrolyze at high temperature. Depolymerization of hemicellulose increased when treatment temperature rose. Moreover, cross-linking of lignin also occurred. This resulted in the reduction of water absorption of heat treated wood.

Ali, Nasko, Bjørn, and Morten (2006) studied the weathering, water absorption, and durability of silicone, acetylated, and heat treated wood. Scots pine (*Pinus sylvestris L.*) sapwood specimens were used. Heat treatment was performed by heating sapwood samples at 240°C. Heat treated samples showed lower water uptake than the other treatments. The result was attributed to the thermal degradation of most hygroscopic polymer in the wood cell wall such as hemicellulose.

Gildas, Mathieu, and Phillippe (2007) examined the chemical reactivity of untreated and heated pine or beech sawdust by measurement in quantity of the hydroxyl group. Heat treatment was applied on the test sample under nitrogen atmosphere at 240°C in an oven for 4 hrs. The result from FTIR analysis showed that reactivity of heat treated sawdust was lower than that of untreated sawdust. Lower reactivity of heat treated wood was due to the decrease in free reactive hydroxyl group in holocellulose (cellulose and hemicellulose). Decreasing wood’s reactivity led to lower hygroscopicity of heat treated sawdust.

Gildas et al. (2007) investigated the effect of heat treatment on O/C ratio of wood. Low O/C ratio indicated high hydrophobicity of fiber. The heat treatment was performed on beech sawdust 240°C in an oven for different times under nitrogen atmosphere. The O/C ratio observed by using X-ray photoelectron spectroscopy (XPS) decreased with the heat treatment. Cross Polarization/Magic Angle Spinning (CP/MAS) $^{13}C$ NMR spectra showed an important degradation of hemicellulose after thermal treatment.z

Derya and Bilgin (2008) investigated the effect of heat treatment on density and swelling properties of red-bud maple (*Acer trautvetteri* Medw.) wood. The samples were heated at 120, 150, or 180°C for 2, 6, or 10 hrs under atmospheric pressure. The results presented that the value of density and swelling were decreased with increasing treatment time and temperature due to a decrease in moisture content.

Katsuya, Tetsuya, and Satoru (2008) monitored hydroxyl group in wood during heat treatment using Near-Infrared Spectroscopy (NIR). Test specimens of sitka spruce (*Picea sitchensis*) were treated at 140°C for different durations (5, 10, 20, 50, and 100 hrs). NIR spectra showed hydroxyl group at 4808 $cm^{-1}$ of the cellulose or hemicellulose which decreased by thermal treatment. This was directly related to the decrease of hydroxyl group on water, cellulose and hemicellulose. The result of weight change showed that the residual weight decreased with treatment time.

### Heat treatment of natural fiber

Yang, Zeng, and Zhang (1995) studied the effect of thermal treatment on the chemical structure and crystallinity of sisal fibers. FTIR spectra did not change when treatment temperature was below 200°C while density and crystallinity increased. This meant that the chemical structure of the sisal fibers was not changed below 200°C while the degree of crystallinity could be increased. This was attributed to the adjustment in molecular structure at evaluated temperature.

Wielage et al. (1999) evaluated the influence of heat treatment temperature and time on mechanical properties of flax fiber. Single fibers of flax were thermally treated at 180, 200, and 220°C for a time period of 15, 30, 45, and 60 min. For single fiber tensile testing, the mechanical properties of thermally treated flax fibers were decreased due to the degradation of fiber at higher temperature and duration of exposure. The influence of temperature higher than 180°C outweighs the influence of the exposure duration.

Shinji (2006) studied mechanical properties of heated manila hemp fiber. The fibers were heated in air at 160, 180, and 200°C for 15, 30, 60, and 120 min. The tensile strength of manila hemp fibers decreased with increasing heating time at 200°C. However, the tensile strength of heat treated manila hemp fibers at 180°C for 30 min was similar to that of non heat treated fibers due to no degradation of fiber.

Jacob, Thomus, and Varughese (2006) studied tensile properties and swelling characteristic of novel woven sisal fabric reinforced natural rubber composites. The surface modification of sisal fabric included alkali, silane, and thermal treatment. Sisal fabric was performed to thermal treatment in an oven at 150°C for 8 hrs. Upon heat treatment, the crystallinity of cellulose increased due to the rearrangement of the molecular structure at evaluated temperature. Swelling index of composites containing heat treated sisal fabric was minimized because the hydrophilic nature of fabric decreased. This showed that heat treatment provided better adhesion and stronger interface than other chemical modifications.

Saikia (2008) investigated structural characteristics of sisal fiber at elevated temperature. The average diameter and density of the fibers were 0.18 mm and 1.57 g/cm$^3$ respectively. The fibers were heated in a convection oven under an air atmosphere at different temperatures, namely 330K, 370K, 410K, 450K, 500K, 530K, and 600K for 3 hrs. X-ray diffraction (XRD) studies of sisal fibers under ambient and heated conditions were performed and scanned in a reflectance mode from $2\theta=4°$ to 40°. FTIR spectra of the fibers were recorded in an air atmosphere on an FTIR spectrometer in the frequency range from 4000 cm$^{-1}$ to 500 cm$^{-1}$. The samples were prepared by mixing sisal fiber with 100 mg of KBr. The result showed that the degree of crystallinity of the heated fiber at 450K was decreased by 10.32%. The heated fiber at 530K showed transformation of the fiber's crystalline structure to an amorphous state. The decrease in crystallinity of the samples annealed could be attributed to the change in dipole interactions. The increase in crystallite size also can be assigned to the effect on weak bend interactions of the crystalline materials in the fibers. The FTIR spectra of sisal under ambient and different annealed condition showed that no significant changes occurred in the IR spectra of the samples annealed at 370K and 450K. However, intensities of the peak resulting from OH in the 3600 cm$^{-1}$ to 3125 cm$^{-1}$ regions decreased very slightly for the sample annealed at 370K. This decrease was attributed to the less of water molecules from the sample.

Yi, Tian, Tong, and Xu (2008) studied on thermal stability and mechanical properties of sisal fiber in cycle process of thermal treatment. Thermal behavior was analyzed with 7.5 mg of sample weight between 30-600°C at 20°C/min under a nitrogen atmosphere. The peak observed at 65°C corresponds to the evaporation of water from the fiber. The second peak at about 350°C was due to the thermal depolymerization of hemicelluloses and cleavage of glycosidic linkage of cellulose. The most of celluloses were decomposed at the temperature of 350°C and dehydration as well as degradation of lignin occurred in the temperature range from 160 to 200°C. Sisal fibers with a length of 50 to 100 mm were roasted in an oven at 185°C for 30 min, 185°C for 5.30 min, 185°C for 10.30 min, and 185°C for 15.30 min. Tensile properties of the sisal fiber were measured at a crosshead speed of 40 mm/min and gauge length of 30 mm. The results showed that the tensile strength decreased gradually with the increasing time of thermal cycles. In the process of thermal treatment, due to some components of fiber decomposing with the increase of times of thermal cycles the molecular mass declined gradually and in the fiber surface, the inanition and disfigurement were formed.

Kaewkuk, S., Sutapun, W., and Jarukumjorn, K. (2009) studied on mechanical properties of heat treated sisal fibers. Heat treatment was performed by heating sisal fiber in an oven at 150, 170, and 200°C with different durations under atmospheric pressure and presence of air. Tensile testing was carried out using LR-5K, Lloyds Instrument Ltd., UK at a crosshead speed of 5 mm/min and a gauge length of 5 cm. Tensile properties of treated fiber at 170°C were higher than those of treated fiber at 150°C and 200°C when treatment time was 30 min because 170°C was the onset of decomposition temperature of hemicellulose. Removal of impurities and hemicellulose resulted in improvement of the strength of treated sisal fibers. In a case of the treated fiber at 200°C which was temperature after onset of decomposition of hemicellulose, the degradation of the fiber was observed and the color of the fiber turned into brown.

#### 2.2.1.2 Plasma treatment

Tu, Young, and Denes (1994) studied on an improvement of the bonding between cellulose and polypropylene by plasma treatment. T-peel test was used to evaluate bonding of cellulose and polypropylene. Oxygen and argon plasmas were used to modify the surface of polypropylene film, while cyclohexane plasma was used to modify the cellulose surface. With the non-reactive argon plasma, the persistence of reactive species such as free radicals was very important for enhancing adhesion. The amount of polar carbonyl groups introduced onto the surface was also an important factor for adhesion improvement. Modification of the cellulose surface to a hydrophobic character with cyclohexane plasma did not improve adhesion to polypropylene.

Hartwig (2002) studied the effect of plasma treatment on surface of cotton fiber. Chemical structure of the surface of cotton fiber was modified by plasma treatment. The topography of the surface of cotton fiber also changed. A highly hydrophobic surface and particular surface topography were occurred by this treatment. This surface modification resulted in a decrease of shrinkage behavior of cotton.

#### 2.2.1.3 Corona treatment

Dong, Sapieha, and Schreiber (1993) studied the effect of corona treatment on mechanical properties of cellulose fiber/polyethylene composites. Corona treatment resulted in a significant increase in strength properties of the composites. Remarkable improvement in ductility had been observed for composites containing 15-30% of the corona modified fiber.

Gassan and Voytex (2000) studied the effect of corona discharge on the properties of jute fiber/epoxy composites. With increasing corona energy, the polar component of the surface of jute fiber was increased. But the oxidation of the fiber surface always occurred when corona energy increased. The result led to a decrease in the yarn tenacity. The adhesion at the matrix-fiber interface might be increased due to the rise of the number of OH and COOH groups. However, improvement in the overall mechanical properties of jute fiber/epoxy composites needed to balance the increase of polarity of fiber surface and the decrease of fiber strength.

### 2.2.2 Chemical modification of natural fibers

#### 2.2.2.1 Alkali treatment

Alkali treatment of natural fiber is one of the most common treatments of the natural fibers as it improves the interfacial adhesion between the fiber and polymer matrix. This process is a purifying treatment that removes impurities such as waxes, pectin, hemicellulose and mineral salts from the fiber. Bisanda (2000) studied the effect of alkali treatment on the adhesion and wettability of sisal/epoxy composites. Sisal fibers were treated in a 0.5 M NaOH solution. The treatment of the fiber showed the improvement of adhesion characteristics because the surface roughness of the fiber increased. The removal of intracrystalline and intercrystalline lignin and other surface waxy substances by the alkalization increased the possibility for mechanical interlocking between fiber and matrix. The alkalization was simple and recommended to produce other sophisticated surface modification treatments on plant fibers.

Ray and Sarkar (2001) studied the changes occurring in rossells fibers after a 5% NaOH solution treatment for different periods for 0, 2, 4, 6, and 8 hrs. A 9.63% weight loss was measured during 2 hrs for the treatment with a drop of hemicellulose content from 22 to 12.90%. The tenacity and modulus of treated fibers were improved by 45 and 79% respectively. The percent breaking strain was reduced by 23% after 8 hrs of the treatment. The crystallinity of the fiber increased only after 6 hrs of the treatment, as evident from the x-ray diffractograms while FTIR measurements showed much of the changes occurring by 2 hrs of the treatment with an increase amount of OH groups.

Min, Ming, Yuan, Gui, and Han, M.Z. (2001) investigated tensile properties of alkali treated sisal fiber. Sisal fibers were immersed in a solution of 2% NaOH for 4 hrs at 60°C. The fibers were then washed thoroughly with water to remove the excess of NaOH, and air dried at 80°C. The fibers were tested by LWK-5 electronic tensile tester at a crosshead speed of 2 mm/min. For each case, 10 fibers were tested at a gauge length of 20 cm. Generally, effects of alkali treatment on the properties of natural fibers depend on the type and concentration of the alkali solution as well as the temperature and time of treatment (Gassan and Bledzki, 1999). The condition of mercerization chosen in this work led to an improvement of tensile strength and elongation at break but a decrease in Young’s modulus. It suggested that sisal fiber became relatively ductile after the removal of some hemicellulose and lignin.

Ray, Sarkar, Basak, and Rana (2002) studied on thermal properties of the treated jute with 5% NaOH for 2, 4, 6, and 8 hrs. Thermal analysis showed the moisture desorption was observed at a lower temperature in the case of all treated fibers. It might be a result of the increase in fineness of the fiber, which provided more surface area for moisture evaporation. The percent degradation of hemicellulose decreased considerably in all the treated fibers. Hemicellulose content was decreased by alkali treatment. The decomposition temperature for α-cellulose of all treated fiber changed from 362.2°C to 384°C, and the residual char formation increased to a significant extent. The enthalpy for the thermal degradation of α-cellulose had shown a decreasing trend for 2 and 4 hrs which could be caused by the initial loosing of the structure.

Sydenstricker, Mochnaz, and Amico (2003) investigated the thermal properties of sisal fiber treated with NaOH solution. Lignin content and density of fiber were reduced with the NaOH treatment. Moreover, moisture absorption was significantly decreased. TGA measurement of NaOH treated fibers showed that the fiber became more thermally resistant.

Sharifah and Martin (2004) studied the effect of fiber alignment and treatment of fiber by alkalization on the mechanical properties of natural fiber composites using polyester resin as a matrix. Hemp fibers were treated in a 6% NaOH solution at 19±2°C for 48 hrs. The surface of the treated fiber appeared to be quite smooth and clean. The surface topography showed the absence of surface impurity such as wax, pectin, hemicellulose and mineral salts. Treatment of fiber by alkalization helped to improve the mechanical interlocking and chemical bonding between the resin and fiber resulting in superior mechanical properties.

Martins, Forato, Mattoso, and Colnago (2006) studied the effect of chemical modification on the structure and morphology of sisal fiber. Mercerization was applied to sisal fibers in order to improve their adhesion in composites materials. The sisal fibers were immersed in NaOH solution with 5 or 10% concentration for 1, 3, and 5 hrs at room temperature, 50, or 80°C. It can be seen that the signals of Nuclear Magnetic Resonance (NMR) spectra of at 21 and 174 ppm due to acetyl groups of hemicelluloses and the signals in the lignin aromatic region 110-159 ppm disappeared, indicating that hemicellulose was removed and lignin was also partially removed. SEM micrographs showed that the fiber surface was cleaned by mercerization.

Mwaikambo and Ansell (2006) studied the effect of alkali treatment on the mechanical properties of sisal fiber bundles. Sisal fibers were soaked in sodium hydroxide solution with concentrations of 0.03, 0.08, 0.16, 0.24 and 0.32 wt% for 48 hrs. They were washed in distilled water to which drops of glacial acetic acid were added to neutralize excess sodium hydroxide. Then they were dried and placed in conditioning chambers for at least 48 hrs. A universal testing machine was used to determine the tensile properties. Thirty two specimens were tested in each case. Tensile strength and Young's modulus of sisal fiber were decreased with an increase in the concentration of NaOH up to 0.03 wt%. Above this concentration, the strength and Young's modulus increased sharply and reached a maximum at 0.16 wt% NaOH and then fell. The fall in tensile strength and Young's modulus between 0.16 wt% NaOH and 0.24 wt% NaOH solution were due to the degradation of the crystalline cellulose in the S2 layer of cell wall. The tensile strength and Young's modulus were increased slightly between 0.24 wt% and 0.32 wt% NaOH due to densification of the crystalline cellulose.

Edeerozey, Akil, Azhar, and Ariffin (2007) investigated morphology and structure changes of NaOH treated kenaf fibers. The fibers were immersed in NaOH solution with different concentrations (3, 6, and 9 wt% NaOH) for 3 hrs at room temperature. SEM micrograph showed wax, pectin, hemicellulose and mineral salts were removed from the fiber surface. Mechanical properties of kenaf fiber were significantly improved by the alkalization treatment as compared to untreated kenaf fiber. The optimum concentration of NaOH was 6 wt%.

#### 2.2.2.2 Silanization

Gonzalez, Uc, Olayo, and Franco (1999) modified short henequen fibers with a 0.5% wt/wt dicumyl peroxide and 1% wt/wt vinyltris (2-methoxyethoxysilane) (silane A-172) coupling agent. The fibers were immersed in the solution for 1 hr. Its deposition mechanism on the fiber surface and the influence of this chemical treatment on the mechanical properties of the composites were investigated. Fourier Transform Infrared Spectroscopy (FTIR) result showed the characteristic absorption bands of -Si-O-Si- at 700, 1030, 1145 and 1187 $\text{cm}^{-1}$ which confirmed the presence of polysilaxanes. The shoulders at 965 and 1200 $\text{cm}^{-1}$ corresponding to the characteristic of the –Si-O-C- bonds seemed to confirm the reaction between the hydrolyzed silane and the henequen fiber. The absorption bands at 860 and 930 $\text{cm}^{-1}$ corresponding to the –Si-OH bond revealed the presence of residual hydrolyzed silane. The results showed the partial removal of lignin and other alkali soluble compounds from the fiber surface by the alkali treatment. The tensile strength of composite using the fibers treated with the silane coupling agent was higher than that of composite using the fibers with no surface treatment. This was because the interaction between the fiber and the matrix was much stronger when the fiber surface was modified by a silane coupling agent.

Min et al. (2001) studied the effect of silane treatment on mechanical properties of sisal fiber reinforced epoxy composites. Sisal fiber was soaked in a solution of 2% aminosilane (KH550, γ-amine propyl trithoxysilane) in 95% alcohol. Crystallinity of sisal fiber was decreased by silane coupling agent treatment. It was generally accepted that when silane coupling agent reacted with hydroxyl groups, alkoxysilanes underwent stages of hydrolysis, condensation, and bond formation. This meant that in addition to the reaction of silanols with hydroxyls of the fiber surface, formation of polysiloxane structures also took place. A large coupling molecule would destroy the packing of cellulose chains to a certain extent. This led to a decrease in crystallinity of sisal fiber. Both tensile and flexural strength of silane coupling agent treated sisal fiber reinforced epoxy composites were slightly higher than those of untreated fiber composites because amine groups of the coupling agent could react with epoxy resin in the curing process.

Abdelmouleh, Boufi, Belgacem, and Dufresne (2007) studied the effect of silane treatment on mechanical properties of alfa fiber/ polyethylene composites. Alfa fibers were immersed in 3 wt% of γ-Methacryloxypropyltrimethoxysilane (MPS) solution for 2 hrs. The 3 wt% of MPS solutions were prepared by dissolving MPS in 80/20 v/v ethanol/water medium. Modulus and tensile strength of composites were improved by the fiber treatment because Si-O of silane coupling agent reacted with OH groups of fiber surfaces. Grafted MPS was reacted with radical species to generate a covalent bond. The radical species may be generated through peroxide decomposition which arose from the thermal oxidation during the processing of the composites. The result of reaction was given to increase of chemical bonding between the fiber and the matrix.

#### 2.2.2.3 Acetylation

Albano, Gonzalez, Ichazo, and Kaiser (1999) studied the effect of acetylated and nonacetylated sisal fiber on thermal degradation of sisal/polypropylene composites. The fibers were immersed in 18% aqueous sodium hydroxide solution at 25°C for 1 hr then soaked in glacial acetic acid for 1 hr. The higher thermal stability of acetylated sisal fiber than untreated fiber might be attributed to the substitution of OH groups by more voluminous ones, which brought about restrictions in the segmental mobility, thereby increasing the stiffness of the cellulose backbone. This was also because of partially removed some components of fiber, such as hemicelluloses during alkali treatment.

#### 2.2.2.4 Functionalization with maleic anhydride

Cantero, Arbeliaiz, Ponte, and Mondragon (2003) studied the effect of fiber treatment with maleic anhydride (MA) on the properties of flax fiber reinforced polypropylene composite. The fiber was esterified during 25 hrs with MA dissolved in boiling acetone (T= 50±5° C). Treated fibers were analyzed by FTIR spectroscopy. The peak between 1800 and 1600 cm$^{-1}$ related with the formation of new ester groups between hydroxyl groups from cellulose and MA. MA treatment led to a more intense peak at about 1735 cm$^{-1}$, associated to carbonyl (C=O) stretching of acetyl groups of hemicellulose due to the esterification reaction. This was worth nothing for flax fiber used that the shape of the 3700-3000 cm$^{-1}$ broad band changed for MA treatment thus indicating a variation on the ratio of intermolecular to intramolecular OH bonds.

### 2.2.3 Interfacial modification of polymer composites by compatibilizer

For the composites based on natural fiber and polypropylene, maleic anhydride grafted polypropylene (MAPP) has been found to be the most efficient compatibilizer in improving interfacial adhesion of natural fiber and polypropylene matrix. Rana et al. (1998) studied the effect of MAPP as a compatibilizer on the mechanical properties of rossells/PP composites. Mechanical properties of the composites were sharp increased and water absorption values were decreased by addition of the compatibilizer. It might be attributed to linkage between the hydrophilic groups of rossells fiber and the carboxyl groups of compatibilizer. At 60 wt% of fiber loading, MAPP improved the flexural strength as high as 100%, tensile strength to 120%, and impact strength (unnotched) by 175%. The improvements were attained even with 1 wt% compatibilizer only.

Joseph et al. (2002) studied the environmental degradation behavior of short sisal/PP composites. Maleated polypropylene (MAPP) was used as a compatibilizer. Water absorption of the MAPP modified composites was reduced when compared with the untreated sisal/PP composite due to better fiber/matrix adhesion. The compatibilizer built up chemical bonds and hydrogen bonds, which reduced the debonding of fiber and matrix. It suggested that both chemical (ester bond) and physical interaction (hydrogen bond) should be formed between the hydroxyl groups of fiber and MAPP. Whereas, the PP chain of MAPP diffused in to the PP matrix to form the physical interaction (entanglement). This was favored a strong interfacial adhesion between the fiber and PP matrix.

Hristov, Lach, and Grellmann (2004) investigated the fracture behavior of PP/wood fiber composites. Maleated polypropylene (MAPP) was used as a compatibilizer. Energy for initiating a crack large increased with adding MAPP. The improvement of interfacial adhesion of compatibilized wood fiber/PP composites led to higher stress distribution which retarded the crack initiation. MAPP toughened the polypropylene matrix and enhanced the total fracture energy of the modified composites.

Arbelaiz et al. (2005) studied the influence of MAPP on mechanical properties of flax fiber bundle/PP composites. The result showed that using MAPP as a compatibilizer, mechanical properties of composites were improved by enhancing the adhesion between flax fiber bundle and PP. MAPP modified composites exhibited a remarkable reduction in water uptake rate due to a better interfacial bonding between fiber and matrix.

Doan, Gao, and Madar (2006) studied the mechanical performances and environmental aging resistance of rossells fiber/PP composites. The addition of 2 wt% MAPP significantly improved the mechanical properties of the composites. An increase of the tensile strength of the rossells/PP composites in humidity aging conditions was attributed to the improvement of interfacial adhesion strength of rossells fibers and PP matrix.

Demir, Atikler, Balköse, and Tıhmınlıoğlu (2006) studied the effect of coupling agent on the mechanical, morphology, and water sorption properties of luffa fiber (LF)/polypropylene. Three different types of coupling agents were (3-aminopropyl)-triethoxysilane (AS), 3-(trimethoxysilyl)-1-propanethiol (MS), and maleic anhydride grafted polypropylene (MAPP). Mechanical test results clearly showed that both silane treatment of luffa fiber and reactive treatment of composites with MAPP during compounding increased the tensile strength and Young's modulus of composites. Water absorption results showed that silane and MAPP treatment reduced the water absorption capacity when compared to untreated composites.

Kim, Moon, Kim, and Ha (2008) studied the mechanical properties of polypropylene/wood fiber composites. Maleic anhydride grafted PP (MAPP) was used as a compatibilizer. The tensile strength of the wood fiber/PP composites was decreased with increasing wt% of the wood fibers. The use of MAPP was helpful to increase the tensile and flexural strength of the wood fiber/PP composites due to increased interaction between the fiber and PP matrix.

## 2.3 The study on properties of natural fiber/polymer composites

### 2.3.1 Mechanical properties

Gassan and Bledzki (1999) investigated mechanical properties of jute fiber reinforced epoxy. The alkali treatment was done by treating the tossa jute fiber yarns with 28 wt% NaOH for 30 min at a temperature of 20°C. Strength and stiffness of composites increased as a consequence of the improvement of mechanical properties of the fiber by NaOH treatment.

Robin and Breton (2001) prepared heat treated wood fiber/high density polyethylene (HDPE) composites. Compounding of spruce wood fiber/HDPE composites was carried out using a two roll mill at 180°C. Test specimens for impact and flexural testing were prepared by an injection molding machine. Impact strength and flexural properties of heat treated wood fiber/HDPE composites were better than of non treated wood fiber/HDPE composites due to more compatible between wood fiber and polyethylene matrix. Morphological analysis indicated a better adhesion between fiber and matrix. There was the wetting of HDPE matrix on heat treated wood fiber. Hence, heat treatment seemed to bring a positive effect onto adhesion of wood fiber and polyethylene matrix.

Arbelaiz et al. (2005) studied the effect of two different maleated polypropylene (MAPP) compatibilizers (Epolene E43 and G3003) on the mechanical properties of flax fiber/PP composites. Tensile strength and Young's modulus were investigated as a function of the amount of compatibilizers. Both the tensile strength and Young's modulus increased with an increase of MAPP contents. The maximum improvement of the tensile strength for E43 and G3003 were 42% and 58% respectively. The maximum values of tensile strength were obtained at 5 to 10 wt% for both MAPP types. The strength of composites with E43 seemed to be more effective until 3 wt% compared to the composites with G3003 whereas beyond this content, composites with G3003 showed better strength performance. This can be explained by G3003 has a lower amount of acid number (amount of maleic groups per chain length), so at low modifier content it has not enough maleic groups to produce an optimum coupling efficiency. At 3 wt% of the compatibilizer, G3003 has enough maleic groups to create interactions with the flax fiber. Thus, a better stress transfer from the matrix to the fiber was expected. E43 has a lower molecular weight and shorter polymer chains than G3003, therefore the chance of entanglements with PP matrix has lower than G3003. The impact strength decreased drastically when the flax fiber was added for both unmodified and MAPP modified composites. Since, when the fiber content was increased, the regions of stress concentrations that required less energy to initiate cracking were created. A reduction of the impact strength was observed at 20 wt% of MAPP. This can be attributed to the migration of a compatibilizer from the fibers to the matrix at a high amount, causing self-entanglement among the compatibilizer chains rather than with the matrix, thus resulting in slippage. The optimum value of compatibilizer content was similar to obtain for tensile strength at 10 wt%.

Demir, Atikler, Balköse, and Tıhmınlıoğlu (2006) studied the effect of coupling agent on the mechanical of luffa fiber (LF)/polypropylene. Three different types of coupling agents: (3-aminopropyl)-triethoxysilane1 (AS), 3-(trimethoxysilyl)-1-propanethiol (MS), and maleic anhydride grafted polypropylene (MAPP) were used. Tensile strength and Young's modulus increased with adding coupling agents due to the better adhesion between the fiber and the matrix. The maximum improvement in the mechanical properties was obtained for the MS treated LF composites. This was due to better adhesion between the filler and the matrix. Better adhesion improved stress transfer through fibers, therefore, increased the tensile strength of composites

### 2.3.2 Thermal properties

Ichazo et al. (2001) studied thermal properties of modified wood flour (WF) reinforced polypropylene composites. The wood flour was treated with 18 wt% solution of sodium hydroxide and with 1 wt% vinyl-tris-(2-methoxyethoxy silane). Maleated polypropylene (MAPP) was used as a compatibilizer. The crystallization temperature ($T_c$) increased approximately by 7°C when the treated WF was added to PP. While the $T_c$ increased approximately by 13°C for the treated WF. These results indicated that the processing of these composites needed molding time and energy less than virgin PP. Melting temperature ($T_m$) practically did not change neither with the addition of WF nor with the different treatments.

Joseph et al. (2003) studied the thermal behaviour of sisal/PP composites by thermogravimetry. Maleated polypropylene (MAPP) was used to modify sisal fibers. The result revealed that fiber filled system degraded later than the PP matrix. It indicated the thermal stability of the composite was higher than the PP matrix. In the case of MAPP modified sisal/PP composites, the extent of degradation at a given temperature was less than that of untreated sisal/PP composite. This was because the improvement of the fiber matrix adhesion can be attributed to the esterification reaction between cellulose fiber hydroxyl groups and anhydride functionality of maleated PP. The incorporation of the sisal fiber in PP caused an apparent increase in the crystallization temperature ($T_c$) and percentage of crystallinity due to fibers acting as a nucleating agent for the crystallization of PP. The treated fiber composites showed better dynamic mechanical properties compared to the untreated system.

Araújo, Waldman, and De Paoli (2008) studied the effect of maleic anhydride grafted polyethylene (MAPE) as a coupling agent on thermal properties of high density polyethylene (HDPE) composites with curaua fiber. Calorimetric characterization of the composites related to the crystallization phenomenon was studied. Addition of the curaua fiber into HDPE increased the crystallinity due to the transcrystallinity effect. However, the presence of the coupling agent decreased this effect due to its reactions with the OH groups at the fiber surface.

### 2.3.3 Rheological properties

George et al. (1996) studied the melt rheological behaviour of short pineapple fiber/low density polyethylene (LDPE) composite. The fibers were first treated with alkali solution and then treated with vinyl tri-2 (ethoxymethoxy silane). The composites were prepared by solution mixing technique. The measurement of rheological behavior was carried out using a capillary rheometer at different plunger speeds. The results showed that the viscosity of the composite increased as a result of chemical treatment. Silane treatment enhanced adhesion at the polymer fiber interface. This improvement was because to $-OR_2$ groups of silane might be hydrolyzed to some extent to form silanols. The resulting –OH group or $-OR_2$ group provided a link to cellulose through their –OH groups by the formation of hydrogen bonds. The long hydrophobic polymer chain of polymerized silane can adhere to LDPE due to van der waal’s type adhesive forces. As a result, the strong interaction was induced at the fiber-matrix interface, resulting an increase in viscosity of the composite.

Nair et al. (2000) studied the rheological behavior of short sisal fiber-reinforced polystyrene (PS) composites using a capillary rheometer. The viscosity of the composite increased with the addition of fibers. An increase in the viscosity was sharper at 30% fiber loading. Generally, the viscosity decreased with incresing temperature of the polymer system. This was due to the decreasing entanglement density and weaker intermolecular interaction at higher temperature. However, sisal/PS composites showed the reverse tendency. The viscosity of the composite increased with temperature. This might be attributing to increased interaction between the fibers and polymer molecules at higher temperature. The viscosity of the sisal/PS composite was found to be lower than that of pure PS due to a higher degree of pseudoplasticity for the composite. There was a sharp decrease in die swell ratio at 10% fiber loading, followed by a leveling off at higher fiber loading. When the fiber loading increased the uniform extrudate was observed.

### 2.3.4 Morphological properties

Ichazo et al. (2001) investigated the fracture surfaces of modified wood flour (WF) reinforced polypropylene composite using a scanning electron microscope (SEM). WF was treated with 18 wt% solution of sodium hydroxide and with 1 wt% vinyl-tris-(2-methoxyethoxy silane). Maleated polypropylene (MAPP) was also used as a compatibilizer. SEM micrograph presented a better polymer filler adhesion with the silane treatment and using MAPP than the untreated WF composite due to an increase of the interface thickness between the WF particles and the polymer matrix.

Hristov, Lach, and Grellmann, (2004) studied the impact fracture of wood fiber/polypropylene (PP) composites modified with maleated polypropylene (MAPP). The fracture surface of unmodified wood fiber/PP composite was mainly characterized by fiber pull-out. It was smooth and clean matrix surface inside the remaining holes. This indicated poor adhesion between the matrix and fibers. When the MAPP was added to the unmodified composite, the interfacial adhesion was noticeably improved. The fiber had been covered with the thin layer by the matrix. The linking in fiber surface to the matrix of MAPP modified composite showed better mechanical properties than that of unmodified composites.

Demir, Atikler, Balköse, and Tıhmınlıoğlu (2006) studied the effect of coupling agents on the tensile properties of luffa fiber (LF)/polypropylene (PP). (3-aminopropyl)-triethoxysilane1 (AS), 3-(trimethoxysilyl)-1-propanethiol (MS), and maleic anhydride grafted polypropylene (MAPP) were used to improve surface adhesion between the fiber and polymer matrix. Scanning electron microscope (SEM) was used to examine the morphology of the LF/PP composites. Fracture surfaces of tensile specimens containing 15 wt% untreated and treated LF were examined. Morphological result demonstrated that better adhesion between the fiber and the matrix was achieved especially for the MS and AS treated LF/PP composites.

Qiu, Endo, and Hirotsu (2006) studied the effect of maleated polypropylene (MAPP) on the morphological properties of fibrous cellulose reinforced polypropylene composite using a scanning electron microscope (SEM). The composites with 30 wt% cellulose content were prepared by melt mixing method. From the fracture surfaces of the PP/cellulose composite, there were large gaps and voids between PP matrices and cellulose fibers. This indicated the interfacial adhesion between cellulose and the PP matrix was very poor. The fracture surfaces of composites with MAPP revealed strong interfacial adhesion between MAPP and cellulose fibers since the cellulose fibers were tightly connected with the matrix.

### 2.3.5 Water absorption

Akinori, Kiichi, and Hikaru (1984) studied the effect of heat treatment on water absorption of wood flour filled phenolics. Water absorption of heat treated wood flour composites was lower than those of untreated wood flour composites because hydrophobic nature of wood flour was increased by heat treatment.

Joseph et al. (2002) studied the effect of maleated polypropylene (MAPP) on the sorption characteristics of sisal/PP composites. The sisal/PP composites were prepared by the melt mixing method at temperature of 170°C and rotor speed of 50 rpm for 10 min. The water absorption rate of treated sisal/PP composites with 20 wt% fiber loading was lower than that of untreated sisal/PP composites. Moisture resistance of the treated sisal/PP composites increased due to an improvement in fiber/matrix adhesion. The enhanced bonding of MAPP treated fiber composites was attributed to the esterification reaction between sisal fiber hydroxyl groups and anhydride part of MAPP, which caused a reduction in interfacial tension and an increase in interfacial adhesion between PP and the fiber.

Arbelaiz et al. (2005) studied the effect of MAPP on water absorption of short flax fiber bundle/polypropylene composites. Sorption characteristics were studied by immersion of the composites in distilled water at room temperature. Water uptake increased with fiber bundle content. MAPP modified composites exhibited a remarkable reduction in water uptake rate due to a better interfacial bonding between flax fiber bundle and PP matrix.

Demir, Atikler, Balköse, and Tıhmınlıoğlu (2006) studied the effect of coupling agent on the mechanical of luffa fiber (LF)/polypropylene (PP). Three different types of coupling agent, (3-aminopropyl)-triethoxysilane1 (AS), 3-(trimethoxysilyl)-1-propanethiol (MS), and maleic anhydride grafted polypropylene (MAPP) were used. Water absorption results showed that silane (AS and MS) and MAPP treatment reduced the water absorption capacity compared to untreated composites due to the better adhesion between the fiber and the matrix. This better adhesion was correlated with mechanical results.

## 2.4 Glass fiber hybridization

One possibility to improve the mechanical properties of composites is to reinforce them with two or more fiber types in a single matrix leading to hybrid composites. Glass fiber hybridization can improve the stiffness, strength, and moisture resistance of the natural fiber/polymer composites. Mishra et al. (2003) studied mechanical performance of biofiber (pineapple leaf fiber and sisal fiber)/glass reinforced polyester hybrid composites. Addition of relatively small amount of glass fiber (by about 8.6 wt%) to the pineapple leaf fiber-reinforced polyester matrix enhanced the mechanical properties of the resulting hybrid composites by about 66%. However, further increase in weight fraction of glass fiber to 12.9 wt%, tensile strength of pineapple leaf/glass fibers hybrid polyester composites was decreased about 10%. It had been observed that water uptakes of hybrid composites were less than that of unhybridized composites. Glass fiber hybridization encouraged mechanical properties, which might be expanded the applicability of these composites in automotive and building products industries.

Arbelaiz et al. (2005) investigated effect of glass fiber hybridization on mechanical properties of flax fiber/polypropylene composites. All hybrid composites had a 30% of fiber content. Glass and untreated flax fiber ratio used were 100:0, 75:25, 50:50, 25:75, and 0:100. Tensile strength of the composites increased with increasing glass fiber contents. Composites with 30 wt% glass fiber (0:100) displayed the highest strength value.

Panthapulakkal and Sain (2007) studied mechanical, thermal properties, and water absorption of hemp/glass fiber-PP composites. Flexural properties and notched Izod impact strength of the composites were enhanced with adding glass fiber. In addition, the incorporation of glass fiber into hemp/PP composites resulted in improved thermal properties and water resistance of the composites.

Velmurugan and Manikandan (2007) investigated the mechanical properties of palmyra/glass fiber hybrid composites. Rooflite (polyester) resin was used as a matrix. Tensile, impact, shear and bending properties were improved with adding glass fiber along with palmyra fiber in the matrix. Moreover, addition of glass fiber with plamyra fiber in the matrix decreased the moisture absorption of the composites.

Jarukumjorn, K., and Suppakarn, N. (2009) examined the effect of glass fiber on mechanical, thermal, rheological, and morphological properties of sisal/PP composites. Incorporating glass fiber into the sisal/PP composites enhanced tensile, flexural, and impact strength without having significant effect on tensile and flexural modulus. In addition, adding glass fiber improved thermal properties and water resistance of the composites. Thermal decomposition temperature of the composites increased with increasing glass fiber content. HDT of PP was considerably increased with adding sisal fibers and further improved by hybridization with glass fibers. However, incorporation of glass fibers into the sisal/PP composites was not notably changed the viscosity.

Nayak, Mohanty, and Samal (2009) studied on thermal properties of short bamboo/glass fiber/polypropylene hybrid composites. Maleic anhydride grafted polypropylene (MAPP) was used as a coupling agent to improve the interfacial interaction between the fibers and matrix. Thermal degradation temperature of composites with MAPP was comparatively higher (about 10°C) than that of the composites without MAPP. This was probably due to the increase in the molecular weight by cross-linking reaction between PP matrix, MAPP and bamboo fiber.

Incorporation of glass fibers resulted in considerable increase in the thermal stability of the composite which was possibly due to the higher thermal stability of glass fiber than bamboo fiber.

# CHAPTER III

# EXPERIMENTAL

## 3.1 Materials

A commercial grade of isotactic polypropylene (PP, 700J) was supplied by Thai Polypropylene Co., Ltd. Maleic anhydride grafted polypropylene with 0.55 wt% of maleic anhydride (MAPP, Fusabond® P MZ 109D, DuPont) was used as a compatibilizer. Sisal fibers (*Agave sisalana*) were purchased from Sisal-Handicraft OTOP Group, Tambon Ban Kao, Amphur Dan Khun Thod, Nakhon Ratchasima, Thailand. Short glass fiber (Chop Vantage® HP 3610, PPG glass fiber) was supplied by Behn Meyer Chemicals Co., Ltd.

## 3.2 Fiber preparation

Sisal fibers were dried overnight before used. These fibers were named “untreated fibers (UT)”.

The untreated fibers were cut into an approximate length of 2 mm. Then, the sisal fibers were treated with 2 wt% NaOH solution for 2 hrs. After that, the fibers were washed with water and dried at 60°C overnight. These fibers were referred “alkali treated fibers (AT)”.

Heat treatment was performed by heating the untreated sisal fibers in an oven at three different temperatures (150, 170, and 200°C) and different durations (5, 15, 30, 45, 60, 90, and 120 min) under an atmospheric pressure and a presence of air.

These fibers were called “heat treated fibers (HT)”. According to the mechanical properties, the heat treated fibers giving the highest mechanical properties at each treatment temperature were chosen to prepare the PP composites.

Short glass fibers (GF) with average length of 3.2 mm and aspect ratio of 320 were heated at 500°C for 4 hrs in order to remove sizing agents.

## 3.3 Composite preparation

Polypropylene and untreated or treated sisal fibers were mixed using an internal mixer (Hakke Rheomix 3000p). The fiber contents were 10, 20, and 30 wt%. The rotor speed was 50 rpm and a mixing temperature was 170°C. After melting PP for 5 min, the fibers were added. The total mixing time was 13 min.

In cases of MAPP modified composites, MAPP was added after melting PP for 3 min and then the fibers were added. For glass fiber hybrid composites, after melting PP for 3 min, MAPP was added. Next, sisal fibers were added and then glass fibers were added after mixing for 6 min. The compounds were ground to prepare test specimens.

Test specimens were prepared by an injection molding machine (Chuan Lih Fa model CLF 80P). The injection was processed at a melting temperature of 170°C, an injection speed of 46 mm/s, a screw speed of 130 rpm, a holding pressure of 1,400 kg/cm$^2$, and a mold temperature of 25°C.

## 3.4 Material characterization

### 3.4.1 Fiber characterization

#### 3.4.1.1 Measurement of fiber dimension

Average lengths and diameters of untreated and heat treated sisal fibers were measured based on 100 samples using an optical microscope (Nikon, model Eclipes E600 POL) with a 10x objective.

#### 3.4.1.2 Thermal properties

Thermal degradation temperature and weight loss of untreated and heat treated sisal fibers were analyzed by a thermogravimetric analyzer (Perkin Elmer, model TGA7). The temperature range was from 30 to 600°C with a heating rate of 10°C/min under a nitrogen atmosphere.

#### 3.4.1.3 Mechanical properties

Tensile properties of untreated and heat treated sisal fibers were tested following ASTM D3822 using a tensile testing machine (Lloyds, model LR-5K) with a load cell of 100 N, a cross head speed of 5 mm/min, and a gauge length of 50 mm.

#### 3.4.1.4 Morphological properties

Surface and cross section morphologies of untreated and treated sisal fibers were examined using a scanning electron microscope (JEOL, model JSM6400) at 10 keV. For cross section morphologies, sisal fibers were embedded in epoxy for 5 min. Transverse sections were cut using a rotary microtome. The samples were coated with goal before examination.

#### 3.4.1.5 Functional groups analysis

FTIR spectra of untreated and heat treated sisal fibers were recorded in an air atmosphere using Fourier transform infrared spectrometer (Bruker, model Tensor 27) in the wavenumber range from 4000 $cm^{-1}$ to 400 $cm^{-1}$, operating in ATR (attenuated total reflectance) mode. Thirty two scans were used at a resolution of 4 $cm^{-1}$.

#### 3.4.1.6 Fiber composition determination

Fiber compositions were determined using a detergent method (Goering and Van Soest, 1970). Hemicellulose and cellulose contents were calculated by the following equation:

$$\%\ \text{Hemicellulose} = \%\ \text{NDF} - \%\ \text{ADF} \tag{3.1}$$

$$\%\ \text{Cellulose} = \%\ \text{ADF} - \%\ \text{ADL} \tag{3.2}$$

where NDF is neutral detergent fiber. ADF is acid detergent fiber and ADL (acid detergent lignin) is quantity of lignin.

### 3.4.2 Composite characterization

#### 3.4.2.1 Thermal properties

Thermal properties of PP and PP composites were examined by a thermogravimetric analyzer (TA, model SDT 2960) and a differential scanning calorimeter (Perkin Elmer, model DSC-7). The measurement was carried out at a heating rate of 20°C/min under a nitrogen atmosphere. TGA and DTGA curves of PP and PP composites were obtained by heating samples under a nitrogen atmosphere at a heating rate of 20ºC/min. DSC thermograms of PP and PP composites were obtained in three steps under a nitrogen atmosphere. The first heating scan was performed by heating a sample from 30ºC to 180ºC at a heating rate of 10ºC/min. Then the sample was annealed at 180ºC for 5 min to remove the thermal history. After that, the cooling scan was begun by cooling the sample to 30ºC at a cooling rate of 10ºC/min. Finally, the second heating scan was performed by heating the sample from 30ºC to 180ºC at a heating rate of 10ºC/min. The crystallinity of the composites was calculated by the following equation:

$$\%\ \text{crystallinity} = (\Delta H_{sample} / \Delta H_f^0\, w) \times 100 \qquad (3.3)$$

where $\Delta H_{sample}$ is the heat of fusion of sample (J/g) obtained from the second heating scan. $\Delta H_f^0$ is the heat of fusion of pure crystalline PP that equals 209 J/g (Arbelaiz, Fernandez, Ramos, and Mondragon, 2006). w is mass fraction of the PP in the composite.

Heat distortion temperature (HDT) was tested following ASTM D648 using HDT testing machine (model HDV 1) under a stress of 0.455 MPa at heating rate of 2º C/min.

#### 3.4.2.2 Rheological properties

Melt flow index (MFI) of PP and PP composites were measured using a melt flow indexer (Kayeness, model 4004) at 170°C and 2.16 kg loading. Viscosity at various shear rates (shear rate ranges 10-1000 $s^{-1}$) was obtained using a capillary rheometer (Kayeness, model D5052m) at 170°C.

### 3.4.2.3 Mechanical properties

Tensile properties of PP and PP composites were tested by following ASTM D638 using a universal testing machine (Instron, model 5565) with a load cell of 5 kN, a crosshead speed of 10 mm/min, and a gauge length of 50 mm.

Unnotch impact strength of PP and PP composites were tested by following ASTM D256 using an impact testing machine (Atlas, model BPI).

Flexural properties of PP and PP composites were examined according to ASTM D790 using a universal testing machine (Instron, model 5565) with a load cell of 5 kN, a crosshead speed of 15 mm/min, and span length of 56 mm.

### 3.4.2.4 Morphological properties

Fracture surfaces of PP composites were studied using a scanning electron microscope (JEOL, model JSM6400) at 10 keV. The composites were freeze-fractured in liquid nitrogen and coated with a thin layer of gold before examination.

### 3.4.2.5 Water absorption

Water absorption of PP composites was performed by following ASTM D570. The specimens were immersed in distilled water at room temperature. The percentage increase in weight during the immersion was calculated by following equation:

$$\text{Water absorption (\%)} = [(w - w_0)/w_0] \times 100 \tag{3.4}$$

where w is wet weight and $w_0$ is dried weight.

# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Effect of heat treatment on physical properties of sisal fibers

### 4.1.1 Mechanical properties

Tensile strength, Young's modulus, and elongation at break of untreated and heat treated sisal fibers at different treatment temperatures and times are shown in Figure 4.1-4.3 and listed in Table 4.1.

In cases of treatment temperature of 150°C, tensile strength of the heat treated fiber was higher than that of untreated fiber. When the treatment times were increased up to 30 min, the highest tensile strength was obtained as shown in Figure 4.5. When the treatment time was more than 30 min, the tensile strength slightly decreased. It may be due to degradation of the fiber by removal of some hemicellulose as mentioned later in 4.1.2.

Tensile strength of heat treated fiber at 170°C increased with increasing treatment time from 5-30 min. After 30 min of treatment time, tensile strength stay almost unchanged. The maximum tensile strength of heat treated fiber was 360 MPa by which it was obtained at treatment time of 30 min.

For the 200°C treated sisal fibers, the highest tensile strength of the treated fiber was obtained at a treatment time of 5 min. After that, when the treatment time was increased, the tensile strength was dropped. In addition, the color of the treated fiber at 200°C turned into brown when the treatment time was longer than

5 min. This was because treatment at 200°C fell in the temperature range of decomposition of hemicelluloses. Therefore, the degradation of the fiber occurred when the treatment time was longer than 5 min as confirmed by SEM micrographs in Figure 4.8-4.9.

Tensile strength of sisal fiber after heat treatment at 150 and 170°C were not difference within 15 min of treatment time. But after 30 min tensile strength of heat treated at 150°C obviously decreased while tensile strength of heat treated at 170°C after 30 min of treatment time unchanged. In a case of heat treatment at 200°C, tensile strength significantly dropped after 5 min of treatment time.

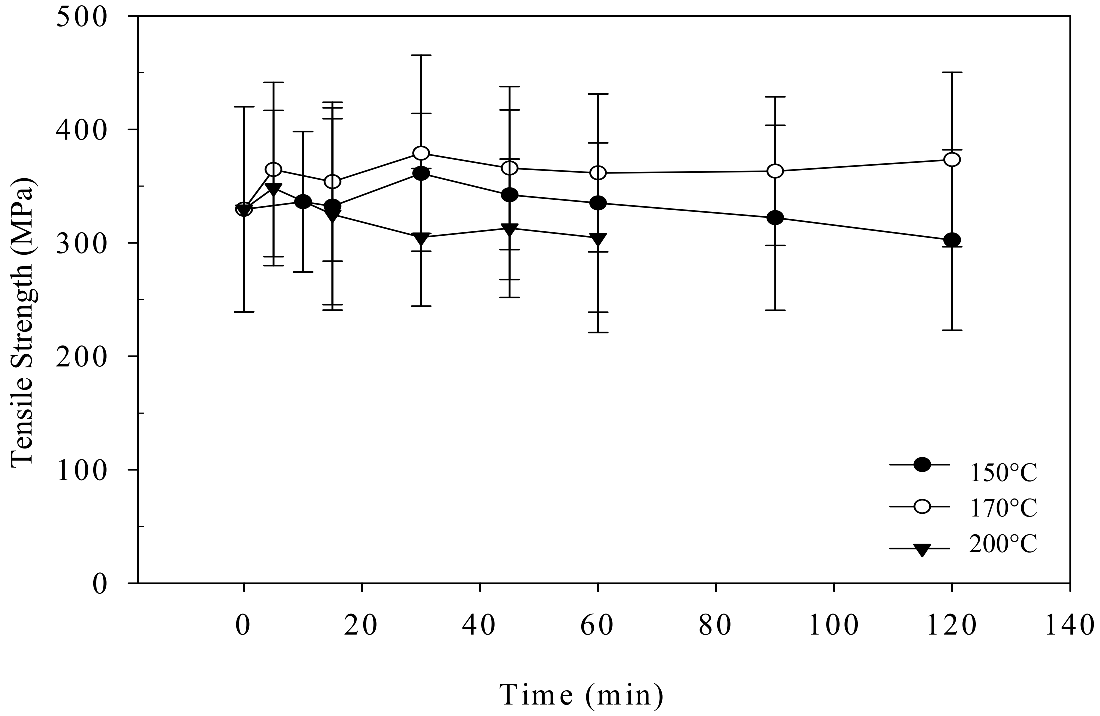


**Figure 4.1** Plot of tensile strength and treatment time of untreated and heat treated sisal fibers with various treatment temperatures.

Young’s modulus of untreated and heat treated fiber at 150 and 170°C showed no significant difference. Increasing treatment time showed no effect on Young’s modulus of heat treated fiber at 150 and 170°C while Young’s modulus of heat treated fiber at 200°C slightly decreased with increasing treatment times as shown in Figure 4.2. Elongation at break of untreated and heat treated fiber also showed no significant difference as shown in Figure 4.3.

According to the mechanical properties, the heat treated fibers at 150 and 170°C for 30 min and 200°C for 5 min were chosen to prepare the PP composites.

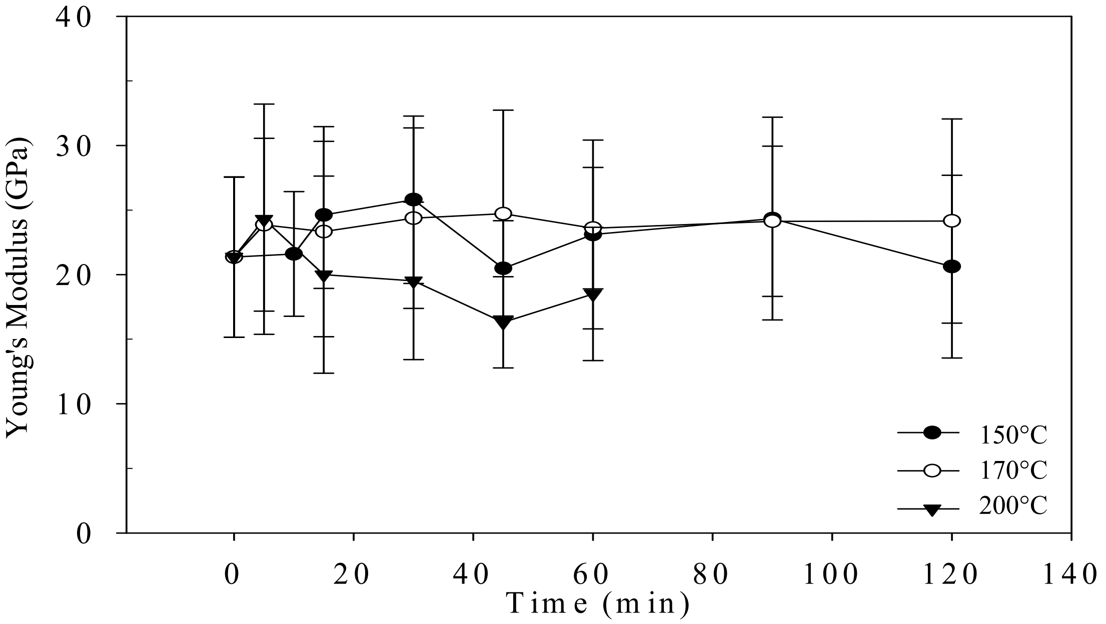


**Figure 4.2** Plot of Young’s modulus and treatment time of untreated and heat treated sisal fibers with various treatment temperatures.

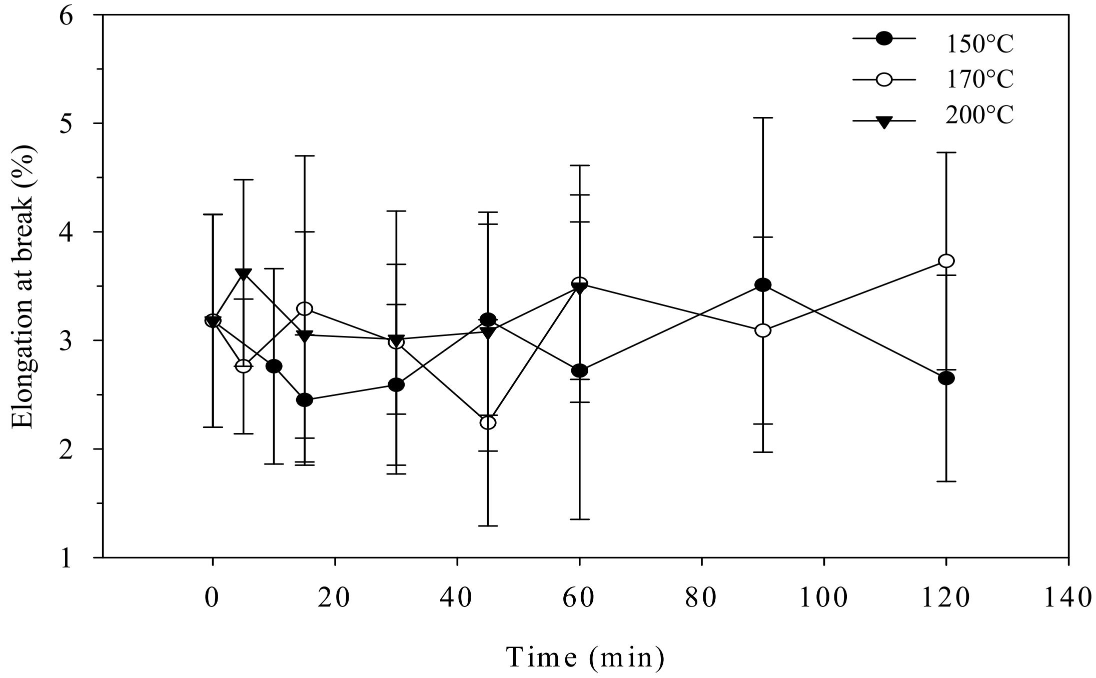


**Figure 4.3** Plot of elongation at break and treatment time of untreated and heat treated sisal fibers with various treatment temperatures.

**Table 4.1** Tensile strength, Young's modulus, and elongation at break of untreated and heat treated sisal fibers.

| **Treatment conditions** | **Tensile strength (MPa)** | **Young's modulus (GPa)** | **Elongation at break (%)** |
|---|---|---|---|
| Untreated | 329.54±90.46 | 21.36±6.20 | 3.18±0.98 |
| 150°C 10 min | 336.27±61.95 | 21.60±4.83 | 2.76±0.90 |
| 150°C 15 min | 332.25±86.74 | 24.62±5.69 | 2.45±0.60 |
| 150°C 30 min | 361.14±52.79 | 25.80±6.48 | 2.59±0.74 |
| 150°C 45 min | 342.36±74.72 | 20.48±3.69 | 3.19±0.88 |
| 150°C 60 min | 335.09±96.28 | 23.11±7.31 | 2.72±1.37 |
| 150°C 90 min | 322.08±81.57 | 24.34±7.85 | 3.51±1.54 |
| 150°C 120 min | 302.49±79.56 | 20.62±7.07 | 2.65±0.95 |
| 170°C 5 min | 364.59±76.83 | 23.86±6.69 | 2.76±0.62 |
| 170°C 15 min | 353.91±69.99 | 23.33±8.14 | 3.29±1.41 |
| 170°C 30 min | 378.98±86.37 | 24.37±6.99 | 2.98±1.21 |
| 170°C 45 min | 365.86±71.89 | 24.71±8.03 | 3.24±0.95 |
| 170°C 60 min | 361.62±69.51 | 23.60±4.70 | 3.52±1.09 |
| 170°C 90 min | 363.20±65.51 | 24.13±5.82 | 3.09±0.86 |
| 170°C 120 min | 373.38±76.83 | 24.15±7.90 | 3.73±1.00 |
| 200°C 5 min | 348.33±68.37 | 24.29±8.92 | 3.62±0.86 |
| 200°C 15 min | 325.10±84.43 | 20.00±7.63 | 3.05±0.95 |
| 200°C 30 min | 304.90±60.72 | 19.52±6.10 | 3.01±0.69 |
| 200°C 45 min | 312.90±61.00 | 16.31±3.53 | 3.08±1.10 |
| 200°C 60 min | 304.53±83.59 | 18.50±5.16 | 3.49±0.85 |

### 4.1.2 Morphological properties

SEM micrographs of surface and cross section of the untreated and 150°C treated sisal fibers with various heat treatment times are shown in Figure 4.4-4.5. After the heat treatment, the surfaces of the treated fibers were cleaner and smoother than that of untreated fiber as shown in Figure 4.4 due to the removal of binding materials e.g., wax, hemicelluloses, and lignin. With increasing treatment time, the surface of the fiber appeared rougher due to more removal of binding materials. This resulted in splitting of fiber bundle.

Figure 4.5 shows SEM micrographs of cross section of untreated and heat treated sisal fibers at 150°C. The shapes of fiber cell of the heat treated fiber were obviously changed. With increasing the treatment time, the size of lumens was transformed from circular shape to oval and emaciated shape. This was due to removal of some free water in lumen of the fiber cell (Tatsuko and Hyoe, 2004). In addition, fiber cell wall separated from the other cell closed by due to the removal of some binding materials and by the removal of water.

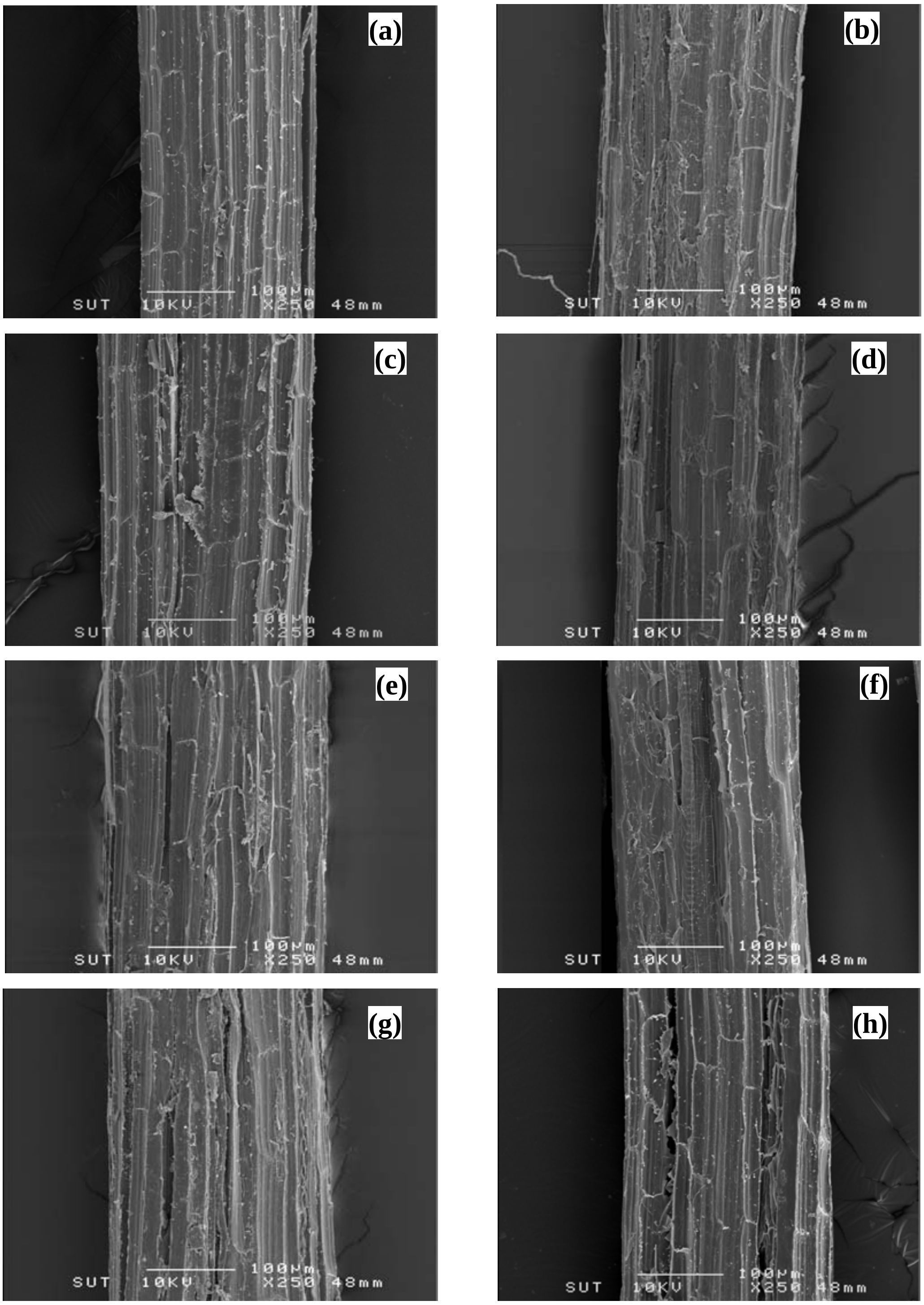


**Figure 4.4** SEM micrographs of sisal surface before (a) and after heat treatment at 150°C for (b) 10 min, (c) 15 min, (d) 30 min, (e) 45 min, (f) 60 min, (g) 90 min, and (h) 120 min.

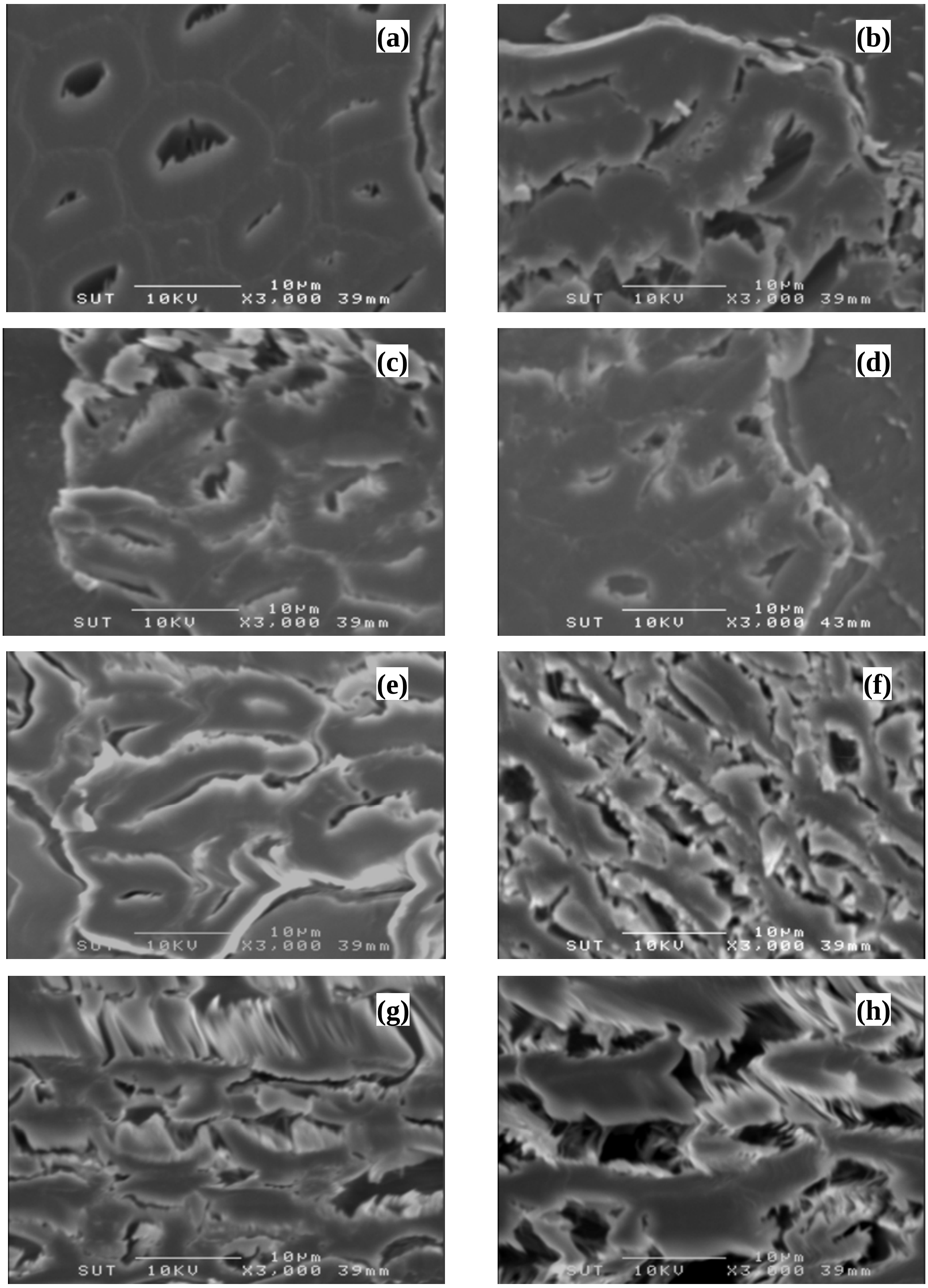


**Figure 4.5** SEM micrographs of cross section of sisal fiber before (a) and after heat treatment at 150°C for (b) 10 min, (c) 15 min, (d) 30 min, (e) 45 min, (f) 60 min, (g) 90 min, and (h) 120 min.

After the heat treatment at 170°C, the surface and cell shape of sisal fiber also changed. Fiber surface became rougher and more splitting with increasing of treatment time as shown in Figure 4.6. Increasing the treatment time resulted in more degradation of low molecular weight substances covering the fiber surface. The change in shapes of fiber cell and lumens of the heat treated fiber at 170°C also found as shown in Figure 4.7. However, when the treatment time was more than 30 min, it was obviously observed some degradation of fiber. The result correlated with a decrease in tensile strength of heat treated fiber when treatment time was more than 30 min.

Figure 4.8-4.9 show SEM micrographs of surface and cross section of untreated and heat treated sisal fibers at 200°C. The surfaces of the heat treated fibers at 200°C were cleaner and smoother than that of untreated fiber. With increasing treatment time, the surfaces of the fiber were rougher. After 5 min of treatment time, fiber cell wall obviously spitted due to more removal of binder materials. This affected a decrease of tensile strength of heat treated sisal fiber at 200°C after 5 min of treatment time.

For 30 min of treatment time, increasing treatment temperature resulted in a rapid change in splitting of fiber, size, and shape of lumen of the fiber cell as shown in Figure 4.10. This was because higher temperature led to more degradation of binder materials on fiber surface and also more removal of water from lumen and cell wall.

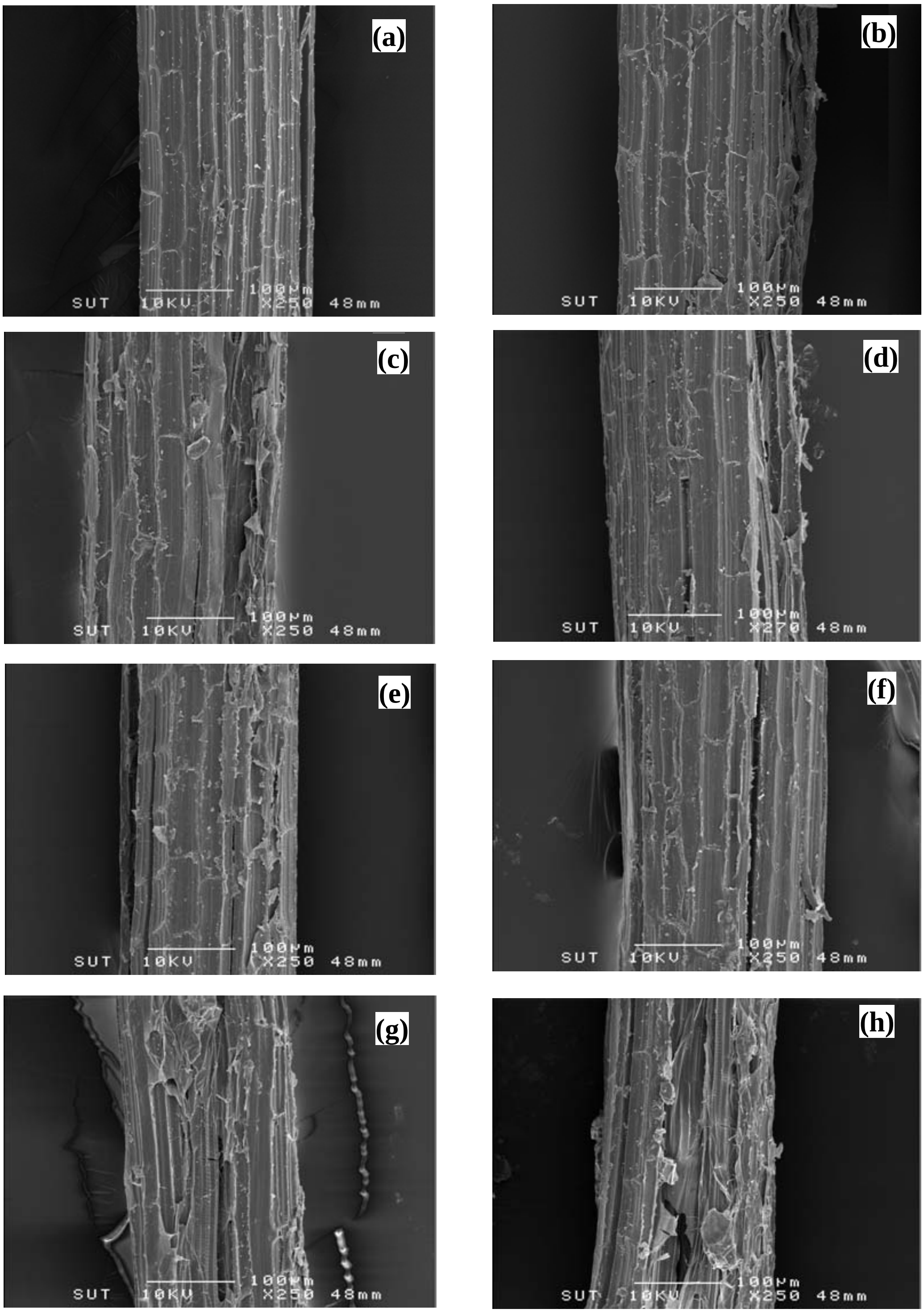


**Figure 4.6** SEM micrographs of sisal surface before (a) and after heat treatment at 170°C for (b) 5 min, (c) 15 min, (d) 30 min, (e) 45 min, (f) 60 min, (g) 90 min, and (h) 120 min.

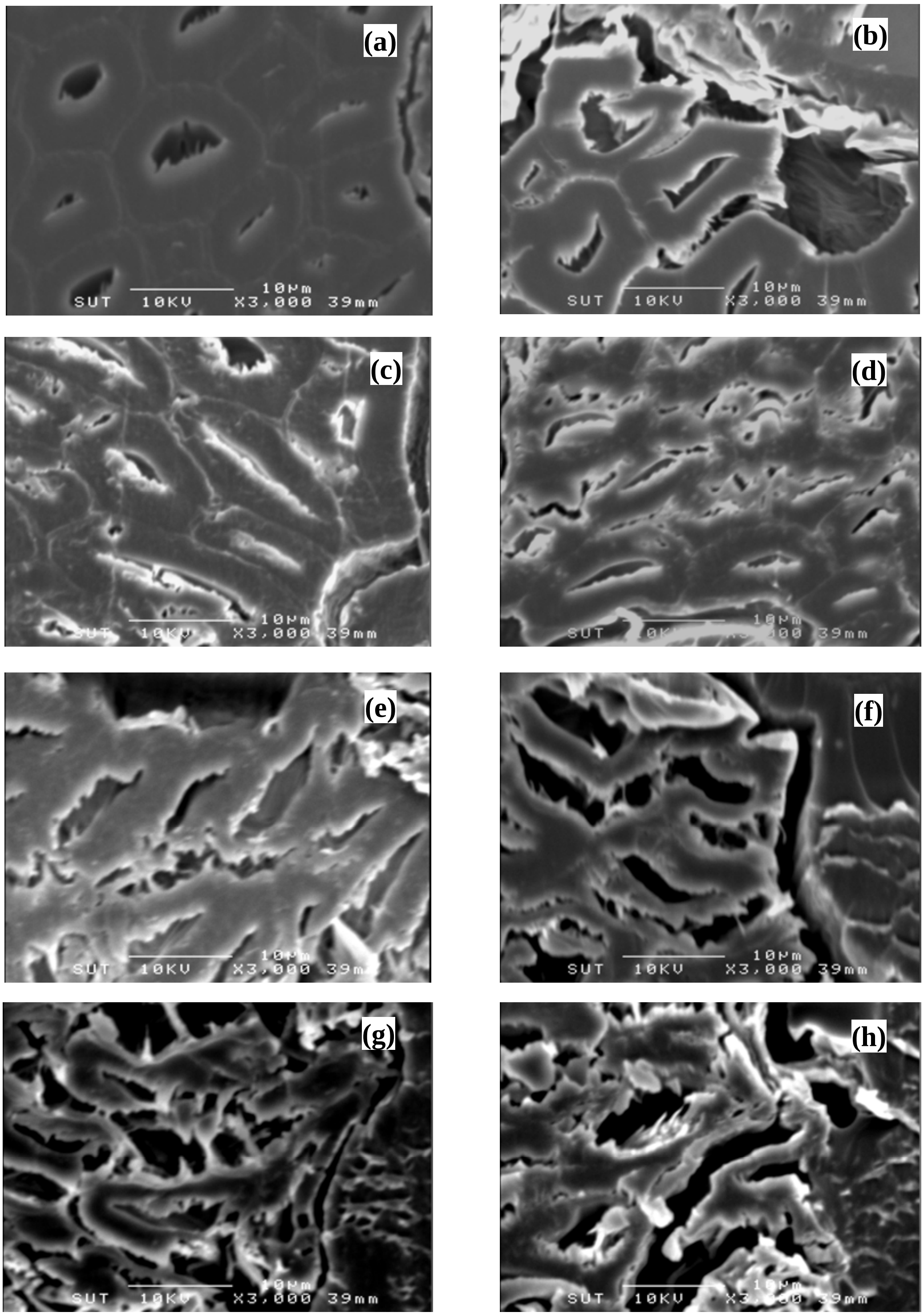


**Figure 4.7** SEM micrographs of cross section of sisal fiber before (a) and after heat treatment at 170°C for (b) 10 min, (c) 15 min, (d) 30 min, (e) 45 min, (f) 60 min, (g) 90 min, and (h) 120 min.

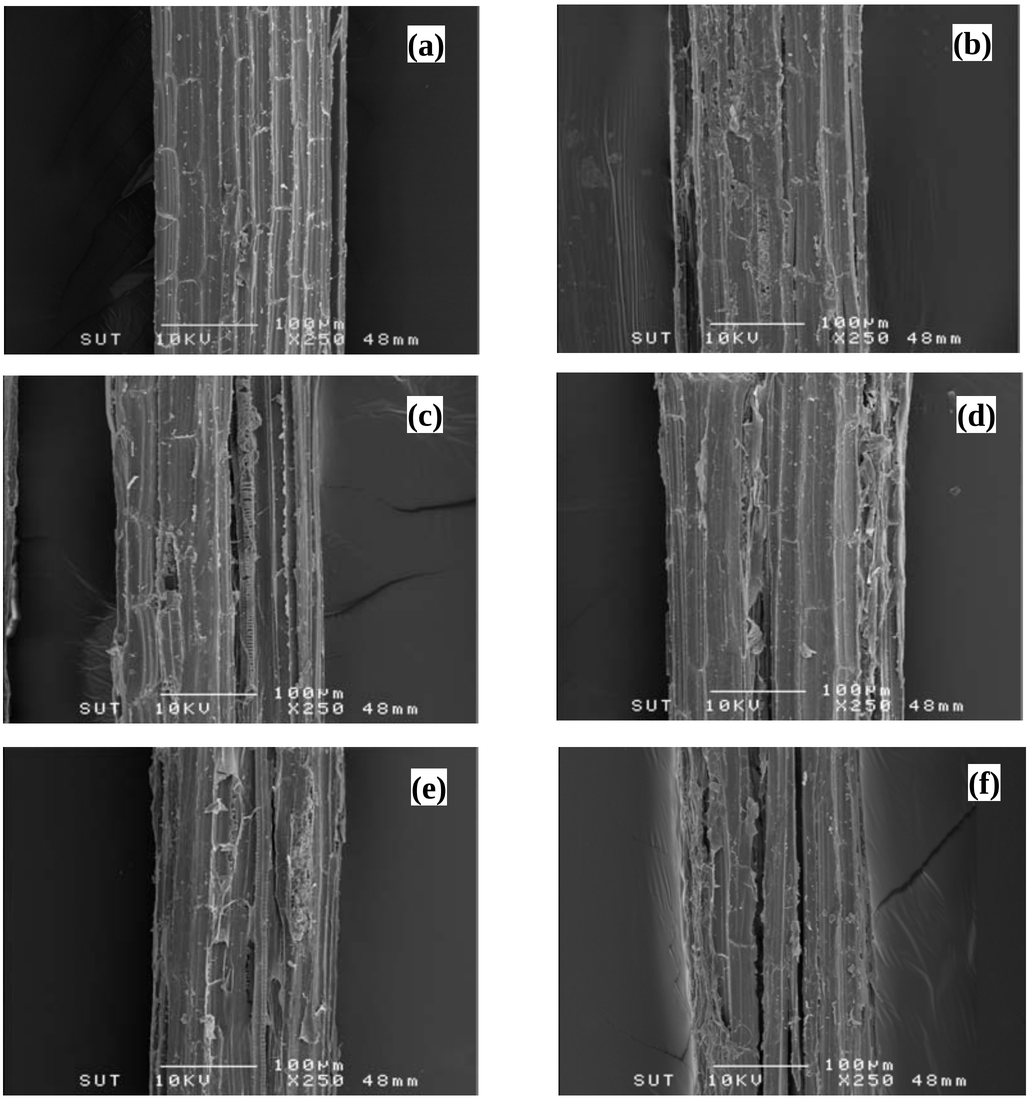


**Figure 4.8** SEM micrographs of sisal surface before (a) and after heat treatment at 200°C for (b) 5 min, (c) 15 min, (d) 30 min, (e) 45 min, and (f) 60 min.

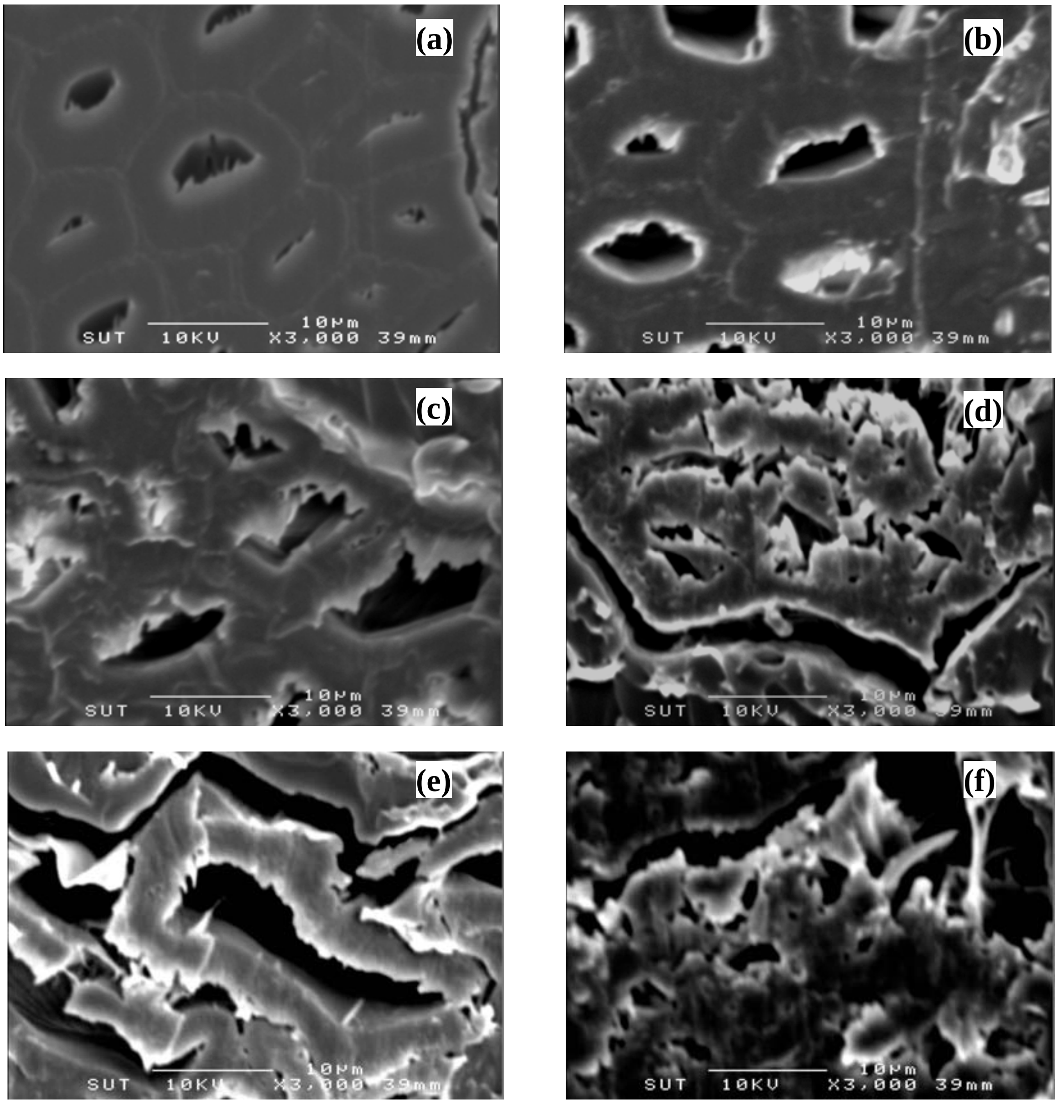


**Figure 4.9** SEM micrographs of cross section of sisal fiber before (a) and after heat treatment at 200°C for (b) 5 min, (c) 15 min, (d) 30 min, (e) 45 min, and (f) 60 min.

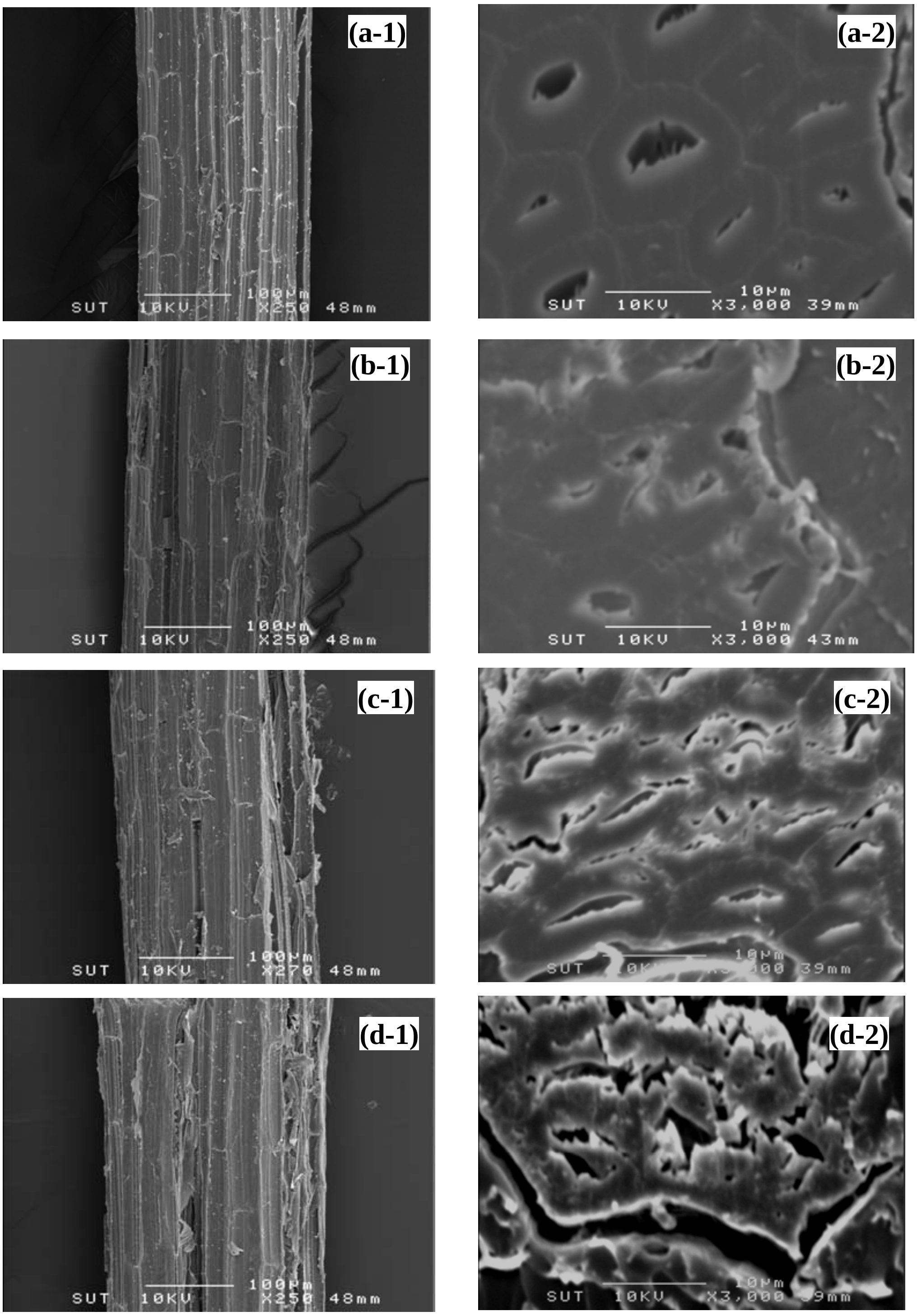


**Figure 4.10** SEM micrographs of surface (1) and cross section (2) of sisal fiber before (a) and after heat treatment at 150°C for 30 min (b), 170°C for 30 min (c), and 200°C for 30 min (d).

### 4.1.3 Thermal properties

TGA and DTG curves of untreated sisal fiber are shown in Figure 4.11. The first transition around 80°C corresponded to the evaporation of moisture. The second transition, observed as a shoulder peak with an onset about 160°C, was caused by the decomposition of low molecular weight compositions, e.g., wax. The third transition at 304°C was the decomposition of hemicelluloses. The forth transition at 361°C was derived from the decomposition of α-cellulose. Choobuatong, N., Meksut, L., and Koochontara, P. (2007) reported that hemicellulose, cellulose, and lignin decomposed in a range of 227-377°C, 277-427°C, and 227-527°C respectively.

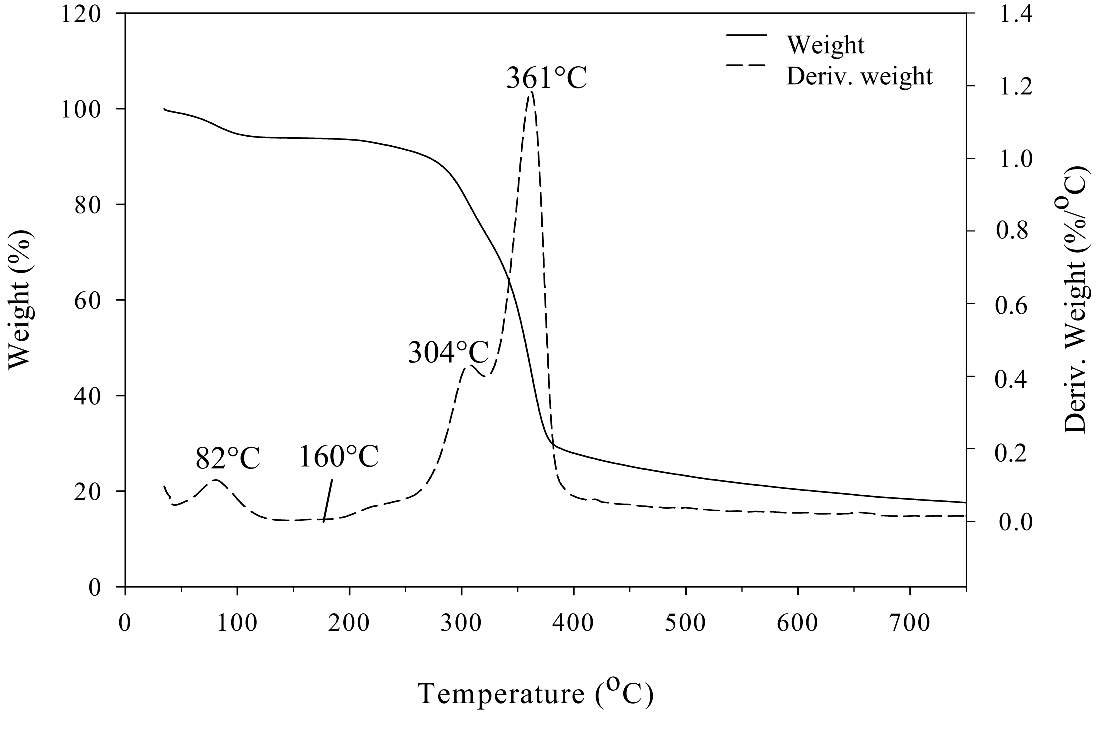


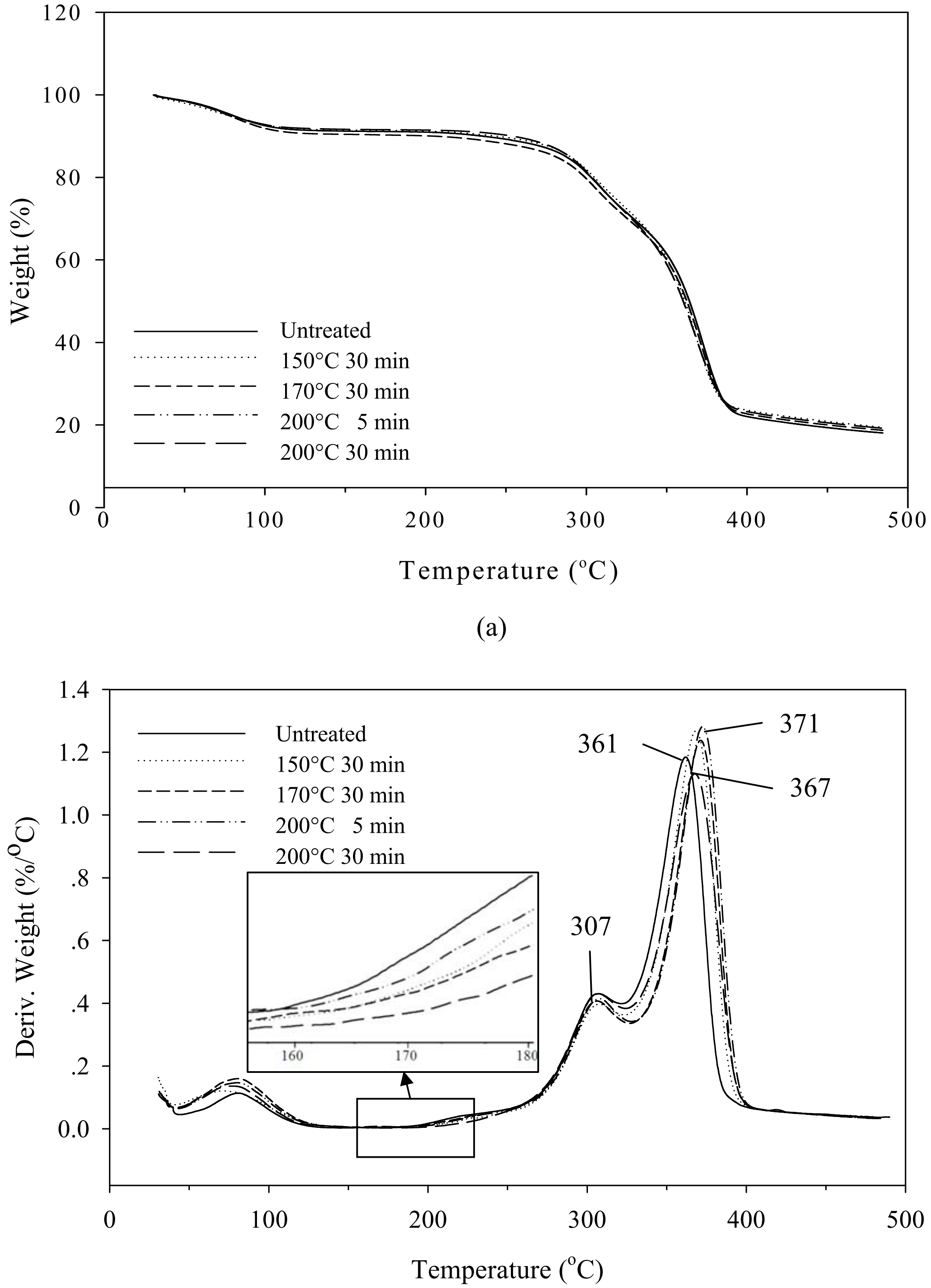
**Figure 4.11** TGA and DTG thermograms of untreated sisal fiber.

TGA and DTGA curves of untreated and heat treated sisal fibers are illustrated in Figure 4.12. All TGA curves showed the first transition around 100°C corresponded to the moisture evaporation. It can be seen that weight loss of the first transition of heat treated fiber decreased when compared to untreated fiber. This indicated that heat treatment process removed 1-2 wt% water in the fiber as numbered in Table 4.2. Katsuya, Tetsuya, and Satoru (2008) also found that water content of heat treated sitka spruce wood was decreased by heat treatment at 140°C.

The treatment at 150°C was the temperature closed to the onset temperature at which low molecular weight compositions would be decomposed. On the other hand, the treatments at 170 and 200°C were the temperature higher than that onset temperature. It was found that this decomposition, the second transition, of the treated fiber shifted to higher temperature. This indicated that treating sisal fiber at 150, 170, and 200°C caused the removal of low molecular weight components resulting in an improvement of thermal stability of the fibers. For 30 min of treatment time, increasing treatment temperature resulted in an increase of onset temperature, as shown in Table 4.2. In addition, for the treatment at 200°C, increasing treatment time resulted in higher onset temperature at which low molecular weight composition decomposed. Wielage et al. (1999) also found that increasing treatment time resulted in an increase of thermal stability of flax fiber. For the longer the period of treatment time, the more impurities and some hemicellulose covering the fiber surface were removed.

For the third transition of the sisal fibers, it was observed that the decomposition temperature of hemicellulose of heat treated sisal fibers was slightly higher than that of untreated fiber. This indicated that the heat treatment was able to remove some part of hemicelluloses having low thermal stability from the sisal fiber. Weiland and Guyonnet (2003) heated beech and maritime pine wood at 230-260°C under nitrogen atmosphere. They found that hemicellulose was removed by this treatment.

For fourth transition, the decomposition temperature of α-cellulose of heat treated fibers also shifted to higher temperature. This indicated that thermal stability of fiber was enhanced. This was because removal of low molecular weight and some of hemicellulose, having low thermal stability, improved thermal stability of α-cellulose. However, heat treated fiber at 200°C for 30 min exhibited a decrease in decomposition temperature of α-cellulose. It may be due to degradation of the fiber.



(a)

(b)

**Figure 4.12** TGA (a) and DTG (b) thermograms of untreated and heat treated sisal fibers.

**Table 4.2** Thermal degradation characteristics of untreated and heat treated sisal fibers.

| Treatment Conditions | 1st Transition | | | 2nd Transition | 3rd Transition | 4th Transition | Final Weight (%) |
|---|---|---|---|---|---|---|---|
| | Onset (°C) | Peak (°C) | Weight loss (%) | Onset (°C) | Peak (°C) | Peak (°C) | |
| Untreated | 43 | 79 | 9 | 160 | 304 | 361 | 22 |
| 150°C 30 min | 45 | 81 | 8 | 165 | 306 | 368 | 19 |
| 170°C 30 min | 46 | 82 | 7 | 167 | 307 | 371 | 18 |
| 200°C 5 min | 45 | 80 | 8 | 164 | 307 | 372 | 18 |
| 200°C 30 min | 46 | 81 | 7 | 171 | 307 | 367 | 19 |

### 4.1.4 Functional groups analysis

FTIR spectrum of the untreated sisal fiber is shown in Figure 4.13 and assigned positions for absorption bands are listed in Table 4.3. A broad absorption band in the region 3600-3100 cm$^{-1}$ corresponded to the O-H stretching vibration. The peaks at 2925 and 2854 cm$^{-1}$ were the characteristic band for the C-H stretching vibration of CH and $CH_2$ in cellulose and hemicelluloses components. The absorbance at 1743 cm$^{-1}$ belonged to the carbonyl C=O stretching vibration of carboxylic acid in lignin or ester group in hemicelluloses. The carboxylic groups may also be presented in the fiber as traces of fatty acids in wax. The absorbance at 1430 cm$^{-1}$ belonged $CH_2$ symmetric bending of cellulose. The absorbance peaks at 1384 cm$^{-1}$ and 1243 cm$^{-1}$ corresponded to the C-O stretching vibration of the acetyl group in lignin and hemicelluloses component, respectively. The peak observed at 1370 cm$^{-1}$ in the spectrum indicated the bending vibration of C-H and C-O groups of the aromatic ring in hemicellulose. The strong absorption peak at 1035 cm$^{-1}$ was ascribed to the C-O stretching which belonged to cellulose. The peak observed at 894 cm$^{-1}$ was attributed to the presence of β-glycosidic linkages between the monosaccharides (Igor, Josè, Debora, Carlo, and Fabrizio, 2010).

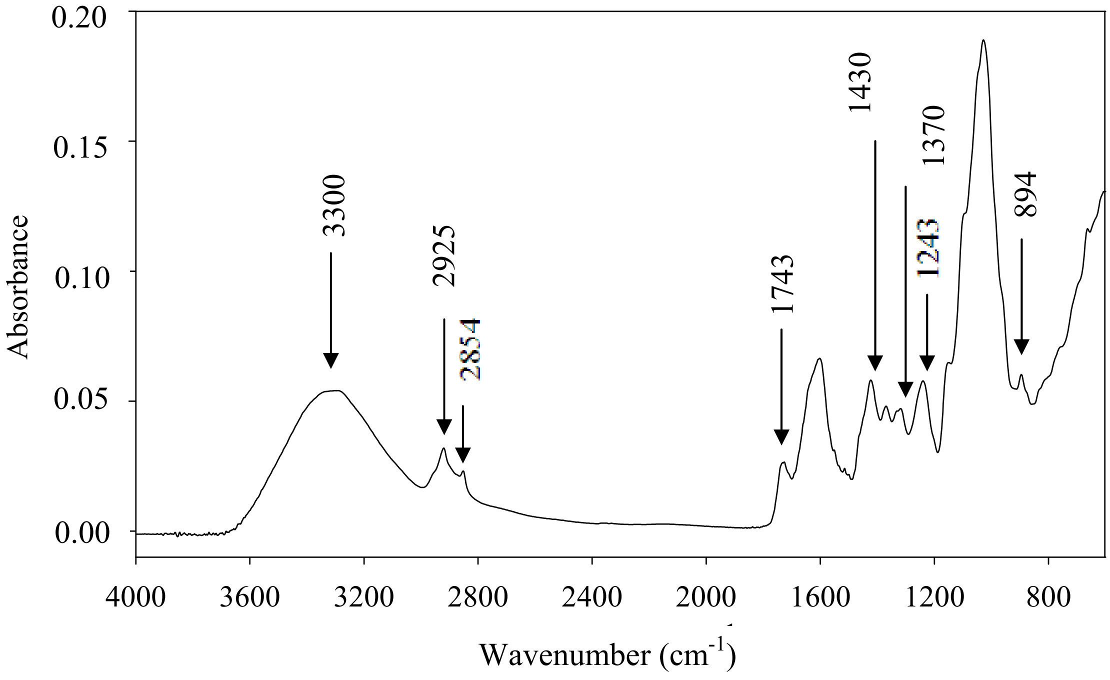


**Figure 4.13** ATR–FTIR spectrum of untreated sisal fiber.

**Table 4.3** Infrared main transitions for untreated sisal fiber (Igor, Josè, Debora, Carlo, and Fabrizio, 2010).

| **Wavenumber (cm$^{-1}$)** | **Vibration** | **Source** |
|---|---|---|
| 3300 | O-H stretching | water |
| 2925 | C-H stretching | cellulose |
| 2854 | $CH_2$ stretching | hemicelluloses |
| 1743 | C=O stretching | lignin, hemicelluloses |
| 1517 | C=C stretching | lignin |
| 1430 | $CH_2$ symmetric bending | cellulose |
| 1384-1243 | C-O stretching | lignin, hemicelluloses |
| 1370 | C-H bending | hemicellulose |
| 1243 | C-O stretching | lignin |
| 1160 | C-O-C anti-symmetrical | cellulose |
| 1035 | C-O stretching | cellulose |
| 894 | β-glycosidic linkages | polysaccharide |

FTIR spectra of untreated and heat treated sisal fibers are shown in Figure 4.14. The absorbance at 1743 $cm^{-1}$ belonged to the carbonyl C=O stretching vibration and 1384 $cm^{-1}$ corresponded to C-O stretching of lignin and hemicelluloses. Weiland and Guyonnet (2003) found that the C=O band (1743 $cm^{-1}$) of carbonyl group in hemicelluloses was decreased by the heat treatment. In addition, peak height ratio of 1430:1370:1243 changed significantly after the treatment. This ratio corresponded to the ratio between cellulose, hemicellulose, and lignin. Heat treated fibers at 150 and 170°C showed an obvious decrease in peak height ratio of these absorption bands due to removal of lignin and hemicelluloses as shown in Table 4.4. In a case of heat treated fiber at 200°C for 5 min, the peak height ratio was closed to the ratio of untreated fiber.

**Table 4.4** Peak heights ratio of 1430:1370:1243 $cm^{-1}$ of untreated and treated sisal fibers.

| **Materials** | **1430:1370:1243 $cm^{-1}$** |
|---|---|
| Untreated sisal | 1:0.123:1.886 |
| Heat treated sisal at 150°C for 30min | 1:0.062:0.584 |
| Heat treated sisal at 170°C for 30min | 1:0.029:0.311 |
| Heat treated sisal at 200°C for 5min | 1:0.138:1.487 |

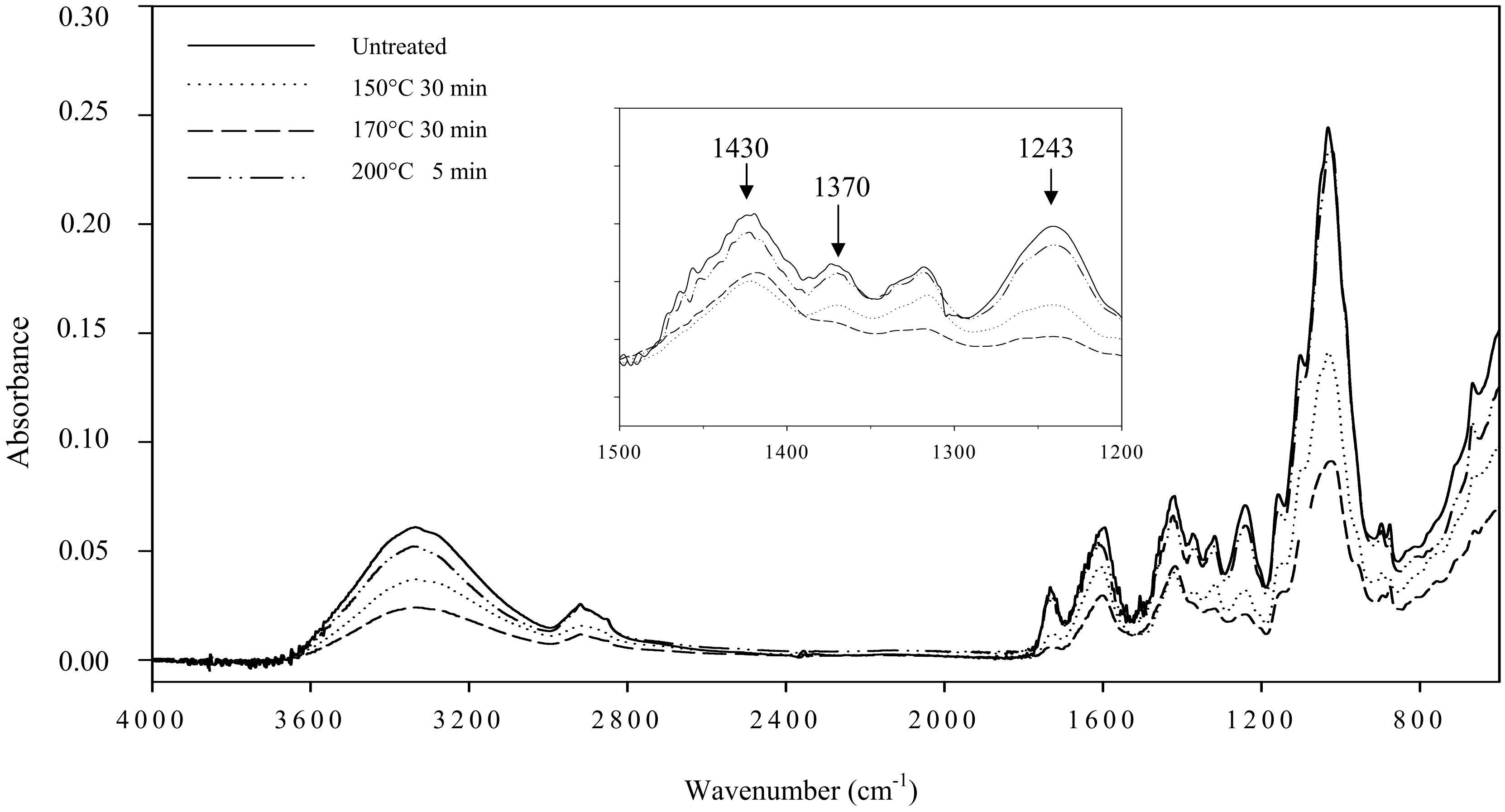


**Figure 4.14** ATR-FTIR spectra of untreated and heat treated sisal fibers

### 4.1.5 Fiber compositions

Fiber composition was obtained via detergent method. Compositions of untreated, alkali and heat treated sisal fiber are listed in Table 4.5. Hemicellulose and lignin of treated fibers were less than that of untreated fiber. During an alkali treatment, some compositions such as hemicellulose, lignin were dissolved or extracted by NaOH solution, resulting in lesser quantity of hemicellulose and lignin (Joseph, P.V., Joseph, K., and Thomas, S., 1999). Therefore, alkali treated sisal fiber had higher content of cellulose than untreated fiber. Brígidaa et al. (2010) reported that the treatment of coconut fibers with NaOCl and NaOH increased the cellulose content of the fibers. This might be explained by partial removal of hemicellulose. In cases of the heat treated fiber, heat treatment at 170°C for 30 min provided the most effective removal of hemicellulose and lignin from the sisal fiber because 170°C was the temperature higher than the onset temperature of hemicelluloses decomposition. Heat treatment of sisal fiber led to degradation of wax and some hemicellulose covering the fiber surface as mentioned in 4.1.2 (Kaewkuk, S., Sutapun, W., and Jarukumjorn, K., 2009). In a case of heat treated fiber at 200°C for 5 min, the fiber composition closed to the composition of untreated fiber. There was no significant change in cellulose content of heat treated sisal fibers.

**Table 4.5** Fiber compositions of untreated and treated sisal fibers.

| **Materials** | **Hemicelluloses (%)** | **Lignin (%)** | **Cellulose (%)** |
|---|---|---|---|
| Untreated sisal | 19.95 | 4.06 | 75.13 |
| Alkali treated sisal | 13.13 | 2.48 | 84.29 |
| Heat treated sisal at 150°C for 30min | 16.46 | 2.68 | 75.79 |
| Heat treated sisal at 170°C for 30min | 15.96 | 2.94 | 75.20 |
| Heat treated sisal at 200°C for 5min | 18.85 | 3.83 | 73.65 |

## 4.2 Effect of interfacial modifications on physical properties of sisal/PP composites

### 4.2.1 Thermal properties

TGA and DTGA thermograms of PP and sisal/PP composites with different interfacial modifications and fiber contents are shown in Figure 4.15-4.17. Decomposition temperatures of PP and cellulose of the composites are listed in Table 4.6. Normally, cellulose decomposed at about 360ºC and PP decomposed about 464°C. Addition of sisal fiber into PP matrix resulted in a slight decrease of decomposition temperature of PP. This was because thermal degradation of sisal fiber was lower than that of PP. The decomposition temperature of cellulose of alkali treated sisal/PP composite was higher than that of untreated sisal/PP composite. This was due to the fact that some components of the fiber such as hemicelluloses, which degraded at a lower temperature, were extracted out during alkali treatment (Joseph, Joseph, and Thomas, 1999). However, additional of alkali treated sisal fiber into PP matrix did not affect the decomposition temperature of PP.

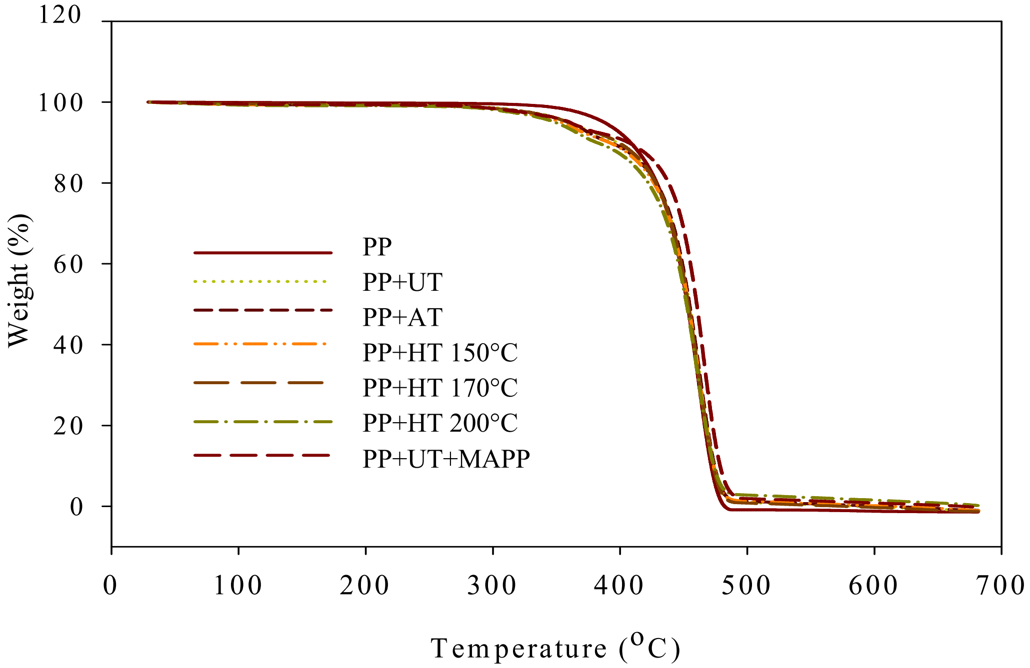
The decomposition temperature of cellulose of heat treated sisal/PP composites slightly increased when compared with untreated sisal/PP composite. This may be attributed to the removal of wax and some hemicelluloses from fiber surface as described in 4.1. Heat treatment at 150, 170, and 200°C exhibited no remarkable effect on decomposition temperature of cellulose. In addition, heat treatment process showed insignificant effect on the decomposition temperature of PP. Decomposition temperature of alkali treated cellulose was higher than that of heat treated cellulose. This was because alkalization provided more effective in removal of impurity, wax, and hemicellulose than heat treatment process.

In a case of addition of MAPP, adding the compatibilizer had a marginal effect on the decomposition temperature of cellulose and PP. Lei, Wu, Yao, and Xu (2007) prepared composites made with HDPE, pine flour and sugar cane bagasse fibers and MAPE. They also found that no significant influence of the compatibilizer was detected on the HDPE degradation. However, Araújo, Waldman, and De Paoli (2008) reported that the HDPE/curaua fibre composite compatibilized with MAPE was less stable than the composites with no compatibilization. One explanation for this fact was that the compatibilized composites presented more interfacial interaction due to reaction between acid groups of the maleic anhydride groups and hydrophilic groups on the fiber surfaces. This larger interaction promoted more interaction between the degradation processes of the two components therefore the degradation of one component may be accelerated the degradation of the other component.

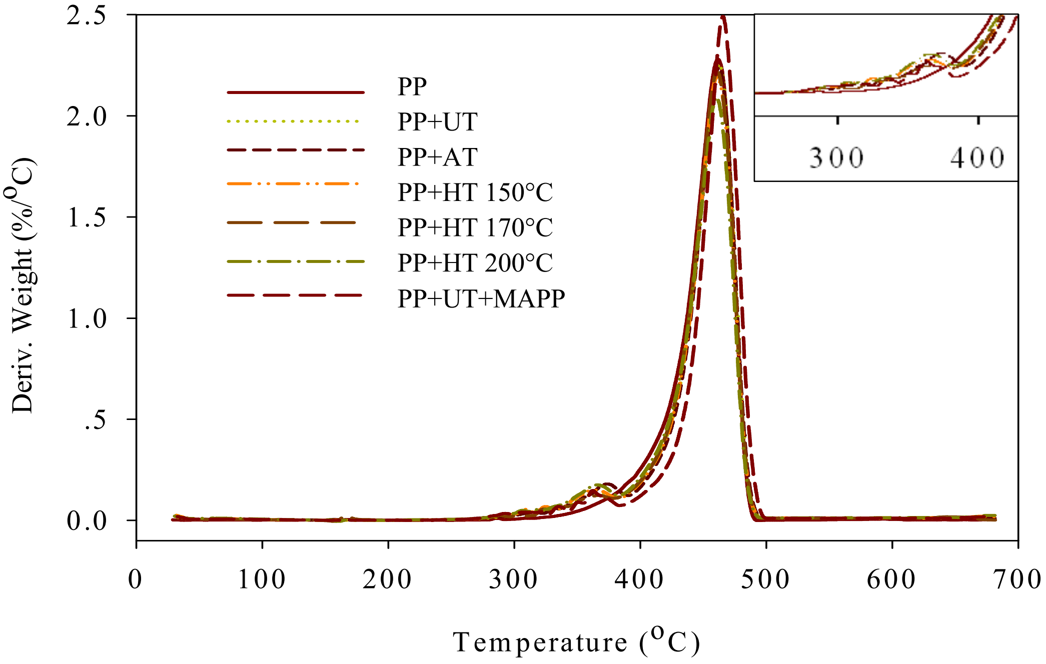
For all of the composites, increasing fiber contents led to a decrease of decomposition temperature of cellulose and insignificant change of decomposition temperature of PP. From the results, addition of alkali treated sisal fiber into PP matrix provided the highest decomposition temperature of cellulose. This was because alkalization showed more effective removal of low molecular weight component from fiber surface than heat treatment process.

**Table 4.6** Decomposition temperatures of PP and sisal/PP composites with different interfacial modifications and fiber contents.

| **Materials** | **Cellulose decomposition temperature (°C)** | | | **PP decomposition temperature (°C)** | | |
|---|---|---|---|---|---|---|
| | **Fiber content** | | | **Fiber content** | | |
| | **10 wt%** | **20 wt%** | **30 wt%** | **10 wt%** | **20 wt%** | **30 wt%** |
| PP | - | | | 464.12 | | |
| PP+UT | 363.16 | 361.97 | 359.98 | 462.12 | 462.15 | 461.27 |
| PP+AT | 374.15 | 373.89 | 371.54 | 462.47 | 462.39 | 462.32 |
| PP+HT 150°C | 365.86 | 362.71 | 360.65 | 462.41 | 462.20 | 462.34 |
| PP+HT 170°C | 366.48 | 364.48 | 362.29 | 462.40 | 462.33 | 462.40 |
| PP+HT 200°C | 364.22 | 362.06 | 360.82 | 462.32 | 462.17 | 461.90 |
| PP+UT+MAPP | 365.23 | 362.96 | 361.56 | 464.59 | 463.96 | 462.63 |

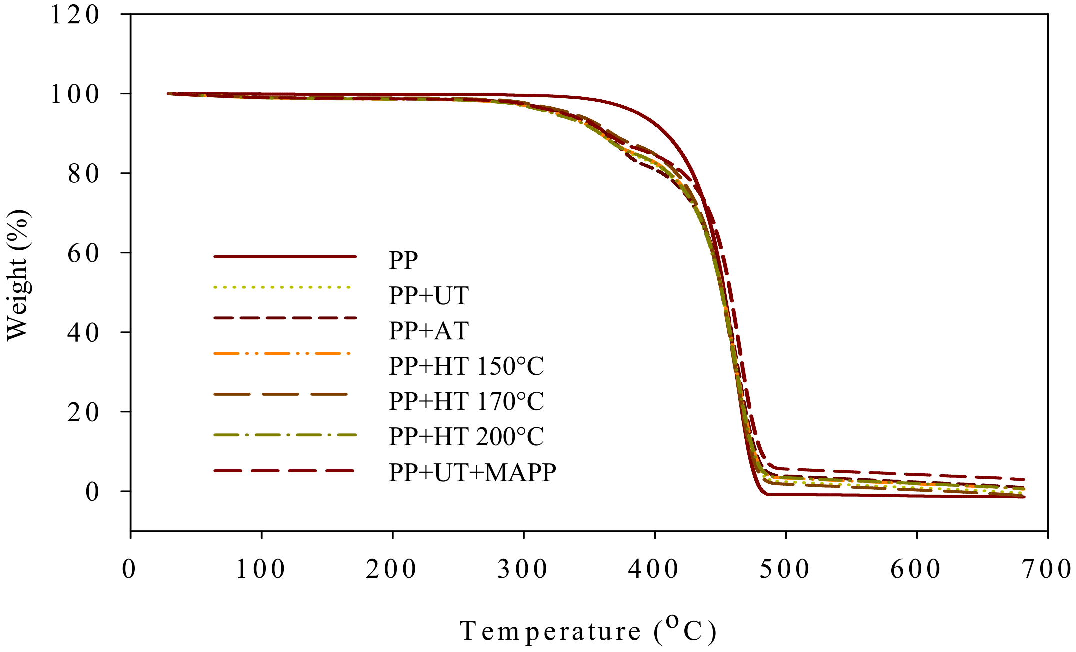


(a)

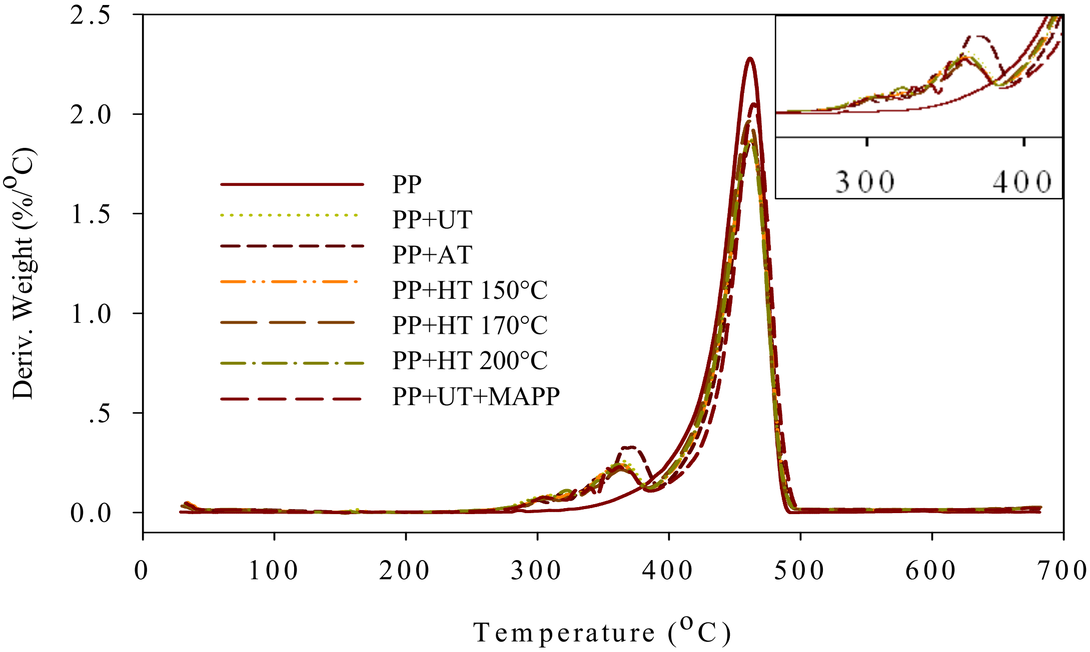


(b)

**Figure 4.15** TGA (a) and DTGA (b) thermograms of PP and 10 wt % sisal/PP composites with different interfacial modifications.

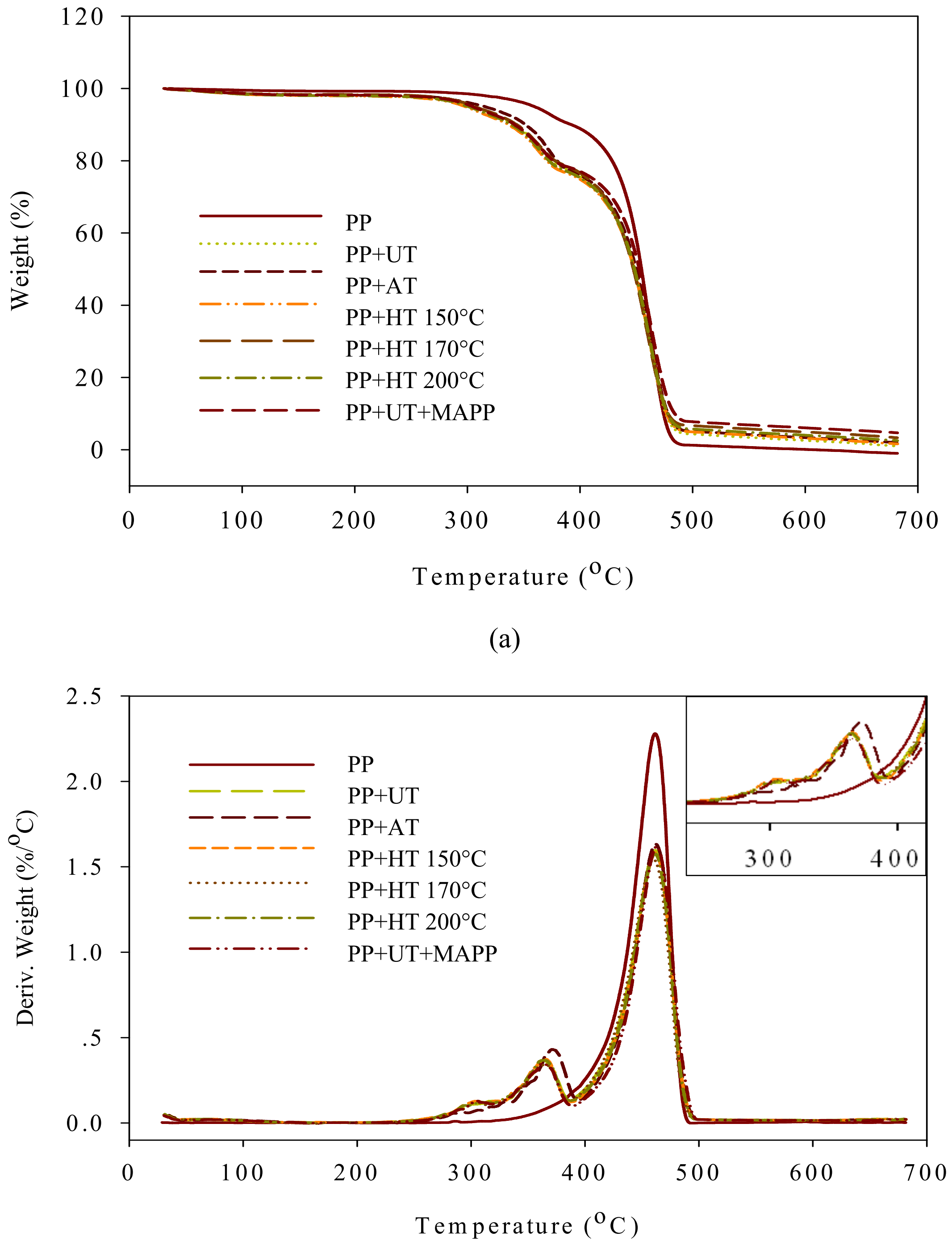


(a)



(b)

**Figure 4.16** TGA (a) and DTGA (b) thermograms of PP and 20 wt% sisal/PP composites with different interfacial modifications.



(a)

(b)

**Figure 4.17** TGA (a) and DTGA (b) thermograms of PP and 30 wt% sisal/PP composites with different interfacial modifications.

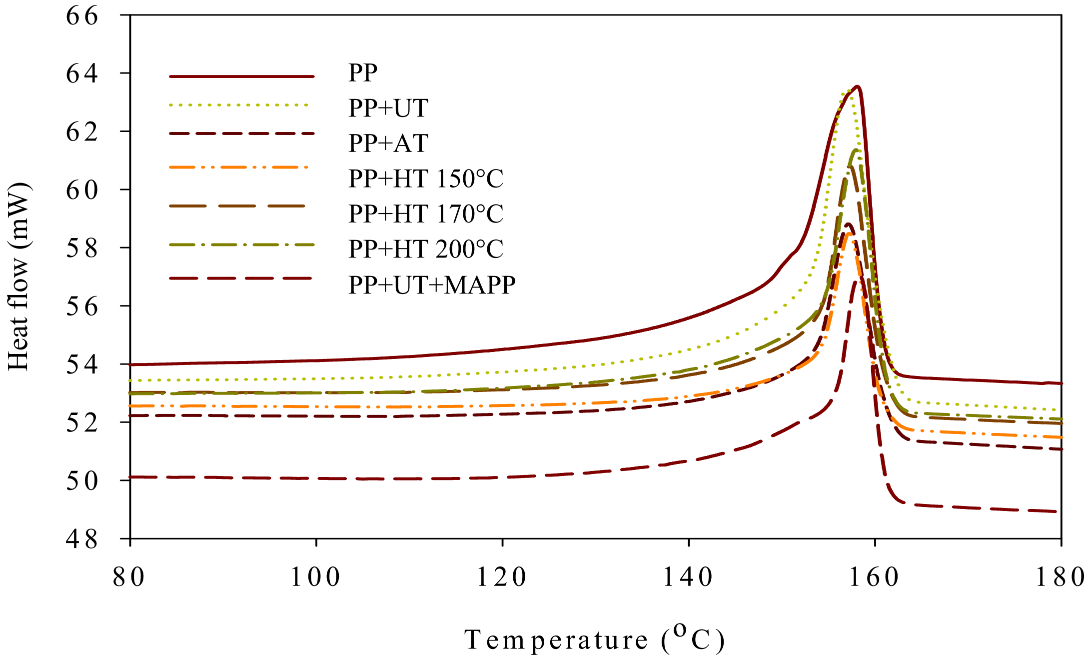
Table 4.7 and Figure 4.18-4.20 show the results from DSC analysis of PP and sisal/PP composites. Melting temperature ($T_m$) of PP did not change with the addition of the sisal fibers. Manchado et al. (2000) also reported that sisal fibers had no effect on the melting temperature of PP composites. It was clear from Table 4.7 that the fiber treatments and adding compatibilizer were only marginal effect on the melting temperature of PP. However, Joseph et al. (2003) reported that fiber surface modification by alkali treatment appreciably changed on melting temperature of PP because the compatibility between the fiber and PP matrix was increased by favoring interaction between the fiber and PP. There was no significant change in melting temperature of PP with increasing sisal fiber contents. Amash and Zugenmaier (2000) also found no significant change in melting temperature at various cellulose contents in PP composites.

Crystallization temperature ($T_c$) of PP slightly increased with adding fibers due to induced crystallization by the fibers. Amash and Zugenmaier (2000) had studied the effect of reinforcing fibers on the crystallization temperature of PP. They had found that crystallization temperature of PP increased with the addition of cellulose fibers due to cellulose fibers acting as a nucleating agent for the crystallization of PP. There was no significant difference in crystallization temperature of composites filled with untreated, alkali treated, heat treated fiber and adding MAPP. However, Joseph et al. (2003) found that the crystallization temperature of PP was further increased by the incorporation of sisal fiber treated with urethane derivative of polypropylene glycol (PPG/TDI), maleic anhydride modified polypropylene (MAPP), and $KMnO_4$ which were further favored the crystallization process. The crystallization temperature of sisal/PP composites slightly increased with increasing sisal fiber contents. This was because the fiber acted as nucleating agents for the crystallization of PP (Amash and Zugenmaier, (2000); Quillin et al., (1994)).

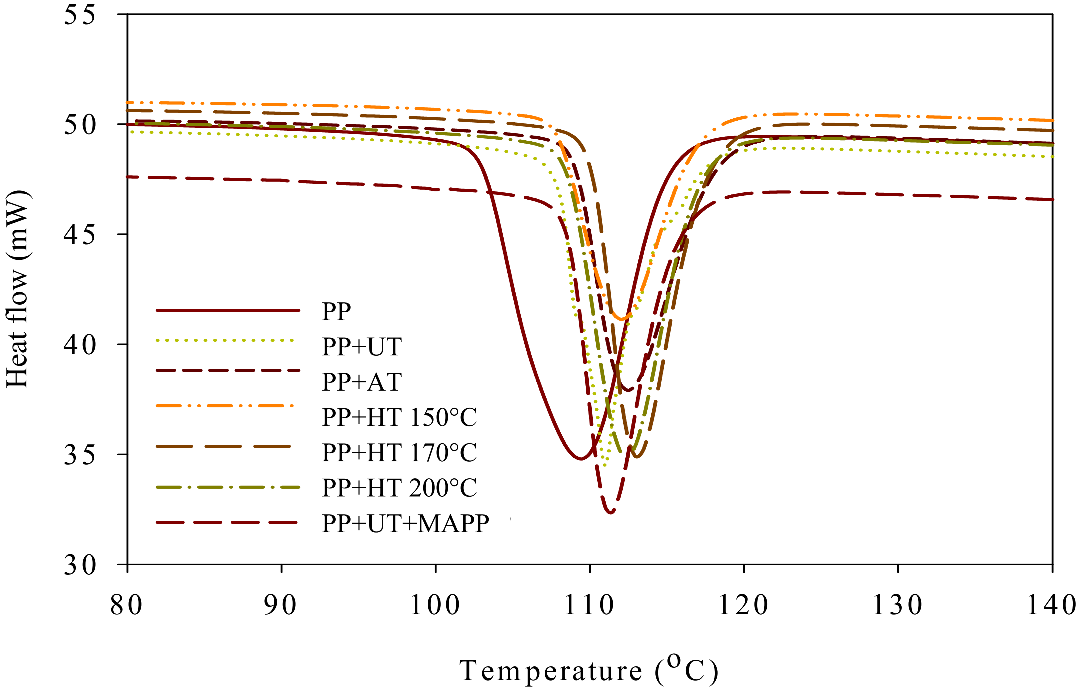
Crystallinity of PP reduced with the addition of fibers. This could be explained that the fibers restricted the molecular mobility in the melt of PP matrix after nucleation leading to the lower crystallinity (Ruksakulpiwat, Y., Suppakarn, N., Sutapun, W., and Thomthong, W., 2007). Interfacial modifications did not significantly affect crystallinity of PP. However, Joseph et al. (2003) showed that the addition of sisal fiber into PP resulted in an increase in crystallinity about 5% and crystallization temperature of the PP matrix due to the nucleating ability of sisal fiber for the crystallization of PP. Addition of toluene-2,4-diisocyanate (TDI) and $KMnO_4$ treated fiber resulted in an increase of crystallinity of PP. Crystallinity of PP also increased with increasing fiber contents.

**Table 4.7** Melting temperature, crystallization temperature, and crystallinity of PP and sisal/PP composites with different interfacial modifications and fiber contents.

| Materials | Tm (ºC) | | | Tc (ºC) | | | Crystallinity (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fiber content | | | Fiber content | | | Fiber content | | |
| | 10 wt% | 20 wt% | 30 wt% | 10 wt% | 20 wt% | 30 wt% | 10 wt% | 20 wt% | 30 wt% |
| PP | 158.0 | | | 109.5 | | | 50.95 | | |
| PP+UT | 157.0 | 157.5 | 157.5 | 111.0 | 112.5 | 113.0 | 36.85 | 38.79 | 40.70 |
| PP+AT | 157.0 | 157.6 | 157.5 | 112.5 | 112.5 | 113.5 | 39.85 | 40.78 | 42.63 |
| PP+HT 150°C | 157.0 | 157.5 | 157.0 | 112.0 | 113.0 | 113.5 | 38.15 | 40.41 | 43.30 |
| PP+HT 170°C | 157.5 | 158.5 | 158.0 | 113.0 | 113.0 | 113.5 | 38.30 | 39.56 | 42.17 |
| PP+HT 200°C | 158.0 | 159.0 | 158.0 | 112.0 | 113.0 | 113.5 | 36.76 | 39.63 | 41.14 |
| PP+UT+MAPP | 158.5 | 159.0 | 158.5 | 111.5 | 112.0 | 113.5 | 37.24 | 39.22 | 42.98 |



(a)



(b)

**Figure 4.18** DSC thermograms of PP and 10 wt% sisal/PP composites with different interfacial modifications (a) heating scan and (b) cooling scan.

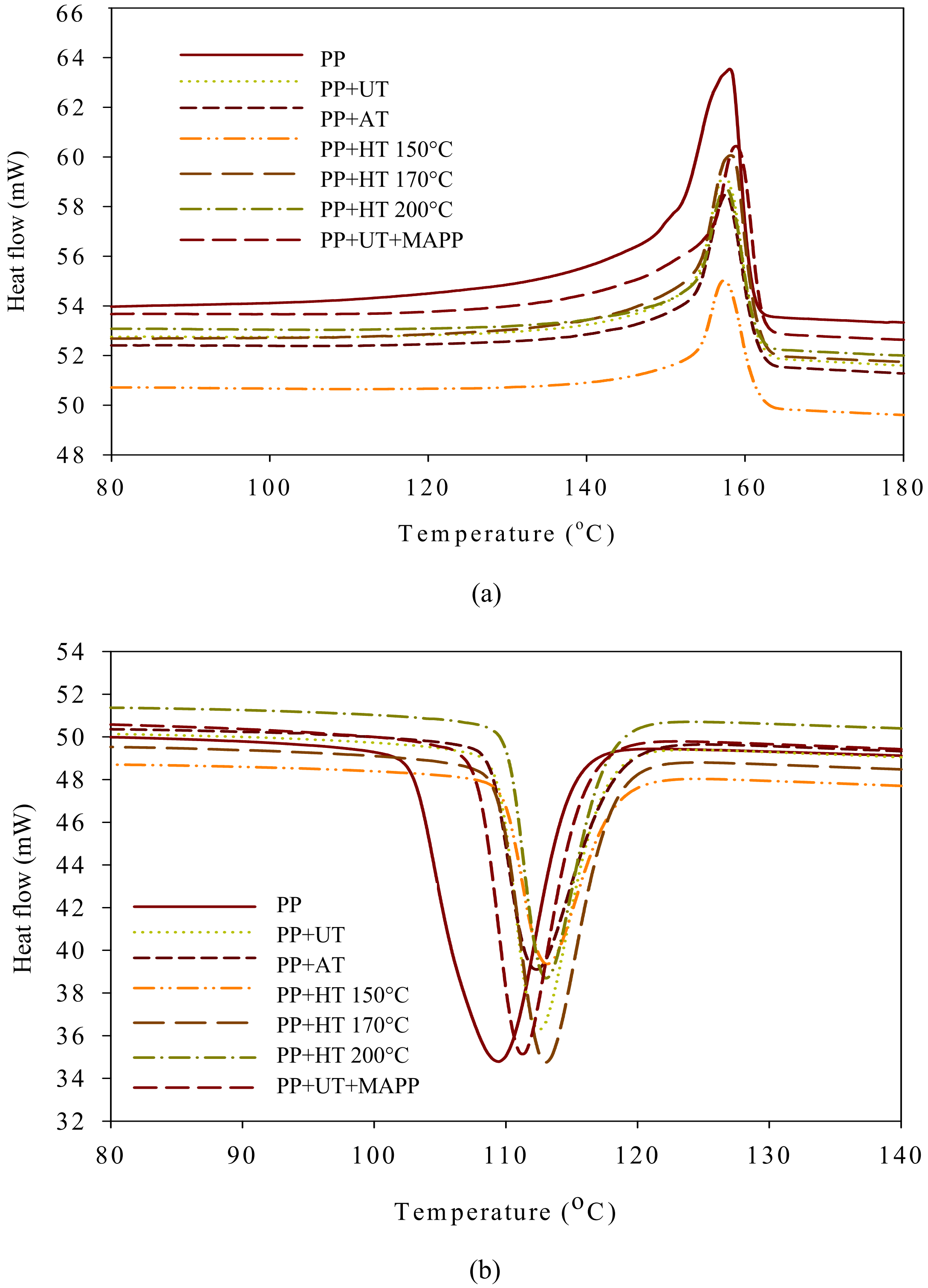
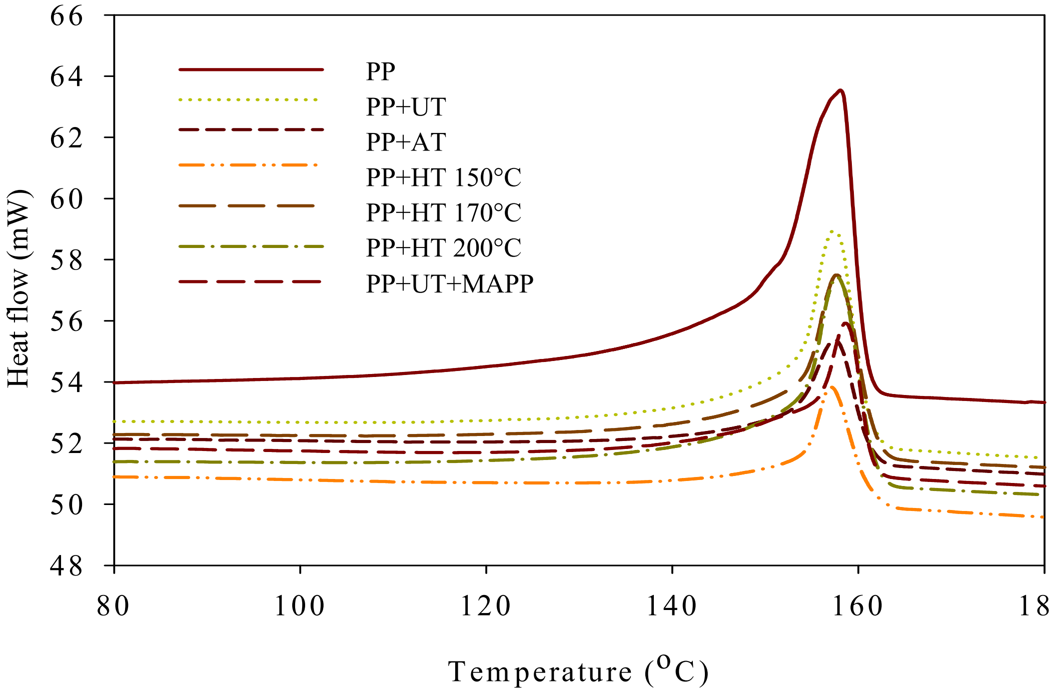
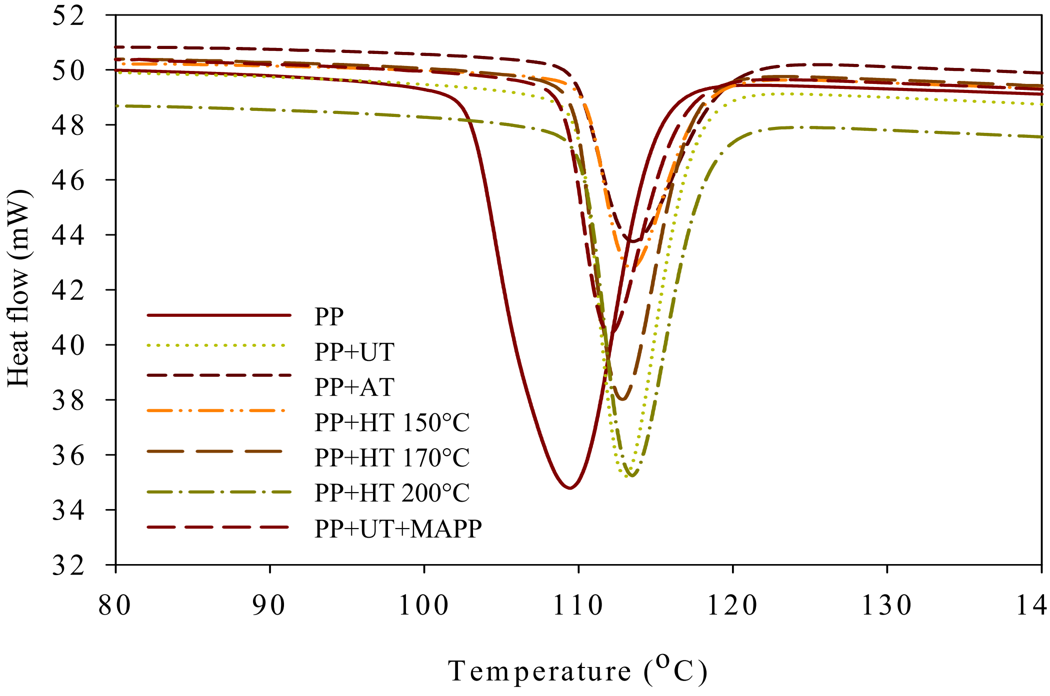


**Figure 4.19** DSC thermograms of PP and 20 wt% sisal/PP composites with different interfacial modifications (a) heating scan and (b) cooling scan.



(a)



(b)

**Figure 4.20** DSC thermograms of PP and 30 wt% sisal/PP composites with different interfacial modifications (a) heating scan and (b) cooling scan.

Table 4.8 shows HDT of PP and sisal/PP composites. HDT of PP increased with adding fibers. As expected, the presence of fiber substantially improved the HDT of PP. With increasing fiber content, HDT of the composites increased. However, the fiber treatments and adding compatibilizer showed no significant difference on HDT of the composites.

**Table 4.8** Heat distortion temperature (HDT) of PP and sisal/PP composites with different interfacial modifications and fiber contents.

| **Materials** | **HDT (°C)** | | |
|---|---|---|---|
| | **Fiber content** | | |
| | **10 wt%** | **20 wt%** | **30 wt%** |
| PP | 82.2±1.0 | | |
| PP+UT | 114.2±0.3 | 123.5±0.7 | 133.5±0.7 |
| PP+AT | 113.7±1.0 | 122.5±0.7 | 134.5±0.7 |
| PP+HT 150°C | 113.5±0.7 | 122.0±0.7 | 135.0±0.7 |
| PP+HT 170°C | 114.0±0.7 | 123.7±0.3 | 134.0±1.4 |
| PP+HT 200°C | 112.7±1.0 | 124.7±0.3 | 134.7±0.3 |
| PP+UT+MAPP | 114.5±0.3 | 124.5±0.7 | 134.5±0.7 |

### 4.2.2 Rheological properties

Melt flow index (MFI) of PP and sisal/PP composites are listed in Table 4.9. MFI of PP decreased with adding fibers. Sisal/PP composites exhibited higher viscosity than PP as shown in Figure 4.21-4.23. In addition, the viscosity of the composites increased with increasing fiber content. This was because the fibers perturbed the flow of polymer and hindered the mobility of chain segments in melt flow. However, the fiber treatments and adding compatibilizer showed no significant effect on MFI and viscosity of the composites. Schemenauer, Osswald, Sanadi, and

Caulfield (2000) also found that the fiber treatments showed insignificant effect on viscosity of jute fiber/polypropylene composites. However, Fung, Li, and Tjong (2002) studied the effect of MAPP on the rheological properties of sisal fiber/polypropylene composites. The results showed that the viscosity of the MAPP modified sisal fiber/PP composites was higher when compared with fiber/PP composites.

**Table 4.9** Melt flow index of PP and PP/sisal composites with different interfacial modifications and fiber contents.

| **Materials** | **MFI (g/10min)** | | |
|---|---|---|---|
| | **Fiber content** | | |
| | **10 wt%** | **20 wt%** | **30 wt%** |
| PP | 3.277±0.0065 | | |
| PP+UT | 2.193±0.0025 | 1.313±0.0029 | 0.283±0.0003 |
| PP+AT | 2.442±0.0011 | 1.251±0.0062 | 0.353±0.0004 |
| PP+HT 150°C | 2.240±0.0108 | 1.027±0.0028 | 0.365±0.0071 |
| PP+HT 170°C | 2.511±0.0079 | 1.261±0.0077 | 0.410±0.0134 |
| PP+HT 200°C | 2.416±0.0040 | 1.212±0.0080 | 0.312±0.0049 |
| PP+UT+MAPP | 1.952±0.0069 | 0.992±0.0056 | 0.474±0.0029 |

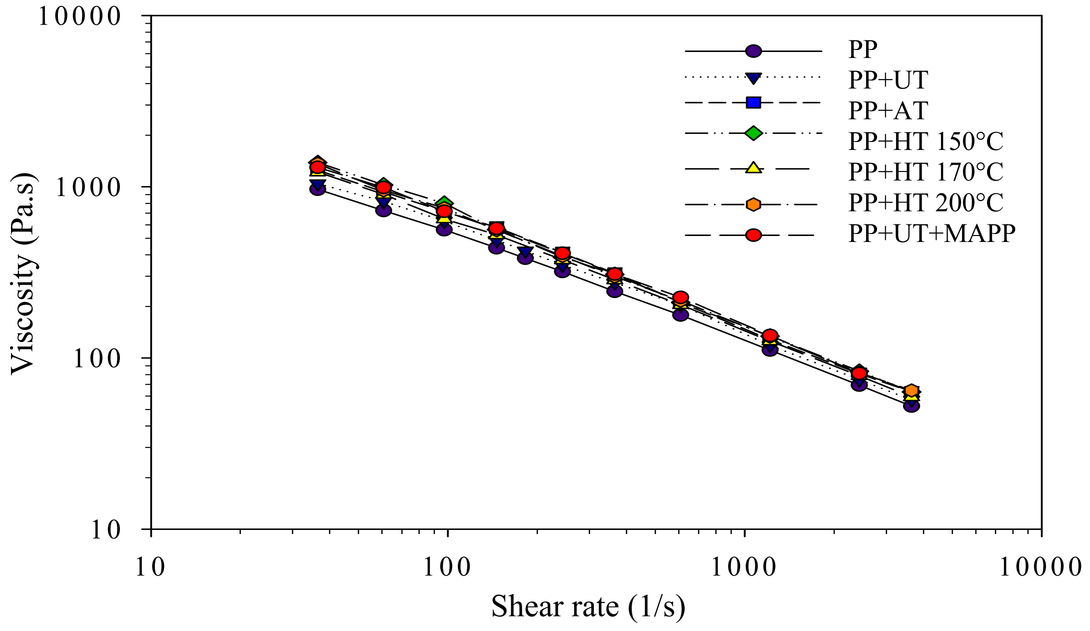


**Figure 4.21** Viscosity at various shear rates of PP and 10 wt% sisal/PP composites with different interfacial modifications.

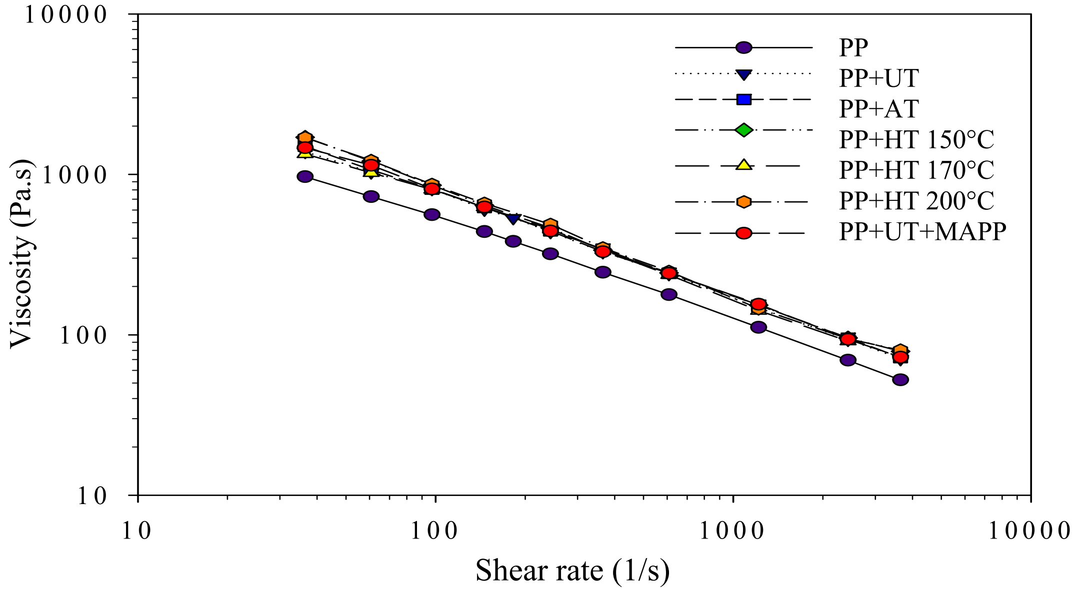


**Figure 4.22** Viscosity at various shear rates of PP and 20 wt% sisal/PP composites with different interfacial modifications.

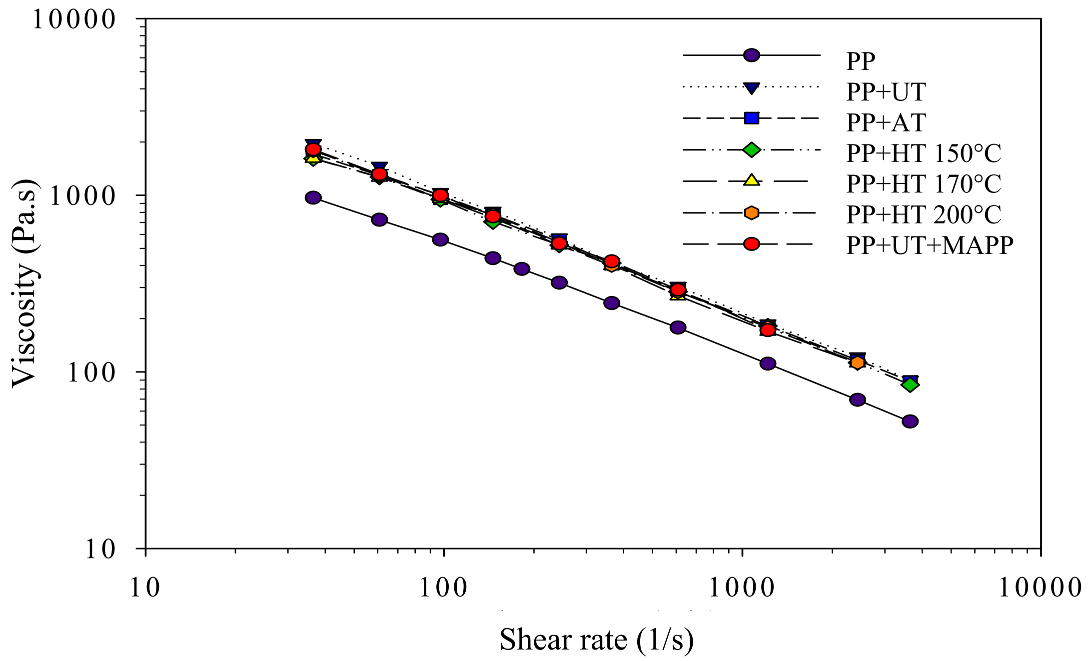


**Figure 4.23** Viscosity at various shear rates of PP and 30 wt% sisal/PP composites with different interfacial modifications.

### 4.2.3 Mechanical properties

#### 4.2.3.1 Tensile properties

Tensile strength, Young's modulus, and elongation at break of PP and sisal/PP composites with different interfacial modifications and fiber contents are shown in Table 4.10. PP was not broken under the testing condition. With incorporating fiber into PP, tensile strength and Young's modulus increased but elongation at break decreased as shown in Figure 4.25-4.27, respectively. This was because tensile strength and Young's modulus of sisal fiber were higher than that of PP (Joseph, Joseph, and Thomas, (1999) and Wambua, Iens, and Verpoest, (2003)). Fung, Li, and Tjong (2002) also observed a decrease in elongation at break and increase in tensile strength and Young's modulus of sisal/PP composites with the addition of the fiber.

Tensile strength, Young's modulus, and elongation at break of alkali treated sisal/PP composites were slightly higher than that of untreated sisal/PP composite. Since, alkalization removed wax, impurity, and some hemicellulose from fiber surface leading to increase the surface area thereby improved the fiber-matrix interfacial adhesion. Joseph, Thomas, and Pavithran (1996) reported that the alkali treated sisal/LDPE composites showed superior tensile properties than untreated composites. This was because alkali treatment improved the fiber surface adhesive characteristics by removal of impurity and some hemicellulose on fiber surface, thereby producing a rough surface topography. In addition, alkali treatment led to fiber fibrillation such as breaking down of the fiber bundle into smaller fibers. This increased the effective surface area available for contacting with the matrix. In other words, alkali treatment reduced fiber diameter and increased the aspect ratio. Therefore, the development of a rough surface topography and enhancement in aspect ratio offered better fiber-matrix interface adhesion and an increase in mechanical properties.

In cases of heat treated sisal/PP composites, PP was filled with sisal fiber treated at different temperature, i.e. 150°C, 170°C, and 200°C. There was no significant difference in the tensile strength, Young's modulus, and elongation at break of heat treated sisal/PP composites. However, the tensile properties of heat treated sisal fiber/PP composites were higher than that of untreated sisal fiber/PP composites. It might be due to removal of some hemicelluloses and impurities on fiber surface. This led to an enhancement in fiber-matrix interfacial adhesion between fiber and matrix. Robin and Breton (2001) also found that mechanical properties of heat treated wood fiber/HDPE composites were better than of non treated wood fiber/HDPE composites due to more compatible between wood fiber and polyethylene matrix.

An increase in tensile strength was observed when MAPP was added into the sisal/PP composites as shown in Figure 4.25. This was attributed to an improvement of surface adhesion between non-polar PP and polar sisal fibers through the linkage between the hydrophilic hydroxyl groups of fibers and the carboxyl groups of the compatibilizer (Rana et al., 1998). Figure 4.24 shows a hypothetical model of hydroxyl groups of fibers and MAPP at the interface. Both chemical (ester bond) and physical interaction (hydrogen bond) should be formed between the fibers and the compatibilizer. PP chain of MAPP diffused into the PP matrix to form the physical interaction (entanglement) (Doan et al., 2005). However, with adding MAPP into sisal/PP composites, there was no significant difference of Young’s modulus and elongation at break of the composites.

Tensile strength and Young’s modulus of sisal/PP composites slightly increased with increasing fiber content while elongation at break decreased as shown in Figure 4.25-4.27 respectively. Joseph et al. (1996) reported that with increasing fiber content, tensile strength of sisal/PP composites increased while elongation at break decreased. This was attributed to difficult slippage of fiber from PP matrix when the fiber content was increased.

From the tensile properties of the sisal/PP composites, MAPP improved the interfacial adhesion of sisal fiber/PP composites more effectively than alkali treatment and heat treatment did.

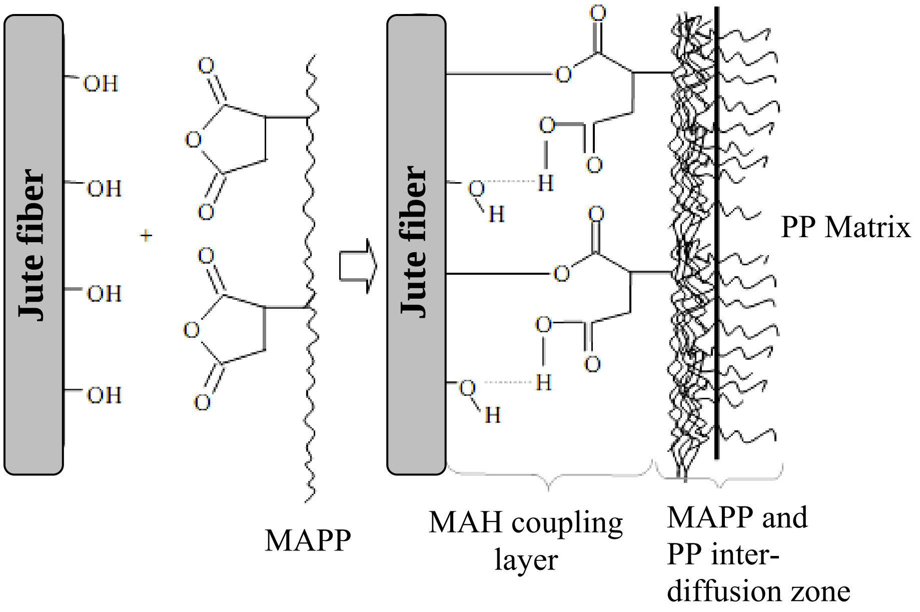


**Figure 4.24** Hypothetical structure of maleic anhydride graft polypropylene (MAHgPP or MAPP) and jute fibers at the interface (Doan et al., 2005).

**Table 4.10** Tensile strength, Young's modulus, and elongation at break of PP and sisal/PP composites with different interfacial modifications and fiber contents.

| **Materials** | **Tensile strength (MPa)** | | | **Young's modulus (GPa)** | | | **Elongation at break (%)** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Fiber content** | | | **Fiber content** | | | **Fiber content** | | |
| | **10 wt%** | **20 wt%** | **30 wt%** | **10 wt%** | **20 wt%** | **30 wt%** | **10 wt%** | **20 wt%** | **30 wt%** |
| PP | NB | | | 0.51±0.01 | | | NB | | |
| PP+UT | 22.62±1.09 | 24.44±0.49 | 25.23±0.45 | 0.70±0.02 | 0.87±0.03 | 0.91±0.03 | 12.50±1.39 | 10.48±0.81 | 6.85±0.65 |
| PP+AT | 24.32±0.51 | 25.37±0.55 | 25.93±0.32 | 0.68±0.04 | 0.85±0.04 | 0.97±0.06 | 14.55±1.85 | 12.35±0.67 | 9.36±0.94 |
| PP+HT 150°C | 24.48±0.46 | 25.14±0.45 | 26.54±0.64 | 0.72±0.03 | 0.85±0.04 | 1.05±0.12 | 14.87±1.70 | 12.11±0.76 | 8.72±0.59 |
| PP+HT 170°C | 24.71±0.59 | 25.51±0.83 | 26.61±0.68 | 0.74±0.02 | 0.93±0.03 | 1.06±0.08 | 15.82±1.91 | 12.10±0.89 | 8.24±1.33 |
| PP+HT 200°C | 23.67±1.13 | 24.43±0.52 | 25.67±0.77 | 0.71±0.02 | 0.87±0.04 | 0.92±0.03 | 13.98±1.71 | 12.46±1.22 | 8.80±1.12 |
| PP+UT+MAPP | 26.99±0.40 | 27.48±0.33 | 28.00±0.50 | 0.73±0.01 | 0.91±0.03 | 1.30±0.12 | 16.60±2.19 | 12.17±0.58 | 8.82±0.57 |

Note: NB = not broken

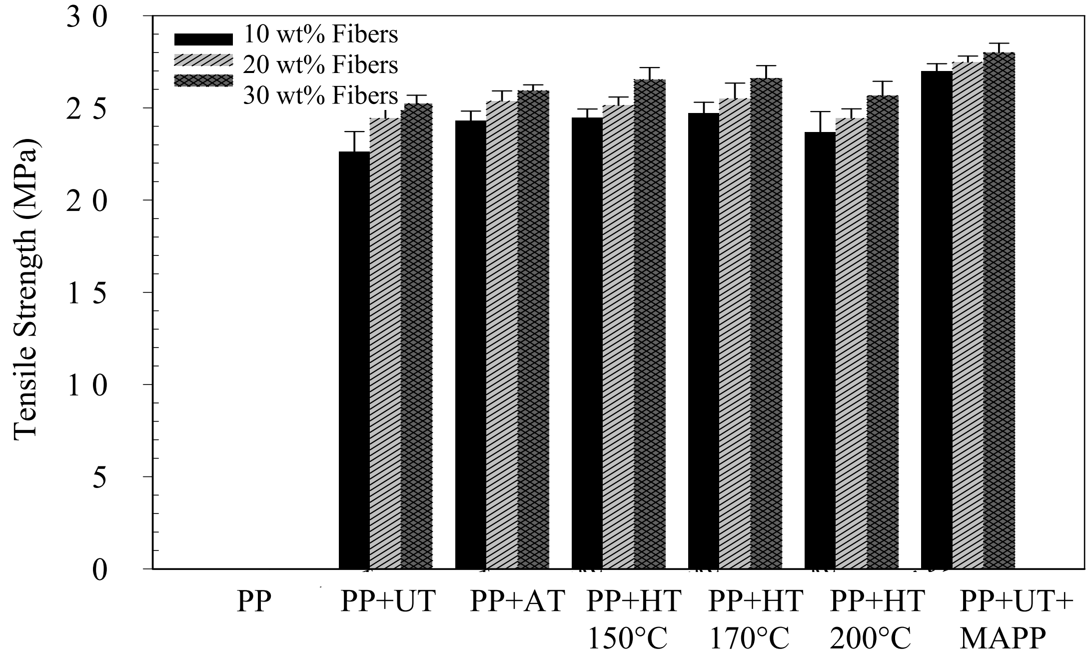


**Figure 4.25** Tensile strength of PP and sisal/PP composites with different interfacial modifications and fiber contents.

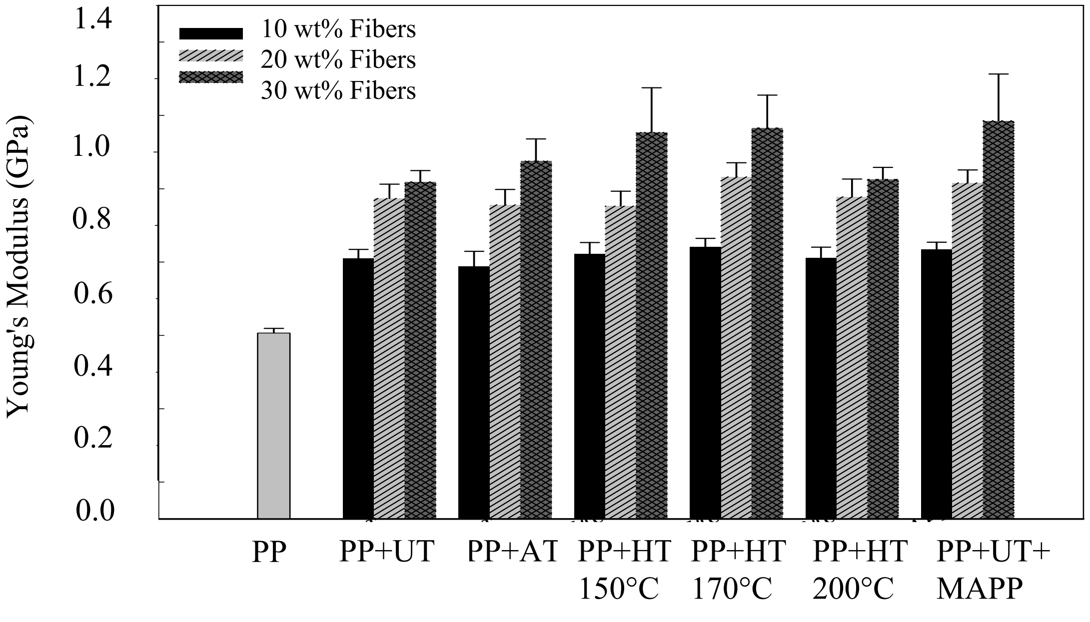


**Figure 4.26** Young's modulus of PP and sisal/PP composites with different interfacial modifications and fiber contents.

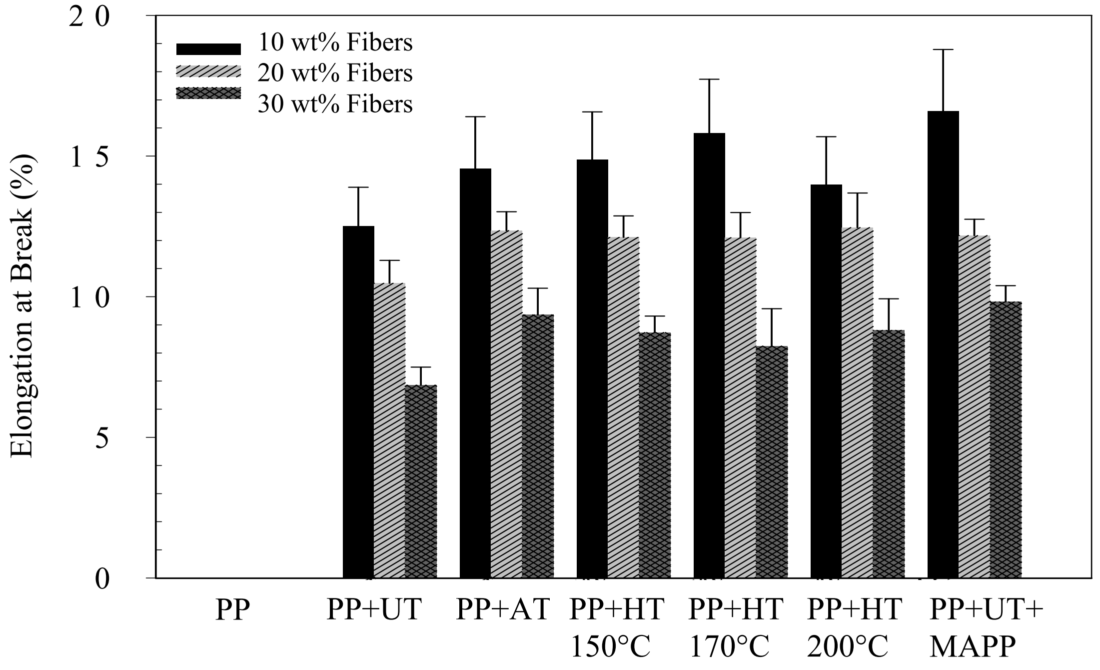


**Figure 4.27** Elongation at break of PP and sisal/PP composites with different interfacial modifications and fiber contents.

### 4.2.3.2 Flexural properties

Table 4.11 shows flexural strength, flexural modulus, and impact strength of PP and sisal/PP composites with different interfacial modifications and fiber contents. Flexural strength and flexural modulus of sisal/PP composites with MAPP were higher than that of untreated sisal/PP composite because of improved interfacial adhesion between fiber and PP matrix (Cantero, Arbelaiz, Ponte, and Mondragon, 2003). However, there was no significant difference in flexural strength and flexural modulus of untreated, alkali and heat treated sisal fiber/PP composites.

In addition, the flexural properties showed the same tendency as the tensile properties that the sisal fiber/PP composites with MAPP have better flexural properties than the composites filled with alkali treated or heat treated sisal fibers. Flexural strength and modulus of alkali, heat treated sisal/PP composites and MAPP modified composites increased with increasing fiber content shown in Figure 4.28 and 4.29 respectively.

**Table 4.11** Flexural strength, flexural modulus, and impact strength of PP and sisal/PP composites with different interfacial modifications and fiber contents.

| **Materials** | **Flexural strength (MPa)** | | | **Flexural modulus (GPa)** | | | **Impact strength (kJ/m$^2$)** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Fiber content** | | | **Fiber content** | | | **Fiber content** | | |
| | **10 wt%** | **20 wt%** | **30 wt%** | **10 wt%** | **20 wt%** | **30 wt%** | **10 wt%** | **20 wt%** | **30 wt%** |
| PP | 47.08±0.13 | | | 1.34±0.04 | | | 79.92±4.25 | | |
| PP+UT | 50.42±0.57 | 52.33±0.30 | 51.19±1.07 | 1.71±0.02 | 2.17±0.08 | 2.76±0.05 | 16.83±2.50 | 15.63±2.90 | 13.62±1.60 |
| PP+AT | 50.61±1.34 | 51.59±0.51 | 52.83±0.33 | 1.75±0.03 | 2.31±0.06 | 2.91±0.10 | 19.32±1.88 | 17.02±2.01 | 14.27±1.50 |
| PP+HT 150°C | 49.47±0.40 | 51.76±1.88 | 52.54±0.56 | 1.76±0.04 | 2.30±0.05 | 2.99±0.05 | 19.57±2.13 | 17.08±2.72 | 14.64±0.80 |
| PP+HT 170°C | 50.17±0.41 | 51.89±0.40 | 53.68±0.44 | 1.84±0.07 | 2.34±0.03 | 3.05±0.17 | 20.38±2.02 | 19.10±1.91 | 16.02±1.93 |
| PP+HT 200°C | 49.79±0.42 | 52.19±0.87 | 52.29±0.60 | 1.72±0.06 | 2.24±0.06 | 2.89±0.08 | 17.52±1.77 | 17.03±1.60 | 16.37±3.62 |
| PP+UT+MAPP | 54.13±0.88 | 54.00±0.56 | 55.83±0.91 | 2.00±0.05 | 2.38±0.06 | 3.40±0.04 | 21.07±2.48 | 19.27±2.84 | 14.98±1.34 |

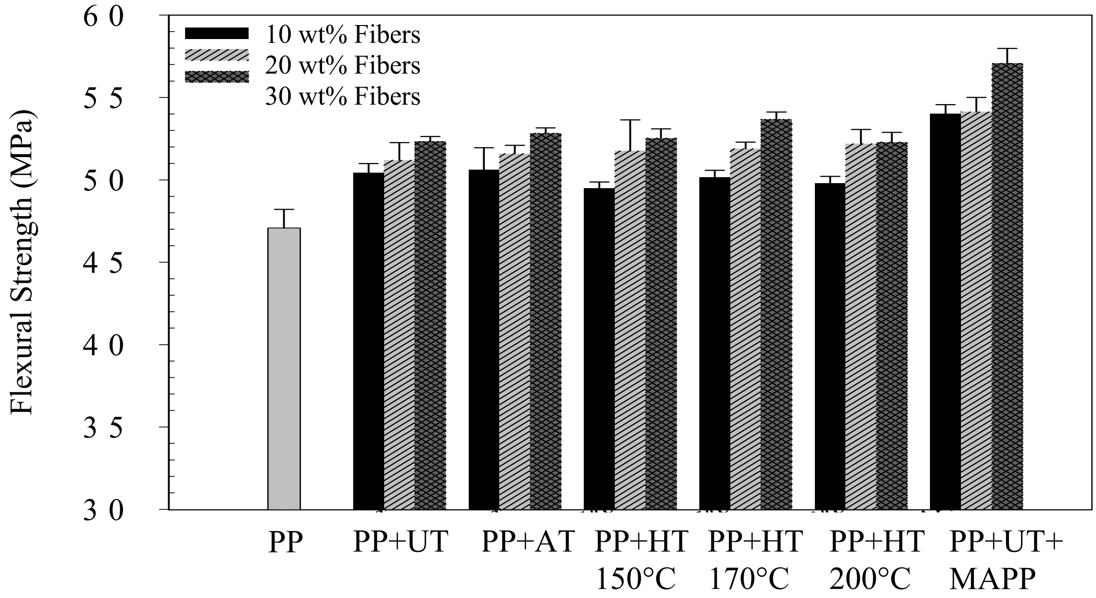


**Figure 4.28** Flexural strength of PP and sisal/PP composites with different interfacial modifications and fiber contents.

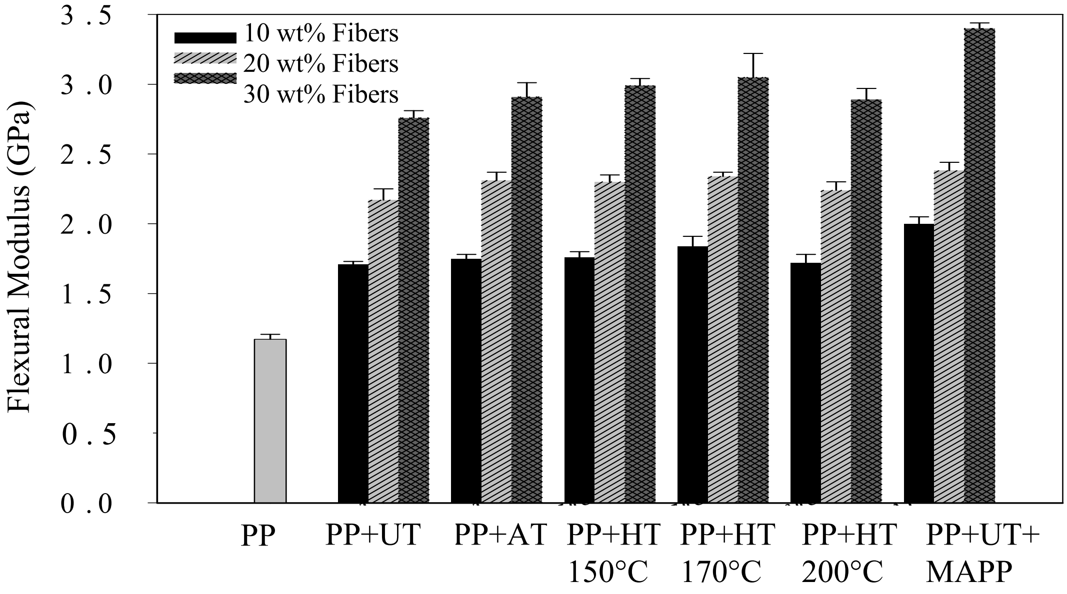


**Figure 4.29** Flexural modulus of PP and sisal/PP composites with different interfacial modifications and fiber contents.

#### 4.2.3.3 Impact properties

Impact strength of PP decreased with adding sisal fiber because the fiber was a stress concentrator as shown in Figure 4.30. Impact strength of alkali treated sisal/PP composite was higher than that of untreated sisal/PP composite due to improved adhesion at fiber-matrix interface (Joseph, P.V., Joseph, K., and Thomas, S., 1999).

Impact strength of heat treated sisal/PP composites was higher than that of untreated sisal/PP composite because there was removal of low molecular weight compound on fiber surface during heat treatment process. This led to more compatible between the heat treated fibers and PP (Kaewkuk, S., Sutapun, W., and Jarukumjorn, K., 2009). Heat treated fiber at different temperatures exhibited no effect on impact strength of the composites.

MAPP modified composites showed higher impact strength value than untreated sisal/PP composite because the interfacial adhesion between the fiber and PP matrix was enhanced (Rana et al., 1998). Moreover, MAPP provided more effective enhancement in impact strength when compared to alkali or heat treatment.

Impact strength of the composites decreased with increasing fiber content. The higher amount of fiber increased a probability of agglomeration and created void in the composites. Karnani, Krishnan, and Naryan, (1997) and Sanadi, Caulfield, Jacobson, and Rowell (1995) found that the impact strength of kenaf/PP composites slightly decreased with increasing kenaf content. This was attributed to an increase in number of void in the composites and crack initiation which led to the composite failure.

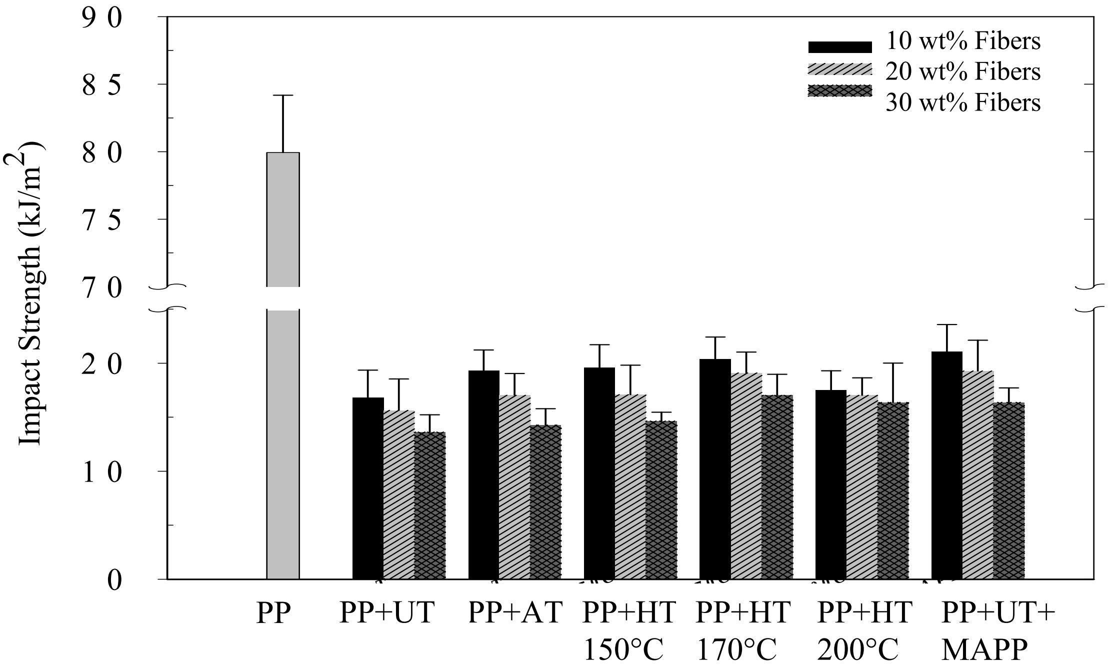


**Figure 4.30** Impact strength of PP and sisal/PP composites with different interfacial modifications and fiber contents.

### 4.2.4 Morphological properties

Surface morphologies of sisal/PP composites are shown in Figure 4.31. The fracture surface of untreated sisal/PP composite in Figure 4.31 (a) presented the wide gap between fiber and PP. Interfacial modifications enhanced the surface adhesion between the fiber and PP. Since the gaps between fiber surface and PP was reduced as shown in Figure 4.31 (b-f). However, interfacial adhesion between the fiber and PP matrix of the alkali treated, heat treated, and MAPP modified composites could not be distinguished. With increasing sisal fiber contents, more agglomeration of sisal fiber was observed, as shown in Figure 4.32. This resulted in lower impact strength of the composites. There was no significant difference in effective of interfacial modification on distribution of the composites.

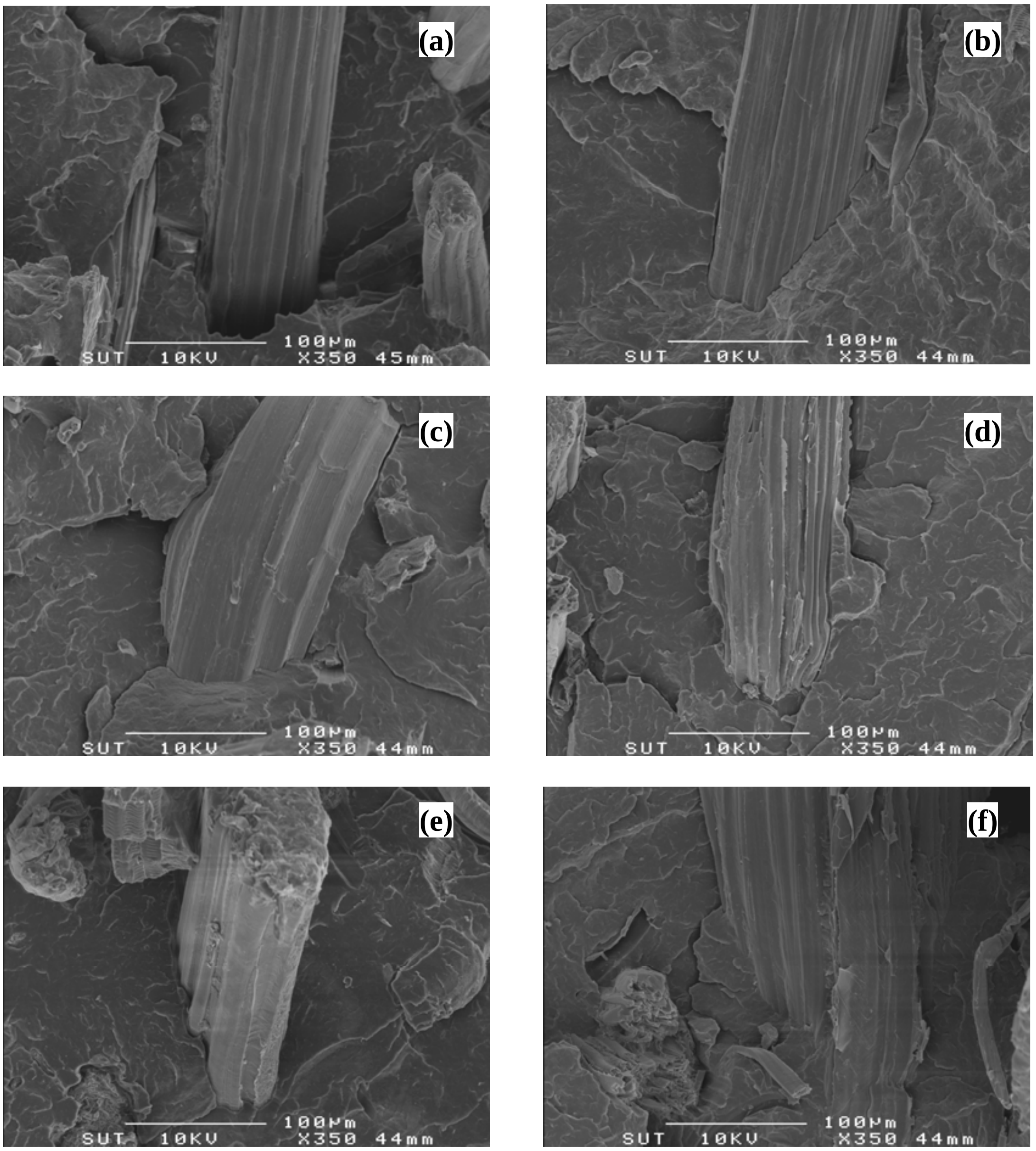


**Figure 4.31** SEM micrographs of surface of UT/PP (a), AT/PP (b), HT150°C/PP (c), HT170°C/PP (d), HT200°C/PP (e), and UT/PP/MAPP (f) composites at 20 wt% fiber content.

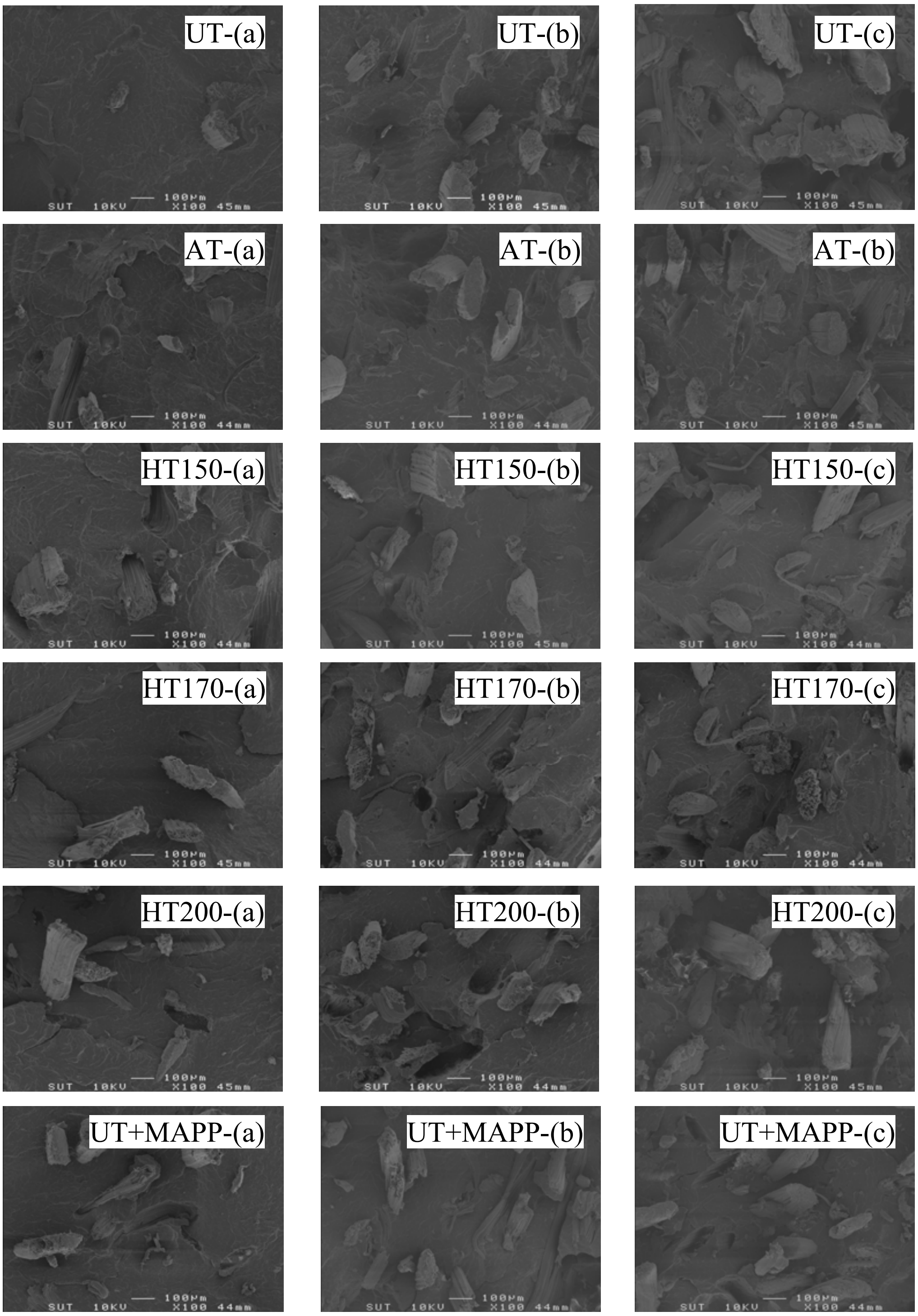


**Figure 4.32** SEM micrographs of surface of sisal/PP composites with different surface modifications and fiber contents; 10 wt% (a), 20 wt% (b), and 30 wt% (c).

### 4.2.5 Water absorption

Figure 4.33-4.35 show the relationship between water absorption and immersion time of PP and sisal/PP composites with different interfacial modifications and fiber contents. Water absorption of sisal/PP composites was higher than that of PP because the hydrophilic character of the sisal fiber led to high moisture absorption of sisal/PP composites. Alkalization, heat treatment, and adding MAPP resulted in a reduction of water absorption of sisal/PP composites.

A decrease in water absorption of alkali treated sisal fiber/PP composite indicated that alkali treatment could be used to reduce the hydrophilicity of sisal fiber/PP composites. Sydenstricker, Mochnaz, and Amico (2003) found that moisture absorption of the alkali treated sisal fiber was significantly decreased when compared with untreated sisal fiber. This was because alkalization removed wax, impurity, and some hemicellulose on fiber surface which were responsible for most water absorption.

A reduction of water absorption of heat treated sisal fiber/PP composites was caused from a decrease of the hydrophilicity of sisal fibers (Follrich, Müller, and Gindl, 2006). Akinori, Kiichi, and Hikaru (1984) studied the effect of heat treatment on water absorption of wood flour filled phenolics. Water absorption of heat treated wood flour composites was lower than those of untreated wood flour composites because hydrophobic nature of wood flour was increased by heat treatment. There was no significant effect of temperature of heat treatment on water absorption of heat treated sisal fiber/PP composites.

With addition of MAPP into sisal/PP composites, the water absorption of the composites was decreased due to the improvement of surface adhesion between fibers and matrix which reduced the water accumulation in the interfacial voids (Thwe and Liao, 2003). Yang, Kim, Park, Lee, and Hwang (2006) reported that MAPP chemically bonded with the –OH groups of the lignocellulosic fibers. The strong interfacial bonding between fibers and polymer matrix caused by the compatibilizing agent limited water absorption of the composites.

Among the interfacial modifications, MAPP modified composites showed the lowest water absorption. In addition, water absorption of the sisal/PP composites increased with increasing fiber content.

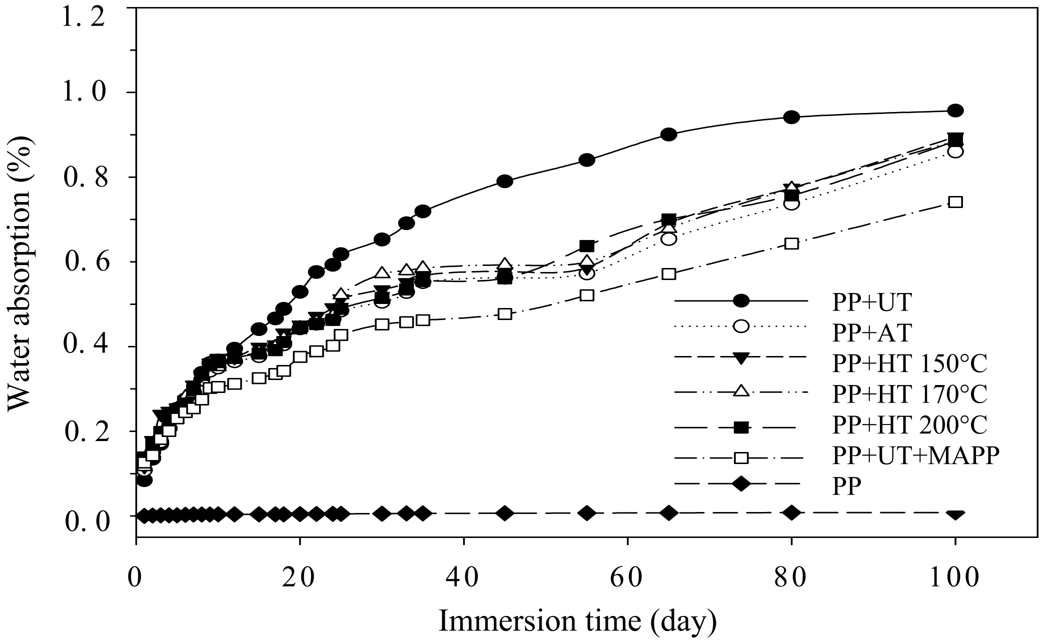


**Figure 4.33** Water absorption of 10 wt% sisal/PP composites with different interfacial modifications.

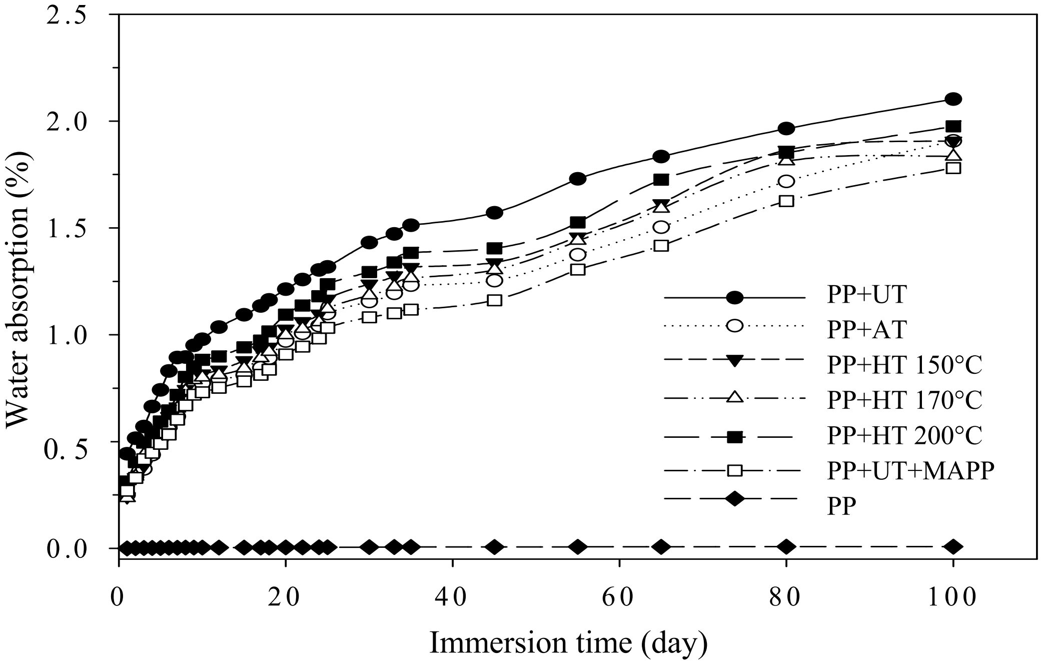


**Figure 4.34** Water absorption of 20 wt% sisal/PP composites with different interfacial modifications.

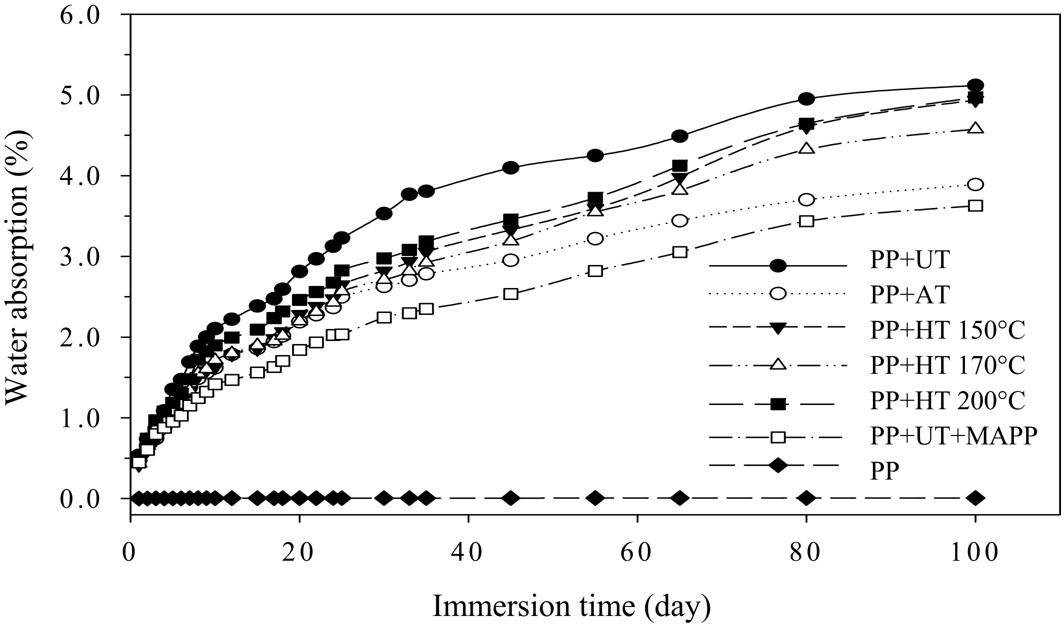


**Figure 4.35** Water absorption of 30 wt% sisal/PP composites with different interfacial modifications.

## 4.3 Effect of glass fiber hybridization on physical properties of sisal/PP composites

In order to evaluate the effect of glass fiber hybridization on the properties of sisal/PP composites, glass fibers (GF) were added into UT and HT sisal/PP composites. The total fiber content was 30 wt%. Sisal and glass fiber ratio was 50:50.

### 4.3.1 Thermal properties

Table 4.12 shows thermal behaviors of PP, sisal/PP composites, glass fiber/PP, and sisal/glass fiber/PP composite. TGA and DTGA thermograms of PP and its composites are displayed in Figure 4.36. In order to examine initial thermal degradation of PP and its composites, $T_{d5}$ and $T_{d50}$ were examined. $T_{d5}$ and $T_{d50}$ were thermal decomposition temperatures at 5% and 50% weight losses respectively. $T_{d5}$ of the sisal/PP composites and the hybrid composites fell in the decomposition range of 308°C and 344°C respectively. Incorporation of sisal fiber into PP resulted in decreasing $T_{d5}$ and $T_{d50}$ of PP because of low thermal stability of sisal fiber. However, adding glass fiber into PP gave a positive impact on $T_{d5}$ and $T_{d50}$ of PP because glass fiber had higher thermal stability than PP.

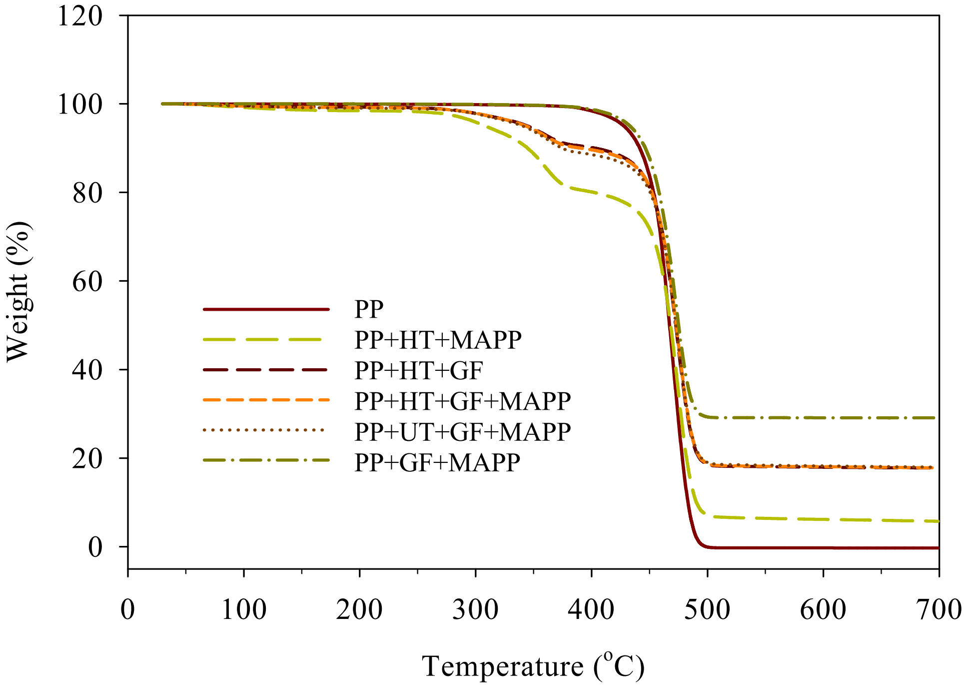
When glass fiber was filled in HT/PP composites, $T_{d5}$ and $T_{d50}$ were improved. Lee and Wang (2006) studied thermal properties of polylactic acid (PLA)/bamboo fiber biocomposite. They found that incorporation of glass fibers into PLA/bamboo composite resulted in a considerable increase in the thermal stability of the composite systems.

MAPP showed insignificant effect on $T_{d5}$ and $T_{d50}$ of HT/GF/PP composite. Both $T_{d5}$ and $T_{d50}$ of HT/GF/MAPP/PP composite were higher than that of UT/GF/MAPP/PP composites. This was because the heat treatment removed some hemicelluloses which degraded at a lower temperature from the fiber resulting in higher thermal stability of HT/GF/MAPP/PP composite.

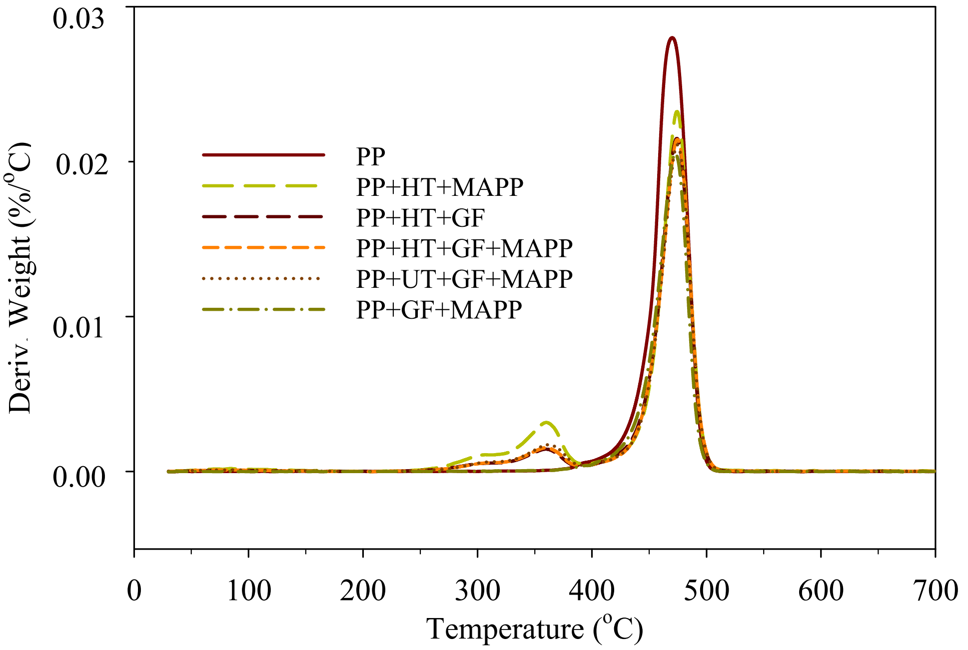
Heat distortion temperatures (HDT) of PP, sisal/PP, sisal/GF/PP, and GF/PP composites are listed in Table 4.12. HDT of PP was remarkably increased with adding sisal fibers. In addition, a remarkable improvement of HDT of PP was observed when glass fibers were incorporated into PP. In general, HDT increased by the addition of the filler. The HDT of HT/PP composites was further enhanced when the glass fibers were added into sisal/PP composites. Panthapukkal and Sain (2007) reported that HDT of the composites was increased with the stiffness of the composites. However, there was no difference on HDT of composites filled with HT and UT sisal fiber. Addition of MAPP into the HT/GF/PP composite resulted in slightly improved HDT of the composite. This behavior was probably due to the increase in interfacial adhesion of fiber and PP matrix (Seung-Hwan and Siqun, 2006).

**Table 4.12** $T_{d5}$, $T_{d50}$ and HDT of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

| **Materials** | **$T_{d5}$ (°C)** | **$T_{d50}$ (°C)** | **HDT (°C)** |
|---|---|---|---|
| PP | 427 | 468 | 82.25±1.0 |
| PP+UT+MAPP | 309 | 469 | 134.50±0.7 |
| PP+HT+MAPP | 308 | 467 | 138.17±0.8 |
| PP+HT+GF | 343 | 472 | 140.17±1.0 |
| PP+HT+GF+MAPP | 344 | 473 | 142.67±0.8 |
| PP+UT+GF+MAPP | 340 | 472 | 141.17±0.7 |
| PP+GF+MAPP | 433 | 475 | 147.83±0.3 |



(a)



(b)

**Figure 4.36** TGA (a) and DTGA (b) thermograms of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

### 4.3.2 Rheological properties

Viscosity, as a function of shear rate, of PP, sisal/PP, sisal/GF/PP, and GF/PP composites are shown in Figure. 4.37. The melt viscosity of PP increased with adding the sisal fibers. However, heat treatment of fiber and a presence of MAPP showed no significant effect on viscosity of sisal/PP composites as explained in 4.2. Moreover, incorporating glass fibers into sisal/PP composites showed no remarkable effect on the viscosity of the sisal/PP composites. This suggested that the glass fibers did not affect the processability of the sisal/PP composites (Jarukumjorn, K., and Suppakarn, N., 2009).

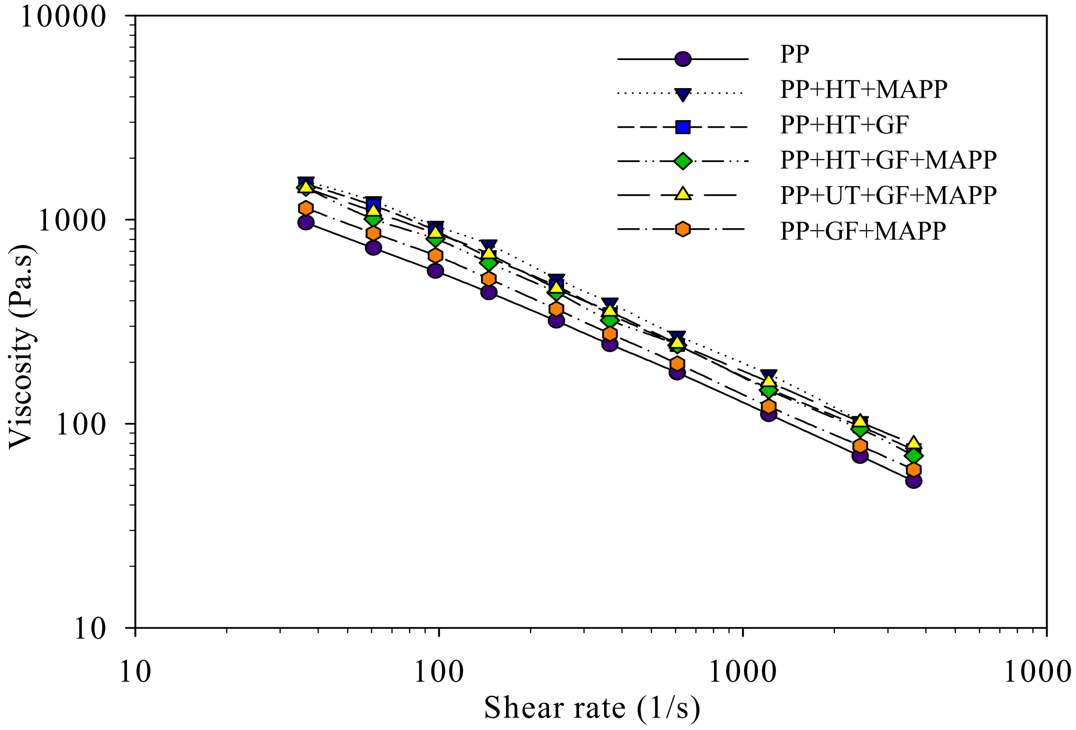


**Figure 4.37** Viscosity at various shear rates of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

### 4.3.3 Mechanical properties

#### 4.3.3.1 Tensile properties

Tensile strength, Young’s modulus, and elongation at break of PP, sisal/PP, sisal/GF/PP, and GF/PP composites are listed in Table 4.13. PP was not broken under the testing condition. Young’s modulus of PP was increased by adding the sisal fiber and glass fiber.

As expected, GF/MAPP/PP composite exhibited superior tensile strength and Young’s modulus than HT/MAPP/PP composite. There was no significant difference in elongation at break and Young’s modulus of sisal/PP composites and hybrid composites as shown in Figure 4.39-4.40. With addition of the glass fibers into the HT/MAPP/PP composite, its tensile strength increased because glass fibers were stronger and stiffer than the sisal fibers. Arbelaiz et al. (2005) reported that the tensile strength and modulus of hybrid glass/flax/PP composites depended on the glass/flax ratio.

MAPP enhanced tensile strength of the HT/GF/PP composite due to improved interfacial adhesion between the fiber and matrix as shown in Figure 4.38.

Tensile strength and Young’s modulus of HT/GF/MAPP/PP composite were higher than that of UT/GF/MAPP/PP composite. This was due to removal of some components of the fiber such as hemicelluloses during heat treatment leading to an improvement of compatibility between the sisal fiber and PP matrix as explained in 4.1.

**Table 4.13** Tensile strength, Young's modulus, and elongation at break of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

| **Materials** | **Tensile strength (MPa)** | **Young's modulus (GPa)** | **Elongation at break (%)** |
|---|---|---|---|
| PP | NB | 0.51±0.01 | NB |
| PP+UT+MAPP | 28.00±0.50 | 1.30±0.12 | 8.82±0.57 |
| PP+HT+MAPP | 28.35±0.95 | 1.44±0.04 | 6.44±0.43 |
| PP+HT+GF | 24.88±1.36 | 1.51±0.05 | 7.60±0.53 |
| PP+HT+GF+MAPP | 32.38±0.98 | 1.54±0.06 | 5.83±0.45 |
| PP+UT+GF+MAPP | 29.17±0.45 | 1.49±0.04 | 5.70±0.32 |
| PP+GF+MAPP | 35.32±0.44 | 1.85±0.04 | 5.83±1.03 |

Note: NB = not broken

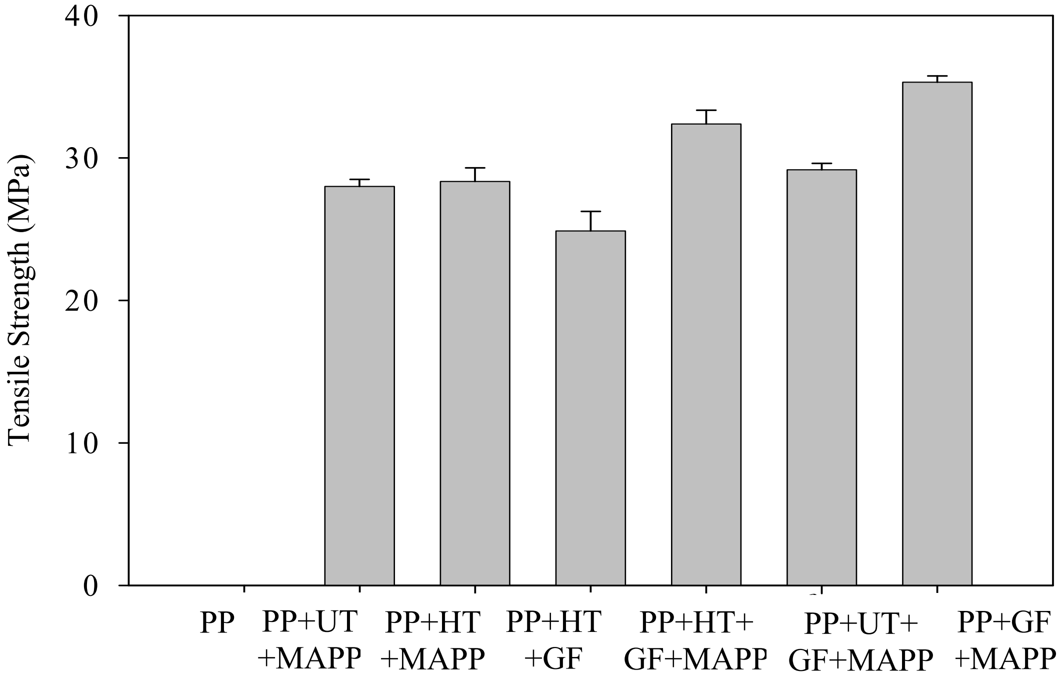


**Figure 4.38** Tensile strength of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

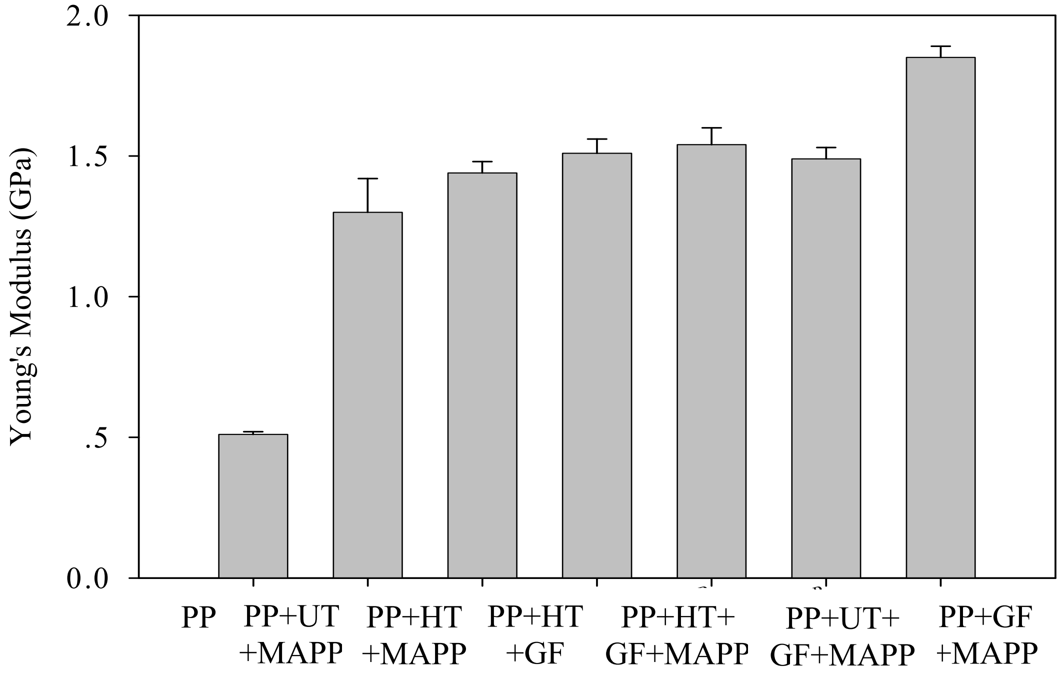


**Figure 4.39** Young’s modulus of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

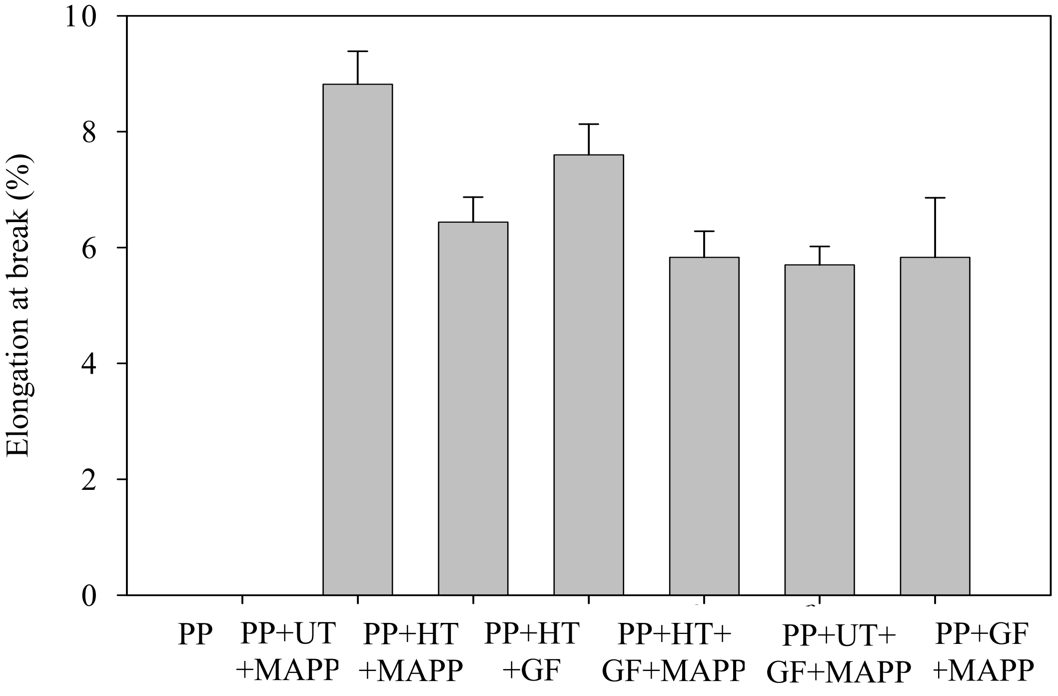


**Figure 4.40** Elongation at break of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

#### 4.3.3.2 Flexural properties

Table 4.14 shows flexural strength, flexural modulus, and impact strength of PP, sisal/PP and sisal/GF/PP composites. Flexural strength and flexural modulus of PP increased with the addition of sisal fiber and glass fiber.

GF/MAPP/PP composite exhibited better flexural strength and flexural modulus than HT/MAPP/PP composite because the strength and modulus of glass fiber were higher than that of sisal fiber. With adding glass fibers into the HT/MAPP/PP composites, flexural strength slightly increased because of stronger and stiffer characteristics of the glass fibers comparing to the sisal fibers (Jarukumjorn, K., and Suppakarn, N., 2009). The result showed the same tendency as the tensile properties of sisal/PP composites as shown in Figure 4.41-4.42. Flexural strength and flexural modulus of HT/GF/PP composites with MAPP were higher than that of the composite without MAPP because of an improvement of interfacial adhesion between fiber and PP matrix.

**Table 4.14** Flexural strength, flexural modulus, and impact strength of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

| **Materials** | **Flexural strength (MPa)** | **Flexural modulus (GPa)** | **Impact strength ($kJ/m^2$)** |
|---|---|---|---|
| PP | 47.08±0.13 | 1.34±0.04 | 79.92±4.25 |
| PP+UT+MAPP | 55.83±0.91 | 3.40±0.04 | 14.98±1.34 |
| PP+HT+MAPP | 56.29±0.79 | 3.46±0.11 | 15.38±3.07 |
| PP+HT+GF | 53.64±0.87 | 3.51±0.08 | 12.66±1.36 |
| PP+HT+GF+MAPP | 58.04±1.57 | 3.53±0.04 | 15.83±2.96 |
| PP+UT+GF+MAPP | 57.75±0.62 | 3.40±0.10 | 15.56±3.57 |
| PP+GF+MAPP | 63.34±1.68 | 3.97±0.29 | 16.14±1.29 |

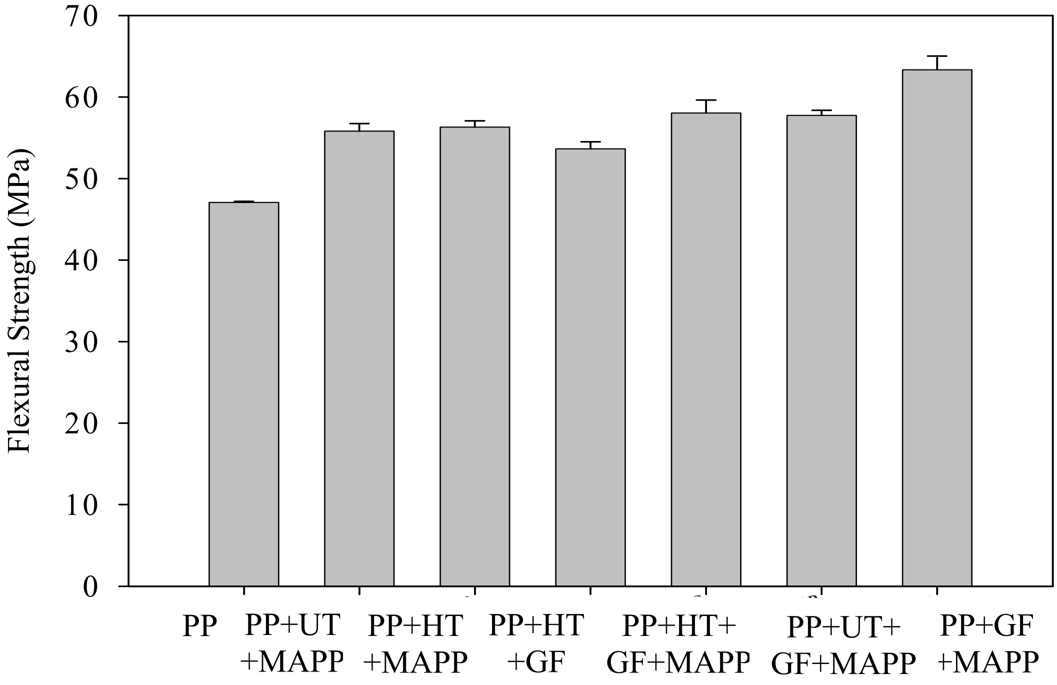


**Figure 4.41** Flexural strength of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

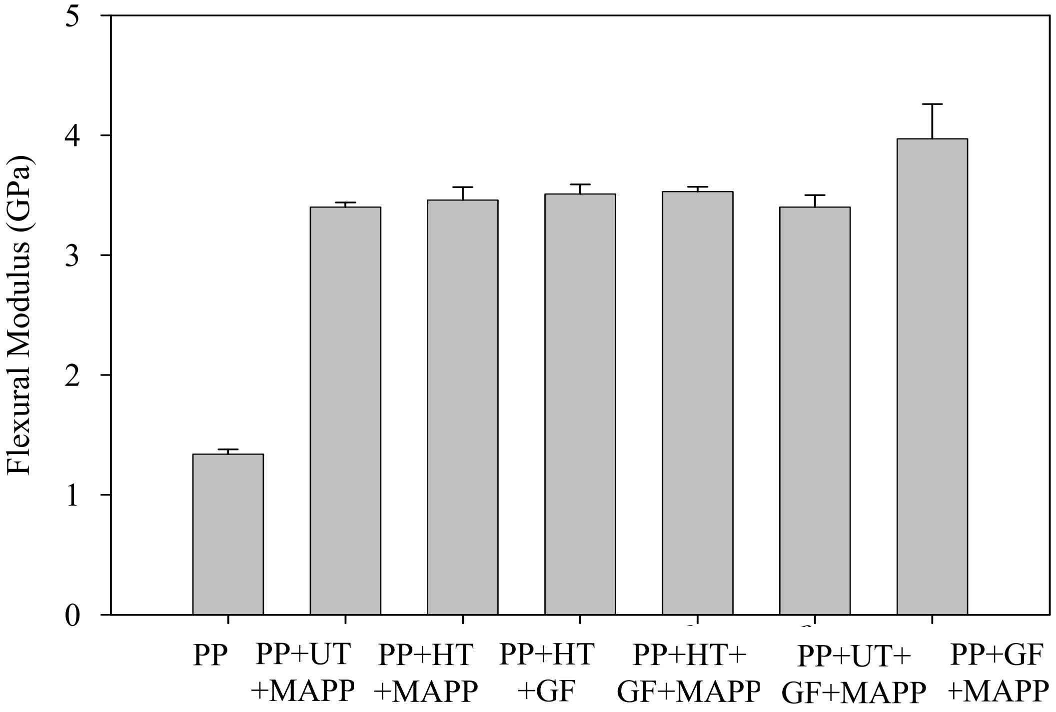


**Figure 4.42** Flexural modulus of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

HT/GF/MAPP/PP composite showed slightly improved flexural strength and flexural modulus compared with UT/GF/MAPP/PP composite. This was because heat treatment gave a positive impact on interfacial adhesion between the sisal fiber and PP matrix.

#### 4.3.3.3 Impact properties

Addition of sisal fibers and glass fiber into PP decreased impact strength of PP. This was because added fiber acted as a stress concentrator. Impact strength of GF/MAPP/PP composite was higher than that of HT/MAPP/PP composites due to improved strength resulted from the glass fibers in the composites (Panthapulakkal and Sain, 2007) as shown in Figure 4.43. Impact strength of HT/MAPP/PP composite slightly increased with adding glass fibers into the composites because of stronger and stiffer characteristics of the glass fibers comparing to the sisal fibers (Jarukumjorn, K., and Suppakarn, N., 2009). Moreover, impact strength of the HT/GF/PP slightly increased when MAPP was added because of enhancement in interfacial adhesion between fiber and matrix.

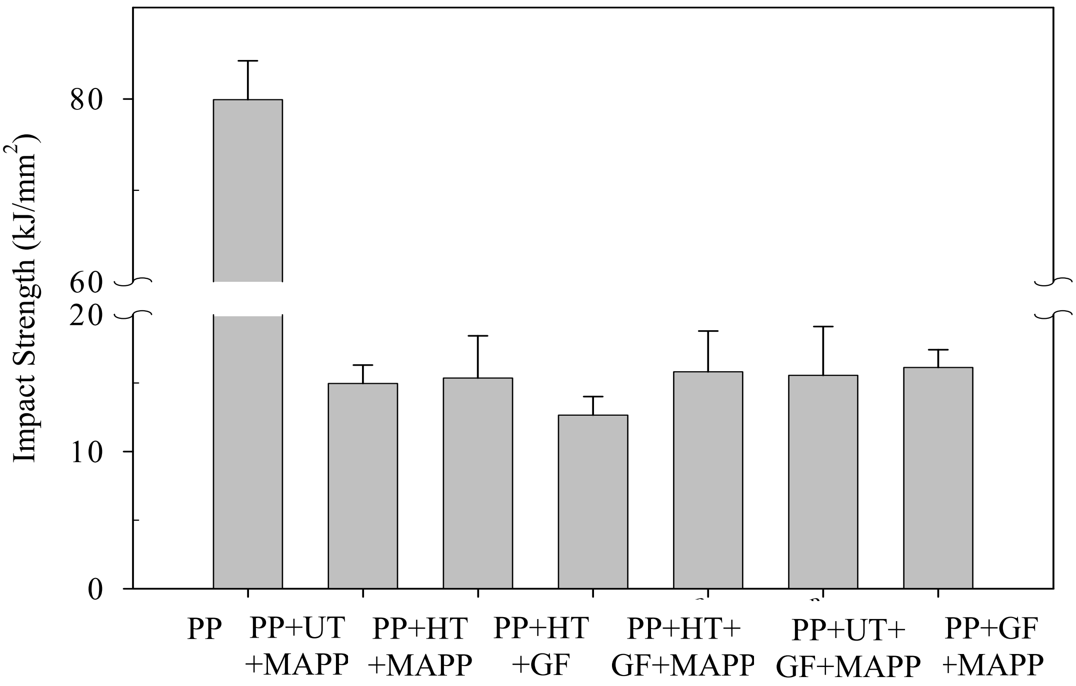


**Figure 4.43** Impact strength of PP, sisal/PP, sisal/GF/PP, and GF/PP composites.

### 4.3.4 Morphological properties

SEM micrographs at 350x of sisal/PP, sisal/GF/PP composites are shown in Figure 4.44. It was found that HT/GF/PP composite showed no gap between fiber and PP as shown in Figure 4.44-b. This result agreed as the system without glass fiber hybridization. Composites with MAPP in Figure 4.45 (b-d) exhibited better adhesions between PP and the fibers than composites without MAPP in Figure 4.45 (a). There was some of PP obviously covered on the fibers. This result was in agreement with those from mechanical tests.

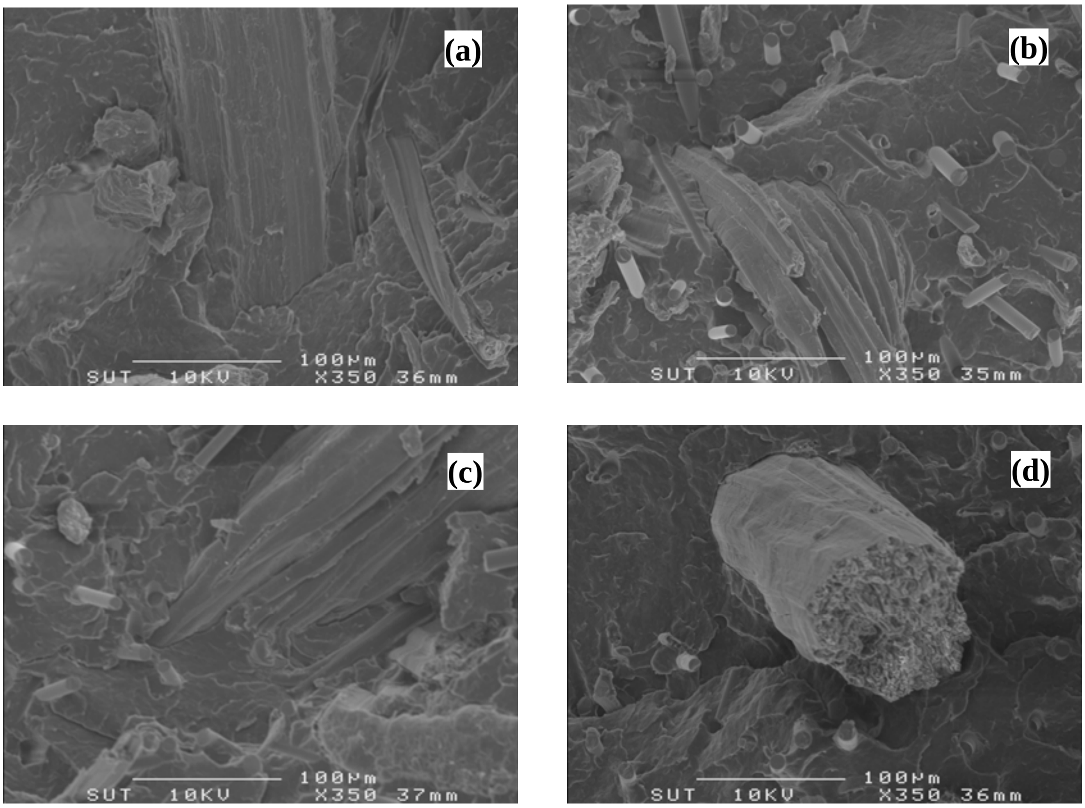


**Figure 4.44** SEM micrographs of (a) HT/MAPP/PP, (b) HT/GF/PP, (c) HT/GF/MAPP/PP, and (d) UT/GF/MAPP/PP composites.

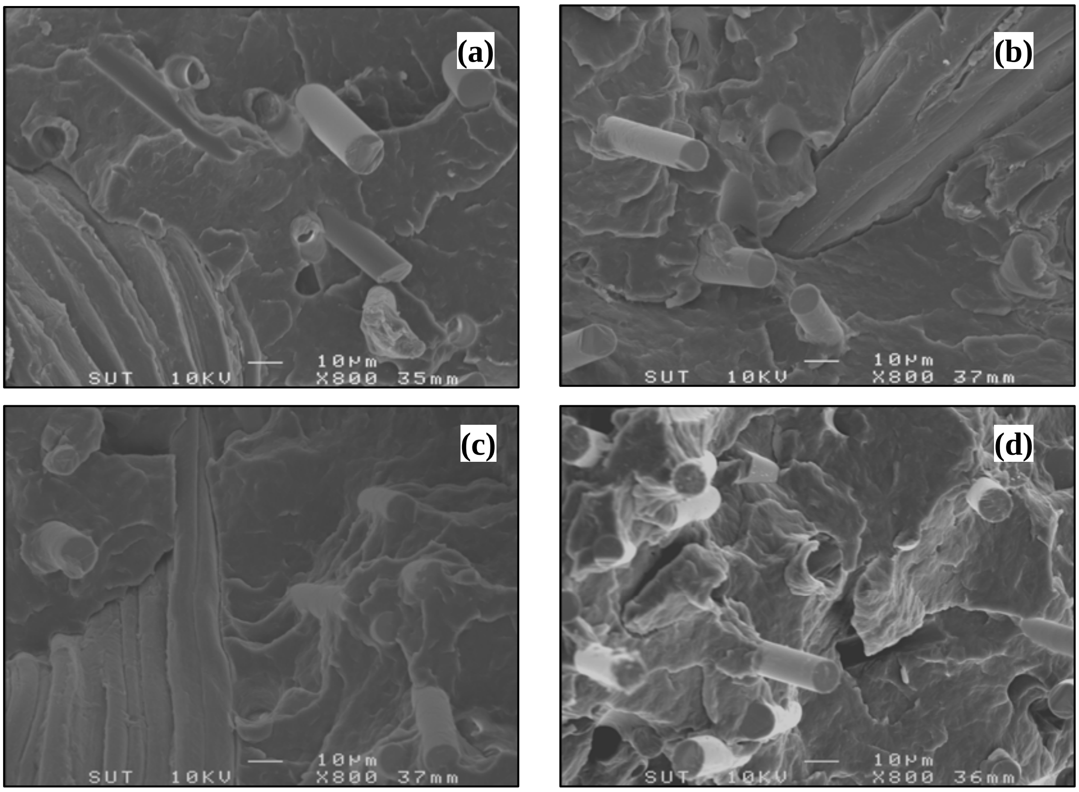


**Figure 4.45** SEM micrographs of (a) HT/GF/PP, (b), HT/GF/MAPP/PP, (c) UT/GF/MAPP/PP, and (d) GF/MAPP/PP composites.

### 4.3.5 Water absorption

Water absorption curves of PP, sisal/PP, sisal/GF/PP, and GF/PP composites are shown in Figure 4.46. Addition of sisal fiber into PP resulted in increasing water absorption of PP. This was due to the hydrophilic character of the sisal fiber leading to high moisture absorption of sisal/PP composites. Water absorption of glass fiber/PP composite was lower than that of sisal/PP composite. This was because glass fiber showed higher moisture resistance than sisal fiber (Arbelaiz, Fernandez, Cantero, Llano-Ponte, Valea, and Mondragon, 2005).

Incorporation of glass fiber into sisal fiber/PP composites decreased the water absorption of the composite. This was attributed to the decrease in hydrophilic nature from the sisal fibers (Jarukumjorn, K. and Suppakarn, N., 2009).

A decrease in water absorption of sisal fiber/PP composites was observed in the composites with MAPP. This was because MAPP improved surface adhesion between fibers and matrix leading to a decrease of water absorption of the composites.

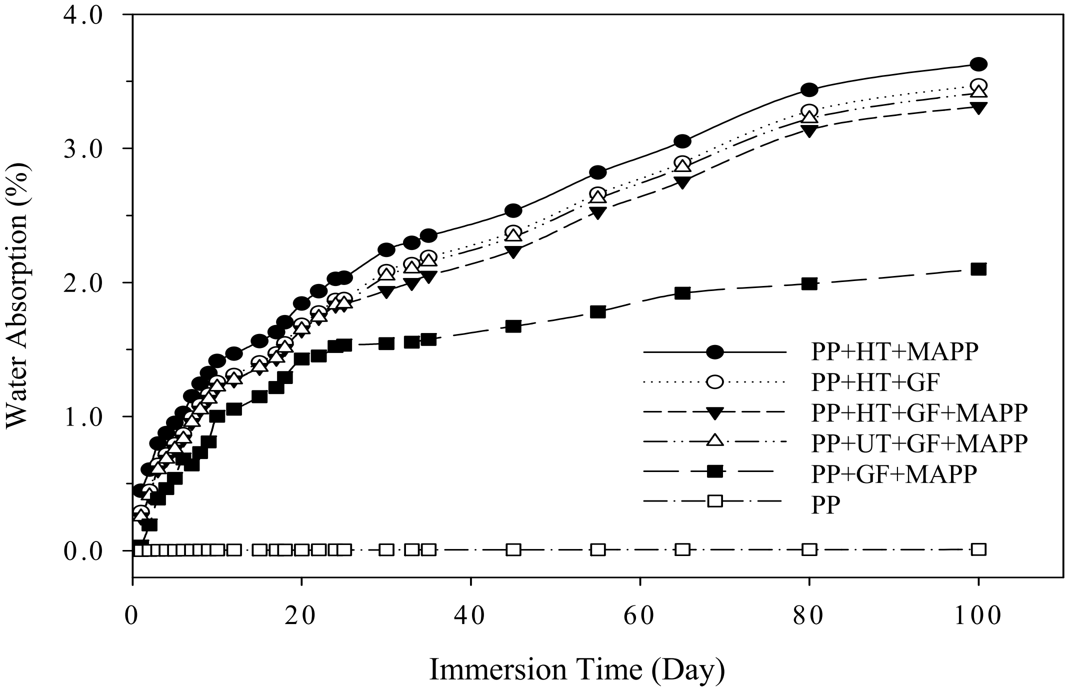


**Figure 4.46** Water absorption of sisal/PP and sisal/GF/PP composites.

# CHAPTER V

# CONCLUSIONS

Mechanical, morphological, and thermal properties of heat treated sisal fibers were studied. Tensile strength of sisal fiber was increased by the heat treatment. Moreover, heat treatment was able to remove low molecular weight compositions, wax, some hemicelluloses, and lignin which have low thermal stability from the fiber surface. Increasing treatment temperature and time resulted in an improvement in thermal stability of sisal fiber. For the treatment at 150 and 170°C, the maximum tensile strength of the treated fiber was obtained at the treatment time of 30 min whereas for the treatment at 200°C, it was obtained at 5 min treatment. This was also confirmed by FTIR analysis and fiber composition analysis. SEM micrographs revealed that the surface of heat treated fiber appeared rougher than the surface of untreated sisal fiber.

With the addition of sisal fibers into PP, crystallization temperature of PP increased while crystallinity of PP decreased. With increasing sisal fiber content, crystallization temperature and crystallinity of PP increased but melting temperature of PP insignificantly changed. The decomposition temperature of cellulose of alkali and heat treated sisal/PP composites and MAPP modified composites were higher than that of untreated sisal/PP composites. With increasing fiber content, the decomposition temperature of cellulose of sisal/PP composites was decreased while the decomposition temperature of PP did not significantly change. The fiber treatments and adding compatibilizer showed no significant effect on MFI, viscosity, and HDT of the composites. The viscosity, HDT, and water absorption of the composites increased with increasing fiber contents.

The incorporation of the sisal fibers into PP enhanced tensile strength, Young’s modulus, and flexural properties while elongation at break and impact strength were decreased. Tensile strength, Young’s modulus, and elongation at break of alkali treated sisal/PP composites were slightly higher than those of untreated sisal/PP composite. Heat treatment at different temperatures, 150°C, 170°C, and 200°C did not significantly affect the tensile strength, Young’s modulus, and elongation at break of heat treated sisal/PP composites. However, the tensile properties of heat treated sisal fiber/PP composites were higher than that of untreated sisal fiber/PP composites. A remarkable increase in tensile strength, flexural properties, and impact strength was observed when MAPP was added into the sisal/PP composites. There was no significant difference on flexural strength and flexural modulus of alkali and heat treated sisal fiber/PP composites. Tensile strength, Young’s modulus, and flexural properties of all composites increased with increasing fiber content. On the other hand, impact strength and elongation at break of the composites decreased with increasing fiber contents. SEM micrographs revealed that the interfacial modifications enhanced the interfacial adhesion between the fiber and PP. However, there was no significant difference in interfacial adhesion of the PP composites when the composite interfaces were modified by alkalization, heat treatment, and addition of compatibilizer. With increasing fiber contents, more agglomeration of sisal fiber within the PP composites was observed.

Addition of glass fibers into sisal/PP composites resulted in considerable increase in the thermal stability and HDT of the composites. Thermal stability of heat treated sisal fiber/glass fiber/PP composites was higher than that of untreated sisal fiber/glass fiber/PP composites. Heat treatment had no effect on HDT, viscosity and water absorption of sisal/glass fiber/PP composites. With an addition of the glass fibers into the sisal/PP composites, tensile strength, Young's modulus, flexural properties, and impact strength increased while water absorption decreased. MAPP not only enhanced the mechanical properties of the composites but also decreased water absorption of sisal fiber/PP composites and sisal fiber/glass fiber/PP composites. Tensile properties, flexural properties, and impact strength of heat treated sisal fiber/glass fiber/PP composites were slightly higher than that of untreated sisal fiber/glass fiber/PP composites.

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# APPENDIX A

# LIST OF PUBLICATIONS

## List of publications

Kaewkuk, S., Jarukumjorn, K., and Sutapun, W. (2009). Effect of fiber treatment on mechanical properties of sisal/polypropylene composites. In **Proceeding of Pure and Applied Chemistry International Conference** 2009. (pp 301-303), Pitsanulok, Thailand.

Kaewkuk, S., Sutapun, W., and Jarukumjorn, K. (2009). Mechanical, thermal and morphological properties of heat treated sisal fibers. In **Proceeding of the 11th Pacific Polymer Conference** 2009. (p 51), Cairns, Australia.

Kaewkuk, S., Sutapun, W., and Jarukumjorn, K. (2010). Effect of heat treated sisal fiber on physical properties of polypropylene composites. **Adv. Mater. Res.** 123-125: 1123-1126.

# EFFECT OF FIBER TREATMENT ON MECHANICAL PROPERTIES OF SISAL/POLYPROPYLENE COMPOSITES

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**Abstract: Sisal fiber reinforced polypropylene composites were prepared by melt mixing. The composites were injection molded for mechanical tests including tensile, flexural, and impact properties. Morphologies of the composites were also examined using scanning electron microscope (SEM). Fiber treatment with alkali and heat were performed to improve interfacial adhesion between the fiber and matrix. Tensile strength of the treated fiber/polypropylene composites was higher than that of the untreated fiber/polypropylene composite due to better surface adhesion between the fiber and matrix. The fiber treatment showed no remarkable effect on Young's modulus, flexural strength, flexural modulus, and impact strength of the composites. SEM micrographs revealed that the fiber treatment enhanced surface adhesion between the fiber and polypropylene matrix.**

## Introduction

Natural fiber reinforced thermoplastic composites are gaining increasing interest. The advantages of natural fibers over synthetic fibers are low density, low cost, environmental friendly, less tool wear during processing, renewability, and biodegradability [1,2].

The main disadvantage of the natural fibers is their hydrophilic nature therefore they are not well compatible with hydrophobic polymer matrix. This results unsatisfactory properties of the composites. The compatibility between the fiber and the polymer matrix can be improved by modification of fiber and/or polymer matrix [3,4].

Many studies have been focused on interfacial modifications by physical and chemical methods. Physical methods include heat [5], plasma [6], or corona treatment [7]. Chemical methods involve the modification of matrix by grafting different monomers [8] or treatment of fiber by alkali solution [9], silane coupling agent [10], maleic anhydride [11] etc. Joseph et al. [12] investigated the effect of fiber treatment with sodium hydroxide (NaOH) on tensile properties of sisal/polypropylene (PP) composites. Alkali treatment reduced the hydrophilic nature of the sisal fiber. Some compositions such as hemicellulose, lignins were dissolved or extracted by NaOH solution during treatment process and thereby improved the fiber-matrix interfacial adhesion. This led to an improvement in tensile properties of the composites. Sharifah et al. [13] studied the effect of fiber alignment and alkali treatment on the mechanical properties of natural fiber composites using polyester resin as a matrix. The surface of the treated fiber appeared to be quite smooth due to absence of surface impurities. Treatment of fiber by alkalization helped to improve the mechanical interlocking and chemical bonding between the resin and fiber resulting in superior mechanical properties.

Heat treatment is an environmental friendly method to improve the compatibility between natural fiber and polymer matrix. Heating cellulose to high temperature changes its physical and chemical properties. Thermal modifications of cellulose result in changes of lignin and hemicellulose that mean less hydroxyl group and more carbon-carbon double bonds. Robin and Breton [5] prepared heat treated wood/high density polyethylene (HDPE) composites. Spruce wood fibers with average length of 1 mm were heated at 230ºC for overnight. There was a higher crystallinity of cellulose occurred after fiber heat treatment. Moreover, when the hemicelluloses were removed the fiber was more hydrophobic. This result led to more compatible between wood fiber and polyethylene matrix. Rong et al. [14] reported that tensile and flexural strengths of heat treated sisal fiber/epoxy composites were higher than that of untreated sisal fiber/epoxy composite due to increase in fiber strength and the adhesion between the fiber and matrix.

In this study, the effect of heat and alkali treatment on mechanical and morphological properties of sisal/PP composites were investigated.

## Materials and Methods

A commercial grade of isotactic polypropylene (700 J) was supplied from Thai Polypropylene Co., Ltd. Sisal fibers were purchased from sisal-Handicraft OTOP group, Amphur Dan Khun Thod, Nakhon Ratchasima. The sisal fibers were cut into a length of 2 mm and treated with 2%wt NaOH solution for 2 hrs. After that, the fibers were washed with water and dried at 60°C overnight.

Heat treatment was performed by heating sisal fiber in an oven at 200°C for 10 min under atmospheric pressure and presence of air.

Polypropylene and sisal fibers were mixed by an internal mixer (Hakke Rheomix 3000p). The fiber content used in this study was 20 wt%. The rotor speed was 50 rpm and the mixing temperature was fixed at 170°C. The total mixing time was 13 min. The test specimens were prepared by injection molding.

Tensile test of PP and PP composites were carried out using an Instron universal testing machine (model 5569) with a load cell of 50 kN, a crosshead speed of 10 mm/min, and a gauge length of 80 mm.

Flexural properties of PP and PP composites were examined according to ASTM D5943 using an Instron universal testing machine (model 5569) with a load cell of 50 kN, a crosshead speed of 15 mm/min, and span length of 56 mm.

Impact properties of PP and PP composites were tested by following ASTM D256 using an Atlas testing machine (model BPI).

Morphologies of the fracture surface of PP composites were examined using a scanning electron microscope (SEM, model JSM 6400). Samples were coated with gold before analysis.

## Results and Discussion

Tensile properties of PP and PP composites are shown in Figure 1. Tensile strength and Young's modulus of PP increased significantly with adding the sisal fiber. When compared to untreated and alkali treated fiber/PP composites heat treated fiber/PP composite showed higher tensile strength due to a better adhesion between the fiber and matrix as seen from SEM micrograph in Figure 4(c). The hydrophilicity of cellulose fiber was decreased by thermal treatment [15]. This led to more compatible between the sisal fiber and polypropylene matrix. No significant difference in Young's modulus of the untreated, heat and alkali treated fiber/PP composites was observed. Alkali treatment gave no impact on tensile properties of the composites. Mohanty and Nayak [16] also found that there was only a minor increase in tensile and flexural strength of the alkali treated jute/HDPE composites compared to untreated jute/HDPE composites. However, some studies have been reported that the alkali treatment enhanced the tensile properties of the composites because the hydrophilic nature of the natural fiber was reduced. Some compositions such as hemicellulose and lignin were removed during the treatment process and thereby improved the fiber-matrix interfacial bonding [12-13].

Flexural properties of PP and PP composites are shown in Figure 2. It was interesting to note that with the addition of sisal fiber into PP flexural modulus remarkably improved while there was a marginal increase in flexural strength. Flexural properties of the composites were not much affected by both heat and alkali treatment.

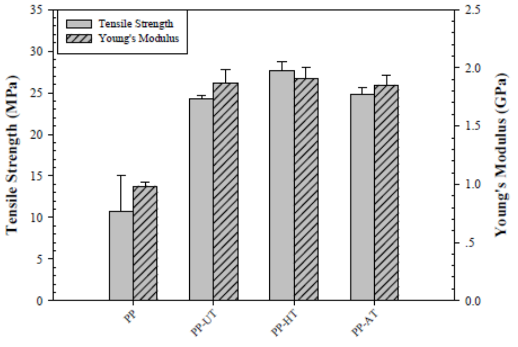

Figure 1. Tensile strength and Young's modulus of PP and PP composites with untreated (UT), heat treated (HT) and alkali treated (AT) sisal fiber.

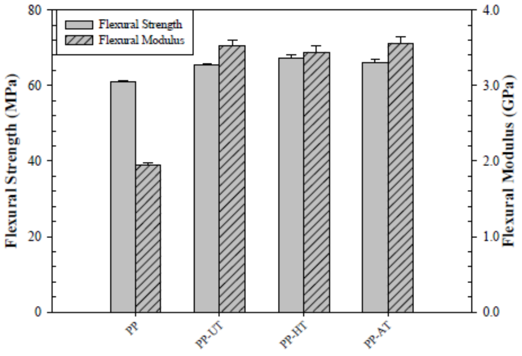

Figure 2. Flexural strength and modulus of PP and PP composites with untreated (UT), heat treated (HT) and alkali treated (AT) sisal fiber.

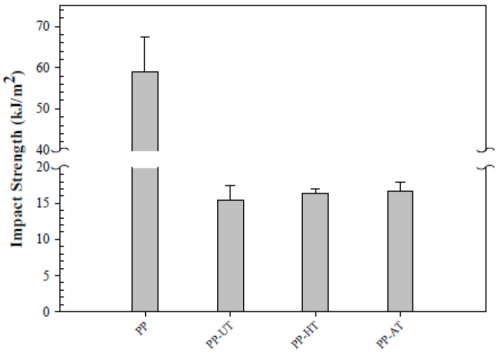

Figure 3. Impact strength of PP and PP composites with untreated (UT), heat treated (HT) and alkali treated (AT) sisal fiber.

Figure 3 shows impact strength of PP and PP composites. Addition of the fiber decreased the impact strength of PP because the fiber was a stress concentrator [17]. There was no significant difference in impact strength of PP reinforced with untreated, heat and alkali treated sisal fiber.

SEM micrographs of PP composites are shown in Figure 4. Fiber surface treatment enhanced the surface adhesion between the fiber and PP. Since the gap between fiber surface and PP was reduced.

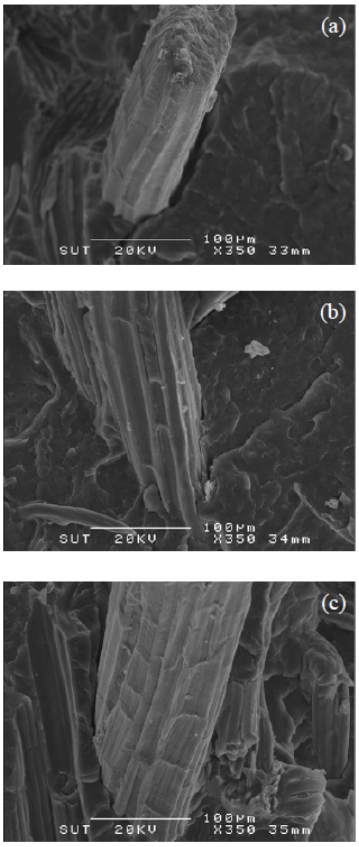

Figure 4. SEM micrographs of of PP composites with untreated (a), heat treated (b) and alkali treated (c) sisal fiber.

## Conclusions

The incorporation of the fiber into PP increased the tensile and flexural properties. Tensile strength of the treated fiber/PP composites was higher than that of the untreated fiber/PP composites due to better surface adhesion between the fiber and matrix. No remarkable effect of fiber treatment on Young's modulus, flexural strength, flexural modulus and impact strength of the composites was observed. The results indicated that there was not much difference in mechanical properties of heat treated and alkali treated fiber/PP composites.

## Acknowledgements

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# Mechanical, Thermal and Morphological Properties of Heat Treated Sisal Fibers

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## Introduction

Heating cellulosic materials e.g. wood or natural fibers results in changes of their physical and chemical properties. Hygroscopicity, swelling, and shrinkage of the materials are reduced.[1] The properties of the heated materials depend on types and properties of the materials, initial moisture content, surrounding atmosphere, treatment time and temperature.[2] Thermal treatment of spruce wood at 200°C remarkably decreased the hydrophilicity of the wood.[3] Yildiz et al.[2] reported that hemicellulose degraded by heat treatment. Loss of hemicellulose affected the strength of wood heated at high temperature. Rong et al.[4] also found that tensile properties of heat treated sisal fiber were higher than that of untreated fiber due to the increased crystallinity of cellulose. The objective of this study is to investigate the effect of treatment times and temperatures on the mechanical, thermal, and morphological properties of sisal fibers. The research is a preliminary work for the further studying the effect of interfacial modifications on the properties of sisal-polypropylene composites.

## Experimental

Sisal fibers were purchased from sisal-Handicraft OTOP group, Nakhon Ratchasima. The diameter of the fiber was 177-360 μm with an average diameter of 243±35 μm. Heat treatment was performed by heating sisal fiber in an oven at 150, 170, and 200°C with different durations under atmospheric pressure and presence of air. Tensile testing was carried out using LR-5K, Lloyds Instrument Ltd., UK at a crosshead speed of 5 mm/min and a gauge length of 5 cm. Thermal degradation of untreated and heat treated sisal fibers were analyzed using Perkin Elmer TGA-7 thermogravimetric analyzer with a heating rate of 10°C/min under a nitrogen atmosphere. Morphologies of fiber surfaces were examined using a scanning electron microscope (SEM, JEOL model JSM 6400).

## Results and Discussion

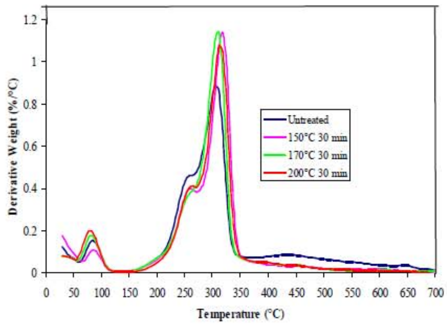

*Figure 1:* DTG curves of untreated and heat treated sisal fiber

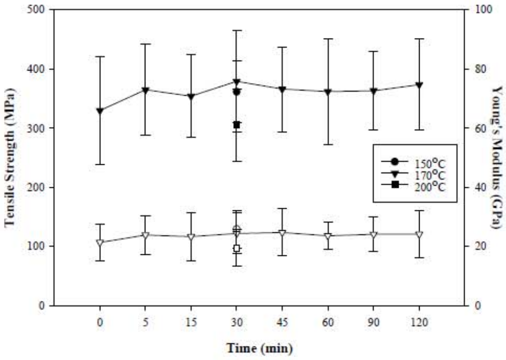

*Figure 2:* Tensile strength (closed symbol) and Young's modulus (open symbol) of untreated and heat treated sisal fiber

DTG curves of untreated and heat treated sisal fibers are shown in Figure 1. The first decomposition peak below 100°C corresponded to the evaporation of moisture. The second decomposition of untreated fiber observed as a shoulder peak around 150°C indicated the onset of decomposition of wax and impurities. The third decomposition peak was the decomposition of hemicellulose. The onset of this decomposition peak was observed around 170°C.[5] The fourth decomposition peak at 320°C was the decomposition of cellulose. In the case of heat treated fibers, weight loss in the second and the third decomposition were a little bit smaller than untreated fiber. This indicated that the heat treatment was able to remove impurities, wax and some hemicellulose from fiber surface. The onsets of decomposition temperature of cellulose of 200°C treated fiber shifted to higher temperature while that of fiber treated at 150°C and 170°C unchanged.

Tensile strength and Young's modulus of untreated and heat treated sisal fibers at 170°C with different treatment times are shown in Figure 2. Tensile strength and Young's modulus of 170°C treated fiber were higher than that of untreated fiber. The treatment for 30 min provided the highest tensile strength. Besides treatment temperature at 170°C, the treatment temperature at 150°C and 200°C which were temperature before and after onset of decomposition of hemicellulose, respectively, were chosen to study the properties of treated fiber. Tensile properties of treated fiber at 170°C were higher than those of treated fiber at 150°C and 200°C when treatment time was 30 min. It might be due to only partial removal of hemicellulose of treated fiber at 150°C as shown in Figure 3(b). In a case of the treated fiber at 200°C, the degradation of the fiber was observed as shown in Figure 3(d) and the color of the fiber turned into brown.

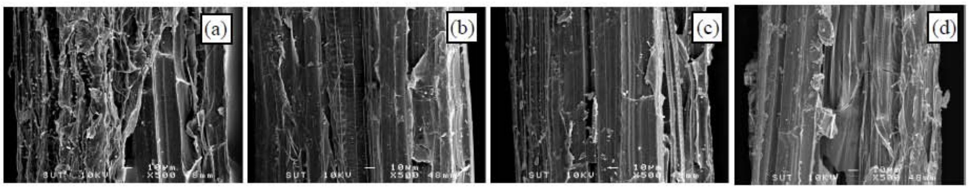

***Figure 3:*** SEM micrographs of untreated fiber (a), heat treated fiber at 150 °C for 30 min (b), heat treated fiber at 170 °C for 30 min (c) and heat treated fiber at 200 °C for 30 min (d).

SEM micrographs of the untreated and heat treated sisal fibers are shown in Figure 3. The surfaces of the treated fibers were cleaner and more smooth than that of untreated fibers due to the removal of impurities and some hemicellulose.

## Conclusions

The impurities, wax and some hemicellulose covering the fiber surface were removed by heat treatment. Removal of impurities and hemicellulose resulted in improvement of the strength of treated sisal fibers. Heat treatment at 170°C for 30 min provided the highest tensile strength of the fiber.

## Acknowledgements

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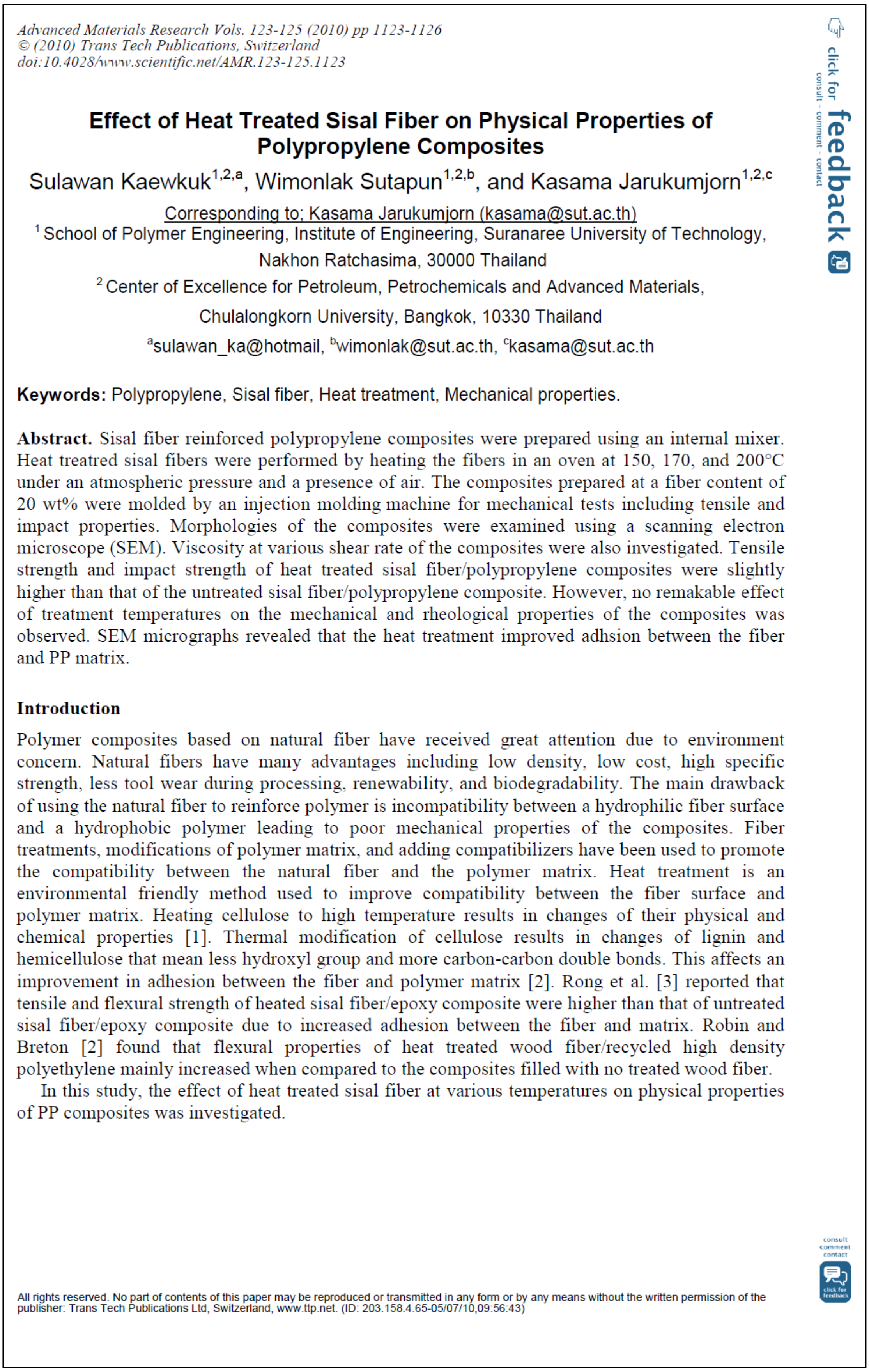

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# Effect of Heat Treated Sisal Fiber on Physical Properties of Polypropylene Composites

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**Keywords:** Polypropylene, Sisal fiber, Heat treatment, Mechanical properties.

**Abstract.** Sisal fiber reinforced polypropylene composites were prepared using an internal mixer. Heat treatred sisal fibers were performed by heating the fibers in an oven at 150, 170, and 200°C under an atmospheric pressure and a presence of air. The composites prepared at a fiber content of 20 wt% were molded by an injection molding machine for mechanical tests including tensile and impact properties. Morphologies of the composites were examined using a scanning electron microscope (SEM). Viscosity at various shear rate of the composites were also investigated. Tensile strength and impact strength of heat treated sisal fiber/polypropylene composites were slightly higher than that of the untreated sisal fiber/polypropylene composite. However, no remakable effect of treatment temperatures on the mechanical and rheological properties of the composites was observed. SEM micrographs revealed that the heat treatment improved adhsion between the fiber and PP matrix.

## Introduction

Polymer composites based on natural fiber have received great attention due to environment concern. Natural fibers have many advantages including low density, low cost, high specific strength, less tool wear during processing, renewability, and biodegradability. The main drawback of using the natural fiber to reinforce polymer is incompatibility between a hydrophilic fiber surface and a hydrophobic polymer leading to poor mechanical properties of the composites. Fiber treatments, modifications of polymer matrix, and adding compatibilizers have been used to promote the compatibility between the natural fiber and the polymer matrix. Heat treatment is an environmental friendly method used to improve compatibility between the fiber surface and polymer matrix. Heating cellulose to high temperature results in changes of their physical and chemical properties [1]. Thermal modification of cellulose results in changes of lignin and hemicellulose that mean less hydroxyl group and more carbon-carbon double bonds. This affects an improvement in adhesion between the fiber and polymer matrix [2]. Rong et al. [3] reported that tensile and flexural strength of heated sisal fiber/epoxy composite were higher than that of untreated sisal fiber/epoxy composite due to increased adhesion between the fiber and matrix. Robin and Breton [2] found that flexural properties of heat treated wood fiber/recycled high density polyethylene mainly increased when compared to the composites filled with no treated wood fiber.

In this study, the effect of heat treated sisal fiber at various temperatures on physical properties of PP composites was investigated.

## Material and methods

A commercial grade isotactic polypropylene (700 J) was supplied from Thai Polypropylene Co., Ltd. Sisal fiber was purchased from sisal-Handicraft OTOP group, Nakhon Ratchasima, Thailand.

**Fiber Preparation.** Sisal fiber was cut into an approximate length of 2 mm. Heat treatment was performed by heating the sisal fiber in an oven at 150°C for 30 min, 170°C for 30 min, and 200°C for 5 min under an atmospheric pressure and in a presence of air. More details of the treatment were reported in Kaewkuk et al. [4].

**Composite Preparation.** The composites were prepared at a fiber content of 20 wt% using an internal mixer (Hakke Rheomix, 3000p). The rotor speed was 50 rpm and the mixing temperature was fixed at 170°C. The total mixing time was 13 min. The test specimens were prepared by an injection molding machine (Chuan Lih Fa, CLF 80T).

**Composite Characterization.** Tensile test of the PP and PP composites were tested by following ASTM D638 using an universal testing machine (Instron, 5565) with a load cell of 5 kN, a crosshead speed of 10 mm/min, and a gauge length of 50 mm. Unnotch impact strength of the PP and PP composites were tested by following ASTM D256 using an impact testing machine (Atlas, BPI). Viscosity at various shear rates (shear rate ranges of 10-1000 $s^{-1}$) were obtained using a capillary rheometer (Kayeness, D5052m) at 170°C. Fracture surfaces of the PP composites were studied using a scanning electron microscope (JEOL, JSM6400) at 10 keV. The composites were freeze-fractured in liquid nitrogen and coated with a thin layer of gold before analysis.

## Results and Discussion

Table 1. Tensile properties and impact strength of PP and sisal/PP composites

| Materials | Tensile strength [MPa] | Young's modulus [GPa] | Elongation at break [%] | Impact strength [kJ/m$^2$] |
|---|---|---|---|---|
| PP | NB | 0.51±0.01 | NB | 79.92±4.25 |
| PP+UT | 24.44±0.49 | 0.87±0.03 | 10.48±0.81 | 15.63±2.90 |
| PP+HT 150°C | 25.14±0.45 | 0.85±0.04 | 12.11±0.76 | 17.08±2.72 |
| PP+HT 170°C | 25.51±0.83 | 0.93±0.03 | 12.10±0.89 | 19.10±1.91 |
| PP+HT 200°C | 24.43±0.52 | 0.87±0.04 | 12.46±1.22 | 17.03±1.60 |

UT: untreated sisal fiber; HT: heat treated sisal fiber
NB = not broken

**Mechanical Properties.** Tensile properties and impact strength of PP and PP composites are listed in Table 1. PP was not broken under the testing condition. With adding fibers into PP, Young's modulus of the composites increased but elongation at break decreased. Tensile strength and Young's modulus of heat treated sisal/PP composites were slightly higher than that of untreated sisal/PP composite. It might be due to a removal of some hemicelluloses and impurities on fiber surface occurred by the heat treatment resulting in the enhancement of interfacial adhesion between fiber and matrix. There was no significant difference in Young's modulus and elongation at break of the heat treated sisal/PP composites. Robin and Breton [2] reported that no significant difference in Young's modulus of the untreated and heat treated wood fiber/HDPE composites was found. However, the heat treatment at various temperatures gave no significant impact on the tensile properties of the PP composites.

Impact strength of PP decreased with adding sisal fiber because the fiber was a stress concentrator as shown in Table 1. Impact strengths of heat treated sisal/PP composites were slightly higher than that of untreated sisal/PP composite because of the removal of low molecular weight compound on fiber surface during heat treatment process. This led to more compatible between the heat treated fibers and PP matrix. However, no remarkable effect of heat treatment on the impact strength of the composites was observed.

**Rheological Properties.** Sisal/PP composites exhibited higher viscosity than that of PP as shown in Fig. 1. This was because the fibers perturbed the flow of polymer and hindered the mobility of chain segments in melt flow. In comparison, the heat treatment process showed no significant effect on the viscosity of the composites. This suggested that the heat treatment did not influence on processing of the composites.

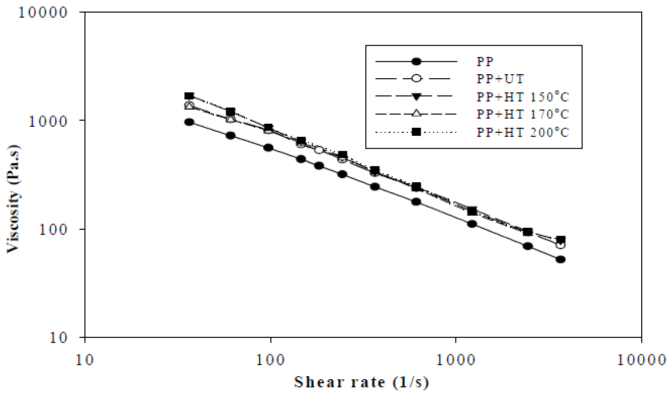
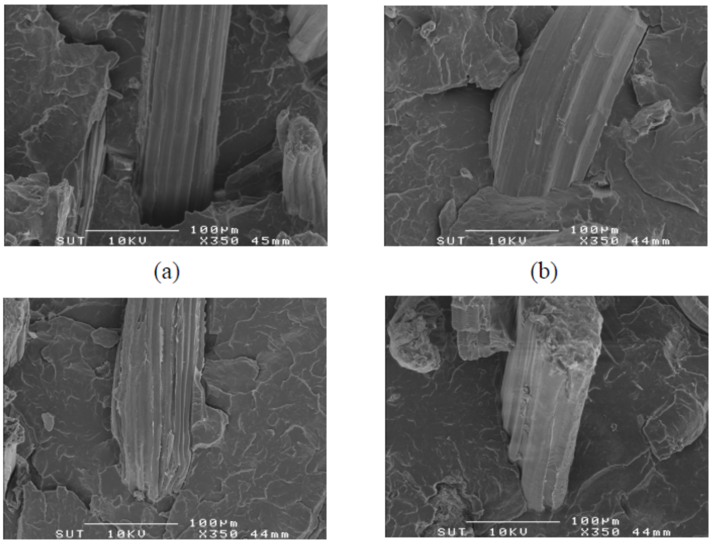


Figure. 1 Plot of viscosity versus shear rates of PP and PP composites prepared with untreated and heat treated sisal fiber at 150°C, 170°C, and 200°C.

**Morphological Properties.** SEM micrographs of PP composites are shown in Fig. 2. The fracture surface of untreated sisal/PP composite in Fig. 2 (a) presented the wider in gab between the fiber and PP matrix. From Fig. 2 (b)-2 (d), the interfacial adhesion between the fiber and PP matrix of the heat treated sisal/PP composites could not be distinguished.



(a) (b)

(c) (d)

Figure. 2 SEM micrographs of surface of (a) UT/PP composite, (b) HT 150°C/PP composite, (c) HT170°C/PP composite, and (d) HT200°C/PP composite.

## Conclusions

Tensile strength and impact strength of heat treated sisal fiber/PP composites were slightly higher than that of the untreated sisal fiber/PP composite. However, there was no remarkable effect of heat treatment on the mechanical and rheological properties of the composites. Surface adhesion between the heat treated fiber and the PP matrix was improved as confirmed by SEM micrographs.

## Acknowledgements

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