EFFECT OF COMPATIBILIZER AND SILANE COUPLING AGENTS ON PHYSICAL PROPERTIES OF NATURAL FIBER-POLYPROPYLENE COMPOSITES

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ผลของสารช่วยให้เข้ากันและสารประสานไซเลนต่อคุณสมบัติทางกายภาพของพอลิเมอร์เชิงประกอบระหว่างเส้นใยธรรมชาติกับพอลิโพรพิลีน

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

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วิทยานิพนธ์นี้เป็นการศึกษาผลของสารช่วยให้เข้ากัน และสารประสานไซเลน ต่อสมบัติทางความร้อน สมบัติทางวิทยกระแส สมบัติทางกล สมบัติทางสัณฐานวิทยา และการดูดซับน้ำของพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใย เส้นใยปอแก้วและป่านศรนารายณ์ถูกใช้ในการศึกษาครั้งนี้ เส้นใยผ่านการทำความสะอาดเบื้องต้นด้วยตัวทำละลายผสม และสารละลายโซเดียมไฮดรอกไซด์ มาเลอิกแอนไฮดรายน์กร๊าฟพอลิโพรพิลีน สารประสานไซเลนชนิดไวนิลไตรเอทรอกซีไซเลน และออกตะเดกซิลไตรเมทรอกซีไซเลน ถูกใช้ในการปรับปรุงการยึดติดที่พื้นผิวระหว่างเส้นใยและพอลิโพรพิลีน พอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยที่ปริมาณเส้นใย 20 เปอร์เซ็นโดยน้ำหนัก ถูกเตรียมโดยใช้เครื่องบดผสมภายใน ชิ้นงานทดสอบถูกเตรียมโดยใช้เครื่องฉีด

การทำความสะอาดด้วยตัวทำละลายผสม และการทำอัลคาไลน์เซชั่น สามารถกำจัดสารน้ำหนักโมเลกุลต่ำ เฮมิเซลลูโลส และลิกนิน ออกจากเส้นใยปอแก้วและป่านศรนารายณ์ได้ ซึ่งส่งผลต่อการลดลงของขนาด และสมบัติการทนแรงดึงของเส้นใย เส้นใยที่มีการดัดแปรด้วยสารประสานไซเลน มีอุณหภูมิการเสื่อมสลายที่สูงกว่าเส้นใยที่ไม่ผ่านการดัดแปร พื้นผิวของเส้นใยที่ผ่านการดัดแปรด้วยสารประสานไซเลน มีลักษณะขรุขระกว่าเส้นใยที่ผ่านการทำความสะอาดด้วยตัวทำละลายผสมและอัลคาไลน์เซชั่น

ความเข้ากันได้ของพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใย สามารถถูกปรับปรุงโดยการใส่มาเลอิกแอนไฮดรายน์กร๊าฟพอลิโพรพิลีน ปริมาณมาเลอิกแอนไฮดรายน์กร๊าฟพอลิโพรพิลีนที่ใช้คือ 1, 2, 4, 6, 8 และ 10 ส่วนใน 100 ส่วนของพอลิเมอร์เชิงประกอบ การยึดติดระหว่างเส้นใยกับเมทริกซ์ ถูกทำให้เพิ่มขึ้นได้ด้วยการใส่มาเลอิกแอนไฮดรายน์กร๊าฟพอลิโพรพิลีนซึ่งนำไปสู่การปรับปรุงสมบัติทางกล มาเลอิกแอนไฮดรายน์กร๊าฟพอลิโพรพิลีน ยังส่งผลต่อค่าอุณหภูมิการตกผลึก ปริมาณผลึก อุณหภูมิการเสื่อมสลายของพอลิโพรพิลีน และอุณหภูมิการบิดงอของพอลิเมอร์เชิงประกอบ ปริมาณมาเลอิกแอนไฮดรายน์กร๊าฟพอลิโพรพิลีนที่เหมาะสมสำหรับพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยปอแก้ว และพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์ คือ 2 ส่วน ใน 100 ส่วนของพอลิเมอร์เชิงประกอบ

ค่าการทนแรงดึงและมอดุลัสของยังค์ ของพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยปอแก้วที่ผ่านการดัดแปรด้วยสารประสานไซเลนชนิดไวนิลไตรเอทรอกซีไซเลน มีค่าสูงกว่าพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยปอแก้วที่ไม่ผ่านการปรับปรุง อย่างไรก็ตาม การใส่เส้นใยปอแก้วที่ผ่านการดัดแปรด้วยสารประสานไซเลน ชนิดออกตะเดกซิลไตรเมทรอกซีไซเลน ไม่ส่งผลเชิงบวกต่อสมบัติทางกล การดูดซับน้ำของพอลิเมอร์เชิงประกอบระหว่าง พอลิโพรพิลีนกับเส้นใยปอแก้ว ที่ผ่านการดัดแปรด้วยสารประสานไซเลนทั้งชนิดไวนิลไตรเอทรอกซีไซเลน และออกตะเดกซิลไตรเมทรอกซีไซเลนจะมีค่าลดลง ในกรณีของพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์นั้น การดัดแปรด้วยสารประสานไซเลนทั้งชนิดไวนิลไตรเอทรอกซีไซเลน และออกตะเดกซิลไตรเมทรอกซีไซเลน ไม่ส่งผลต่อสมบัติทางความร้อน สมบัติทางกล และสมบัติทางวิทยกระแส แต่ค่าการดูดซับน้ำมีแนวโน้มต่ำกว่าพอลิเมอร์เชิงประกอบที่ไม่ผ่านการปรับปรุง เวลาการดัดแปรของสารประสานไซเลน ทั้งชนิดไวนิลไตรเอทรอกซีไซเลนและออกตะเดกซิลไตรเมทรอกซีไซเลน ไม่ส่งผลอย่างมีนัยสำคัญต่อสมบัติทางกลของพอลิเมอร์เชิงประกอบพอลิโพรพิลีน

พอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยปอแก้ว ให้ค่าการทนแรงดึง และมอดุลัสของยังค์ ต่ำกว่าพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์ ในกรณีของพอลิเมอร์เชิงประกอบที่ไม่ผ่านการการปรับปรุง สำหรับการปรับปรุงด้วยมาเลอิกแอนไฮดรายน์กร๊าฟพอลิโพรพิลีนนั้น พอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยปอแก้ว ให้ค่าการทนแรงดึง และมอดุลัสของยังค์ สูงกว่าพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์

สาขาวิชา <u>วิศวกรรมพอลิเมอร์</u>	ลายมือชื่อนักศึกษา_______________________
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THANATIWAT NARAPRATEEP : EFFECT OF COMPATIBILIZER AND SILANE COUPLING AGENTS ON PHYSICAL PROPERTIES OF NATURAL FIBER-POLYPROPYLENE COMPOSITES. THESIS ADVISOR : ASST. PROF. KASAMA JARUKUMJORN, Ph.D. 118 PP.

PP/ NATURAL FIBERS/ COMPOSITE/ MAPP/ SILANE COUPLING AGENT

In this thesis, the effects of compatibilizer and silane coupling agents on thermal properties, rheological properties, mechanical properties, morphological properties, and water absorption of fibers-PP composites were studied. Rossells and sisal fiber are used in this study. The fibers were pretreated with mixed solvent and sodium hydroxide (NaOH) solution. Maleic anhydride grafted polypropylene (MAPP), vinyltriethoxysilane (VTES) and octadecyltrimethoxysilane (OTMS) were used to improve the surface adhesion between the fibers and PP. The fibers-PP composites with 20 wt% fibers loading were prepared using an internal mixer. The test specimens were molded using injection molding machine.

Cleaning with mixed solvent and alkalization were able to remove low molecular weight species, hemicellulose and lignin from the rossells and sisal fibers. This resulted in the decreasing of diameter and tensile strength of the fibers. Silane treated fibers had higher degradation temperature than untreated fibers. Surface of silane treated fibers was rougher than the fibers that cleaning with mixed solvent and alkalization.

Compatibility of the fibers-PP composites could be improved by adding MAPP. MAPP contents were 1, 2, 4, 6, 8, and 10 phr. The adhesion between fibers and matrix was enhanced with addition of MAPP leading to improve the mechanical properties. MAPP also affected on crystallization temperature, crystallinity, decomposition temperature of PP, and HDT of the composites. The optimum content of MAPP for rossells-PP composites and sisal-PP composites was 2 phr.

Tensile strength and Young's modulus of VETS treated rossells-PP composites were higher than that of unmodified rossells-PP composites. However, adding OTMS treated rossells into PP yielded no positive on impact strength, tensile strength and Young's modulus. Water absorption of both VTES and OTMS treated rossells-PP composites slightly decreased. In the case of silane treated sisal-PP composites, both VTES and OTMS treatment did not affect on the thermal, mechanical, and rheological properties but water absorption slightly lower than unmodified composite. Treatment times of both VTES and OTMS showed no significant effect on mechanical properties of PP composites.

Rossells-PP composite gave lower tensile strength and Young's modulus than sisal-PP composite in the case of unmodified composites. For the MAPP modification, rossells-PP composite gave higher tensile strength and Young's modulus than sisal-PP composite.

School of Polymer Engineering
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SYMBOLS AND ABBREVIATIONS

% = Percent

ºC = Degree Celsius

μm = Micrometer

cm = Centimeter

Deriv. = Derivative

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

rpm = Revolution per minute

SYMBOLS AND ABBREVIATIONS (Continued)

wt% = Percent by weight

wt/v = Weight by volume

wt/wt = Weight by weight

CHAPTER I

INTRODUCTION

1.1 General introduction

The natural fibers reinforced thermoplastics have gained more attention because of their good processability, high specific modulus, and ability to be recycled. Comparing with traditional reinforcing materials e.g. glass and carbon fibers, natural fibers have many advantages such as low cost, low density, reduced tool wear, biodegradability, and renewability. (Valadez-Gonzalez, Cervantes-Uc, Olayo, and Herrera-Franco, 1999). In addition, natural fibers reduce skin dermal and respiratory irritation during handling compared to glass fibers (Arbelaiz et al., 2005). The natural fiber-reinforced thermoplastic composites are widely used in many applications such as automotive parts e.g. door panels in Mercedes, rear-shelf panel of the 2000 Chevrolet, and a part of golf cars produced in Germany (George, Sreekala, and Thomas, 2001).

Jute and sisal fibers are widely used to reinforce plastics due to high tensile strength and stiffness (Bledzki and Gassan, 1999). Moreover, they are readily available from natural sources at a low price (Valadez-Gonzalez, Cervantes-Uc, Olayo, and Herrera-Franco, 1999). They compose of cellulose, hemicellulose, lignin, pectin, waxes, and water-soluble substances. These components have physical and mechanical properties that make them suitable to reinforce plastics. Cellulose, hemicellulose, and lignin are the basic components that involve in the physical properties of fibers.

Hemicellulose is responsible for the biodegradation, moisture absorption, and least thermal resistance whereas lignin couples fiber bundles together and thermally stable (Bledzki and Gassan, 1999).

Polypropylene (PP) is one of the most popular matrices to produce natural fibers reinforced composites. The advantages of PP are low cost, easy molding, low processing temperature, and high heat stability. However, main disadvantage of using natural fibers to reinforce PP is their hydrophilic nature that lowers the compatibility with the hydrophobic PP. The compatibility between natural fibers and PP matrix can be improved by chemical modifications of the fibers or addition of compatibilizers.

Maleic anhydride grafted polypropylene (MAPP) is known to be an effective compatibilizer for natural fibers-PP composites (Arbelaiz et al., 2005). MAPP is able to compatibilize polar natural fibers and non-polar polymer matrix. The chemical (ester bond) and physical interaction can be formed between hydroxyl groups of the fibers and anhydride groups of MAPP. While PP chains of MAPP diffuse into the PP matrix, by which the physical interaction (entanglements) is formed. Therefore, the surface adhesion between fibers and matrix can be improved by use of MAPP compatibilizer (Doan et al., 2006).

Furthermore, chemical modification of natural fibers with silane coupling agents enhances surface adhesion between fibers and hydrophobic PP due to the reduction of hydrophilic nature of fibers. Varma, Krishnan, and Krishnamoorthy (1987) studied the treatment of jute fibers with γ-aminopropyltrimethoxy silane, which is capable of reacting with hydroxyl groups of fibers. The result showed that the water uptake of the treated fibers is reduced because of the reduction of hydrophilic nature of the fibers. In addition, treatment of flax fibers with vinyltrimethoxysilane (VTMS) highly decreased the polarity of the fibers and reduced the hydrophilic nature of the fibers (Cantero et al., 2003).

1.2 Research objectives

The main objectives of this study are as follow:

(i) To investigate thermal properties, rheological properties, mechanical properties, morphological properties, and water absorption of rossells-PP and sisal-PP composites.

(ii) To evaluate the effect of compatibilizer and silane coupling agents on the properties of the rossells-PP and sisal-PP composites.

(iii) To compare the mechanical properties of rossells-PP composites and sisal-PP composites.

1.3 Scope and limitation of the study

In this study, rossells and sisal fibers were used to reinforce polypropylene. The effect of compatibilizer and fiber treatment with silane coupling agents on thermal properties, rheological properties, mechanical properties, morphological properties, and water absorption of fibers-PP composites were studied. The fibers were cleaned with solvent mixtures and sodium hydroxide (NaOH) solution. Maleic anhydride grafted polypropylene (MAPP), vinyltriethoxysilane (VTES) and octadecyltrimethoxy silane (OTMS) were used to improve the surface adhesion between fibers and matrix. The composites with 20 wt% fibers loading were prepared using an internal mixer, and the test specimens were molded by injection molding machine. The effects of compatibilizer contents at 1, 2, 4, 6, 8, and 10 phr and silane treatment times at 3 and

24 hrs on the properties of rossells-PP and sisal-PP composites were investigated. In addition, the mechanical properties of rossells-PP composites and sisal-PP composites were compared.

CHAPTER II

LITERATURE REVIEW

2.1 Interfacial modification of fiber and matrix

2.1.1 Fiber surface treatments

2.1.1.1 Alkalization

Several researchers investigated the effect of alkalization on thermal and physical properties of natural fiber in the past decade. Bisanda (2000) examined the effect of alkali treatment on the wettability and coherence of sisal-epoxy composites. The sisal fiber was treated with a 0.5% Sodium hydroxide (NaOH). The results presented that surface adhesion between sisal and epoxy was enhanced due to a reduction of surface tension and an increase of surface roughness of fibers. Improvements in the compressive strength and water resistance of the resulting composites were found. The removal of intracrystalline and intercrystalline lignin and other surface waxy substances by the alkalization enhanced the possibility for mechanical interlocking and chemical bonding.

Ray and Sarkar (2001) investigated the changes occurring in jute fibers after a 5% NaOH solution treatment for different periods of 0, 2, 4, 6, and 8 hrs. A 9.63% weight loss was measured during 2 hrs of 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, and the percent breaking strain was reduced by 23% after 8 hrs of the treatment. The crystallinity of the fibers increased only after 6 hrs of the treatment, as evident from the x-ray diffractrograms. In addition, FTIR spectrums presented the change of 2 hrs fiber treated with an increment of OH groups.

Ray, Sarkar, and Bose (2002) examined the impact fatigue behavior of vinylester matrix composites reinforced with untreated and alkali treated jute fibers. Longer time of alkali treatment increased the crystallinity and gave better fiber dispersion due to the removal of hemicellulose. The alkalization at 4 hrs was the optimum treated time to improve the interfacial bonding and fiber strength. The flexural strength of alkali treated jute fiber composites was higher than the untreated jute fiber composites. This might be caused the alkali treated jute fiber was more surface area to adhere polymer matrix due to the splitting of microfibrillar as evident from SEM micrographs.

Ray, Sarkar, Basak, and Rana (2002) treated jute fiber with 5% NaOH for 2, 4, 6, and 8 hrs. The results of thermal analysis showed that the moisture desorption was observed at a lower temperature in the case of all treated fibers. It might be a result of fiber fineness, which provided more surface area for moisture evaporation. The moisture loss of alkali treated jute fiber for 6 and 8 hrs decreased due to the increase of crystallinity of fibers. The percent degradation of hemicellulose decreased considerably in all the treated fibers. This was a fact that the hemicellulose content was reduced by the alkalization. The decomposition temperature for α-cellulose of all treated fibers changed from 362.2ºC to 384ºC, and the residual char formation increased to a significant extent. In addition, the enthalpy of α-cellulose degradation slightly decreased due to the loss of hemicellulose.

Mwaikambo and Ansell (2002) studied thermal resistance, crystallinity index, and surface morphology of untreated and alkali treated natural fibers. The concentration of NaOH solution affected on thermal resistance of the fibers. DSC results showed a rapid degradation of cellulose between 0.8 and 8% NaOH, beyond these the degradation was found to be a little. There was insignificant drop in the crystallinity index of hemp fiber while sisal, jute, and kapok fibers slightly increased in crystallinity index at the NaOH concentration of 0.8-30%. SEM micrograph of all untreated fibers showed a relatively smooth surface whereas, all alkali treated fibers showed uneven surfaces due to the loss of low molecular weight species and hemicellulose.

Sydenstricker, Mochnaz, and Amico (2003) studied the thermal properties of NaOH treated sisal fibers. Lignin content and density of fibers were reduced with NaOH treatment. In addition, NaOH treatment affected on a significant reduction in moisture absorption of sisal fiber. TGA thermograms showed the NaOH treated fiber became more thermally resistant than the untreated fiber.

Razera and Frollini (2004) investigated the effect of NaOH treatment on the physical properties of jute-phenolic resin composites. Jute fiber was treated with a 5% NaOH solution. The tensile strength, impact strength, and elongation at break of NaOH treated fiber composites were the highest while the water uptake was the lowest. SEM micrograph of the impact fracture surface revealed that the alkali treated fibers embedded with the matrix greater than untreated fibers. Furthermore, the pull-out mechanism could be observed in the case of untreated jute fiber. The improvement of surface adhesion between jute fibers and phenolic resin might be caused from the NaOH treatment contributed the reaction of hydroxymethyl and hydroxyl groups of phenolic resin and jute fibers, respectively.

2.1.1.2 Silanization

Varma, Krishnan, and Krishnamoorthy (1987) studied the treatment of jute fibers with γ-aminopropyltrimethoxy silane. The moisture uptake of the silane-treated fibers reduced approximately by 30-40%. A decrease of weight loss in the region 50-150ºC of the treated fibers indicated that this treatment had imparted the moisture repellency from the fibers. Silane-treated jute fibers showed an increase in the residual weight, perhaps because silicon moieties were incorporated on the fibers.

Herrera-Franco and Aguilar-Vega (1997) studied the mechanical properties of silane-treated henequen fiber-LDPE composites. The modified fiber with a vinyltris (2-methoxy-ethoxy) silane was carried out in a 1 wt% carbon tetrachloride at 70ºC with dicumyl peroxide as the catalyst. SEM micrograph of the failure surface of the composite revealed that silane-treated fibers were still coated with the matrix. The use of silane coupling agent resulted in a small increment in the mechanical properties of the composites, which was attributed to an improvement in the surface adhesion between fibers and the matrix. In addition, silane coupling agent could be used to improve a fiber dispersion of the composite.

Valadez-Gonzalez, Cervantes-Uc, Olayo, and Herrera-Franco (1999) modified short henequen fibers with a 0.5% wt/wt dicumyl peroxide and 1% wt/wt vinyltris (2-methoxy-ethoxy) silane coupling agent. The fibers were immersed in silane solution for 1 hr. Its deposition mechanism on the fiber surface and the influence of this chemical treatment on the mechanical properties of the HDPE composites were investigated. FTIR spectra of silane treated fibers revealed the absorption bands at 700, 1030, 1145 and 1187 cm^{-1}, which were assigned to -Si-O-Si- bond. The shoulders at 965 and 1200 cm^{-1} indicated the characteristic of the -Si-O-C- bond that came from the reaction of silane and the henequen fibers. The absorption bands at 860 and 930 cm^{-1} corresponding to the -Si-OH bond revealed the presence of residual hydrolyzed silane. The partial removal of lignin and other alkali soluble compounds from the fiber surface by the alkali treatment increased the absorption of the silane coupling agent. The tensile strength of modified composite was higher than the unmodified composite. The interaction between the fiber and the matrix was enhanced when the fiber surface was modified with the silane coupling agent. The interaction between silane-treated fibers and polymer matrix seem to be stronger than that of the untreated fibers. The fracture surface of modified composite revealed both fiber and matrix failed simultaneously. The fiber pulled out was not observed.

Singh, Gupta, Verma, and Tyagi (2000) treated sisal fibers with γ-methacryloxypropyltrimethoxysilane (silane A-174) coupling agent. An irregular physisorption/chemisorption of coupling agent reduced the hydrophilicity of the fibers. The water absorption of treated fibers had been reduced significantly similar to the polar component of surface free energy. When treated sisal fiber was used as reinforcement in an unsaturated polyester resin matrix, the composites absorbed less moisture than those prepared from untreated fibers. Tensile strength and flexural strength improved about 15-33% and 21-29%, respectively. Surface modification of the fiber enhanced surface adhesion because it was involved in chemisorbed layers on the fiber surface and chemical bond formation with the unsaturated polyester resin.

2.1.1.3 Treatment with maleated polypropylene

Gassan and Bledzeki (1997) studied the effectiveness of maleated polypropylene (MAPP) as a coupling agent in the jute-PP composites. The fibers were first dewaxed in an alcohol solution for 24 hrs to remove the weaving size (potato starch and waxes). The MAPP treatment was carried out in the toluene solution with different MAPP contents at 100ºC for 5 and 10 min. The effectiveness of the treatment depended on concentration and treatment time. The most noticeable increase in performance was obtained with a 5 min application of the MAPP in a toluene solution of 0.1 wt%. Flexural strength of MAPP treated jute-PP composites was higher than that of unmodified fibers composites. Flexural strength and modulus of MAPP treated jute-PP composites were increased by 40% and 90%, respectively. The cyclic-dynamic values indicated that the coupling agent reduced the progress of damage. The dynamic strength of MAPP modified fiber composites was raised by about 40%. SEM micrograph of composites demonstrated that fiber pull-out was reduced after the modification of fibers with MAPP. The improvement in fiber-matrix adhesion was due to the chemical bonds between fiber and matrix. This caused an increase in stress transfer from matrix to fibers.

Cantero, Arbelaiz, Ponte, and Mondragon (2003) studied the treatment of flax fiber with MAPP. A 5 and 10 wt% MAPP were dissolved in boiling xylene. The fiber was soaked in the solution at a ratio of 1:25 (wt/v) for 5 or 6 min. The test specimens containing 30 wt% flax fiber had been formed by twin-screw extrusion and injection molding. FTIR spectrum of MAPP treated fiber revealed the formation of new ester groups (1800 and 1600 cm^{-1}) between hydroxyl groups of cellulose and MAPP. The MAPP treatments of flax fiber seem to be effective treatment to improve the compatibility between flax fiber and PP matrix. The MAPP treatment reduced a polar component and surface energy of the fiber. Thus, the wettability of flax fiber with PP matrix could be improved by the action of MAPP treatment due to the reduction of polar component and surface energy of the fiber.

2.1.1.4 Acetylation

Rana, Basak, Mitra, Lawther, and Banajee (1997) studied thermal properties and surface morphology of acetylated jute fibers. The derivative thermo gravimetric analysis (DTGA) curves of acetylated jute fibers presented that the shoulder of hemicellulose decomposition was missing and weight loss at the major degradation step (373ºC) increased. The main decomposition temperature increased from 363.0 to 373.0ºC, which indicated that the thermal stability of the acetylated jute fibers was higher than untreated fibers. DSC thermograms of acetylated jute fibers showed that the moisture content at the first peak was very low (1.6%) and the main decomposition peak was shifted to a higher value (370.8ºC). This revealed that the thermal stability of the acetylated jute fibers was improved. SEM micrographs presented that the acetylation could be reduced the gaps between the fibrils of the fiber. These might be due to the reaction of the acetyl group and hydroxyl groups of the fiber.

Mwaikambo and Ansell (1999) studied the effect of chemical treatments on the physical and thermal properties of hemp, sisal, jute, and kapok. The natural fibers had been treated with various concentrations of NaOH solution with the objectives of removing surface impurities and developing fine structure. The same fibers were also acetylated with and without an acid catalyst to graft acetyl groups onto the cellulose structure in order to reduce the hydrophilic tendency of the fibers and enhance weather resistance. After alkali treatment, the surface topography of the natural fibers was clean and rough except kapok fibers. X-ray diffraction presented that the crystallinity index of the fibers slightly increased at low NaOH concentration. However, at high NaOH concentrations the crystallinity index of fiber was lower than that of low NaOH concentration. DSC thermograms of the fibers also indicated that the reduction in the crystallinity index was optimized at elevated temperatures with the increase of NaOH concentration and grafting percent. Alkalization and acetylation had successfully modified the structure of the natural fibers and improved the performance of natural fiber composites by promoting better fiber to resin bonding.

Albano, Gonzalez, Ichazo, and Kaiser (1999) studied the effect of acetylation on thermal degradation of sisal fiber. The shoulder of hemicellulose decomposition of acetylated sisal fiber was missing and weight loss at the major degradation step (385ºC) increased. This might mean that the acetylation increased the thermal stability of fiber. The residue left at 427ºC of acetylated sisal fiber was less than the untreated sisal fiber due to the loss of volatile products that did not contribute to char formation. The higher thermal stability of acetylated sisal fiber than untreated fiber might be attributed to the substitution of OH groups, which brought about restrictions in the segmental mobility, thereby increasing the stiffness of the cellulose backbone.

Ichazo, Albano, and Gonzalez (2000) studied the influence of acetylation on the surface morphology of sisal-PP composites. The microfibers forming of acetylated sisal fibers could be seen clearly. This treatment affected on the wettability property and the fibrillation. The improvement in the wettability property and enhancement in aspect ratio offered better fiber-matrix interface adhesion and an increase in mechanical properties. Furthermore, the treatment produced a number of small voids on the sisal surface that promoted mechanical interlocking between the fiber and matrix.

2.1.1.5 Functionalization with maleic anhydride monomer

Cantero, Arbelaiz, Ponte, and Mondragon (2003) investigated 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. The test specimens containing 30 wt% flax fiber had been formed by twin screw extrusion and injection molding. The spectrums zone between 1800 and 1600 cm^{-1} of FTIR analysis related to the formation of new ester groups between hydroxyl groups of cellulose and MA. MA treatment led to more intense peak at about 1735 cm^{-1}, associated with carbonyl (C=O) stretching of acetyl groups of hemicellulose due to the esterification reaction.

Arbelaize, Fernandez, Ramos, and Mondragon (2006) studied the effect of MA treatment on the thermal stability of flax fiber. Flax fiber was treated with 10 wt% MA for 25 hrs. MA was dissolved in boiling acetone at temperature of 50±5ºC. The result of thermogravimetric analysis (TGA) indicated that the treated flax fiber became more hydrophobic after the treatment. Moisture content of MA treated flax fiber was lower than that of the untreated fiber.

2.1.1.6 Functionalization with other monomers or polymers

Escamilla et al. (1999) investigated the properties of cellulose fibers and polymethyl methacrylate (PMMA) or polybutylacrylate (PBA) grafted cellulose fibers. The results showed that the molecular weight of grafted cellulose fibers decreased while the crystallinity increased with an increment of initiator (cericammonium nitrate) concentration. The amorphous zone of the fibers was exposed to the oxidation by the initiator. Therefore, the elastic modulus and tensile strength were reduced at a high initiator concentration. During the grafting process, the degradation of cellulose was partially inhibited. The effect of initiator on the mechanical properties was less affected in the grafted cellulose fiber. Mechanical properties of PMMA- or PBA-grafted cellulose fiber were lower than that of ungrafted cellulose fiber. The reduction of the elastic modulus of grafted fiber was independent of the amount of grafted PMMA or PBA, but the tensile strength decreased with the PBA content on the PBA-grafted fiber. The mechanical properties of PMMA-grafted cellulose fiber were superior to PBA-grafted cellulose fiber when they were used to reinforced plasticized PVC composites.

Saha, Das, Basak, and Mitra (2000) improved mechanical properties and dimensional stability of jute-based polyester composite by cyanoethylation process. An acrylonitrile monomer was used to react with the hydroxyl groups of fiber constituents. IR result showed that the extent of cyanoethylation increased with an increase of the reaction time. Water absorption and thickness swelling of composites were much reduced. The mechanical properties of the modified fiber composites improved remarkably due to better bonding at the fiber-matrix interface. This effect was more pronounced with a higher degree of cyanoethylation. The fractured surface of cyanoethylated jute composite showed the excellent retention of resin on broken fiber ends while the unmodified jute composite revealed a clean fiber and holes of fibers in the matrix.

Mishra, Misra, Tripathy, Nayak, and Mohanty (2001) studied the graft copolymerization of acrylonitrile (AN) on chemically modified sisal fibers using a combination of sodium periodate ($NaIO_4$) and copper sulfate ($CuSO_4$) as initiators. The effect of reaction medium, variation of time and temperature, concentration of $CuSO_4$, $NaIO_4$ and AN, and the liquor ratio on the percentage of graft yield had been investigated. $[IO_4^-] = 0.008$ mol.L^{-1} and $[Cu^{2+}] = 0.002$ mol.L^{-1} produced an optimum grafting for use of 0.1 g chemically modified sisal fiber and 1 ml AN at 60ºC. At low percent grafting (5% grafting), the fiber gave the best tensile strength and modulus. The AN-grafted sisal fibers were expected to act as compatible reinforcing fibers with several hydrophobic resin systems both thermoplastics and thermosetting.

2.1.2 Addition of compatibilizer

Rana et al. (1998) studied the effect of MAPP as a compatibilizer on the mechanical properties of jute-PP composites. The sharp increase in the mechanical properties and decrease in water absorption values after addition of the compatibilizer were found. It might be attributed to linkage between the hydrophilic groups of jute and anhydride groups of the compatibilizer. At 60 wt% of fiber loading, MAPP improved the flexural strength as high as 100%, tensile strength 120%, and impact strength (unnotched) 175%. The improvement was attained even with 1% compatibilizer only.

Rana, Mitra, and Banerjee (1999) studied the effect of MAPP as a compatibilizer on the improvement in the molecular interaction between jute and PP. The dynamic properties of different weight fractions of jute fiber indicated a possible improvement in the molecular interactions with the presence of the compatibilizer. The reduction of modulus retention term with the weight fraction of jute fiber also indicated the effect of compatibilizer.

Joseph, Rabello, Mattoso, Joseph, and Thomas (2002) studied the environmental degradation behaviour of short sisal-PP composites. MAPP was used as a compatibilizer. Water absorption of modified sisal-PP composites was reduced compared with the untreated sisal-PP composite due to the improvement in fiber-matrix adhesion. The compatibilizer built up chemical bonds and hydrogen bonds, which reduced the moisture-caused fiber-matrix debonding. The reduction of hydrophilic nature of sisal fiber resulted in a strong interfacial adhesion between fibers and PP matrix.

Doan, Gao, and Madar (2006) studied the mechanical performances and environmental aging resistance of natural fiber reinforced polypropylene composites. The addition of 2 wt% MAPP significantly improved the adhesion strength with jute fibers and affected the mechanical properties of composites. Tensile strength of fiber actually increased with jute fiber cross-sectional area at a constant gauge length, and associated with its perfect circle shape. An increase of the tensile strength of the jute-PP composites in humidity aging conditions was attributed to the improvement in interfacial adhesion strength.

2.2 The study of composite properties

2.2.1 Thermal properties

Ichazo, Albano, Gonzalez, Perera, and Candal (2001) investigated thermal properties of modified wood flour (WF) reinforced polypropylene composite. The WF was treated with 18 wt% NaOH solution and then treated with 1 wt% vinyltris (2-methoxy-ethoxy) (VTES) silane. In addition, MAPP was used as a compatibilizer to improve the thermal properties of composites. The crystallization temperature (T_c)

increased about 7ºC when the untreated WF was added to PP. While, T_c increased about 13ºC both VTES treated WF-PP composites and MAPP compatibilized WF-PP composites. The increasing of T_c indicated that the processing of these composites need less molding time and energy than virgin PP since it had a short time for cooling. Melting temperature (T_m) practically did not change neither with the addition of WF nor with the different treatment.

Joseph et al. (2003) studied the thermal behaviour of sisal-PP composites by thermogravimetric analysis. MAPP was used as a compatibilizer. The extent of degradation of MAPP modified sisal-PP composites at a given temperature was less than that of unmodified sisal-PP composite. The improvement in the fiber matrix adhesion could be attributed to the esterification reaction between cellulose fiber hydroxyl groups and anhydride functionality of MAPP. The incorporation of sisal fiber in PP caused an apparent increase in the crystallization temperature (T_c) and percentage of crystallinity. The MAPP modified sisal-PP composites showed superior percentage of crystallinity compared with the unmodified composite.

Qiu, Endo, and Hirotsu (2006) studied the effect of MAPP on thermal properties of fibrous cellulose reinforced polypropylene composite. The fibrous cellulose was prepared by the manufacturer of cotton, which consisted of 99% alpha cellulose and numerous hydroxyl groups. The composites with a 30 wt% fibrous cellulose were prepared by internal mixer at the temperature of 190ºC, rotor speed of 55 rpm for 20 min. The addition of cellulose resulted in a remarkable increase in crystallization temperature (T_c) and onset temperature (T_{onset}) of PP matrix. This was attributed to the cellulose fibers acted as an efficient nucleating agent for the crystallization of PP. When MAPP was used as a compatibilizer, the nucleation rate of the composite was increased. This was indicated a strong interaction between cellulose fibers and the PP matrix, which compatibilized by MAPP. Thus, the nucleating activity of cellulose fibers for PP was improved. However, the improvement in nucleating rate induced by MAPP was maintained constantly after MAPP reached to a critical amount.

2.2.2 Rheological properties

George, Janardhan, Anand, Bhagawan, and Thomas (1996) studied the melt rheological behaviour of short pineapple fiber reinforced low density polyethylene composite. The fibers were first treated with alkalization, and then treated with vinyltris (2-methoxy-ethoxy) silane. The composites were prepared by solution mixing technique. The measurement of rheological behaviour was carried out using capillary rheometer at different plunger speeds. The viscosity of the composite was increased with the chemical treatment. Silane treatment enhanced adhesion at the polymer-fiber interface. This was attributed to the reaction between $-OR_2$ groups of silane and –OH groups of fiber. The resulting of –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 could adhere to PE due to van der Waal’s type adhesive forces. Therefore, the adhesion between polymer and fiber was enhanced and affected on the increasing of the viscosity.

Nair, Kumar, Thomas, Schit, and Ramamurthy (2000) studied the rheological behaviour of short sisal fiber reinforced polystyrene (PS) composites as a function of fiber loading, fiber length, shear rate, and temperature. 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 of PS decreased with increasing of temperature. However, the viscosity of sisal-PS composites increased with the increasing of temperature. This might be due to the change of interaction between the fibers and polymer molecules at a higher temperature. Melt flow index of the sisal filled PS composite at a given temperature was lower than that of pure PS. This suggested that degree of pseudoplasticity of the composite was higher than pure PS. The die swell ratio was decreased rapidly at 10% fiber loading, followed by a leveling off at higher fiber loading. The uniform extrudate was observed at lower than 10% fiber loading but the maximum distortion and non-uniformity of the extrudate was observed at 10% fiber loading.

Fung, Li, and Tjong (2002) studied the effect of MAPP on the rheological properties of sisal fiber reinforced polypropylene composites. The MAPP modified sisal fiber-PP composites had lower melt viscosities than the unmodified sisal fiber-PP composite as indicated by torque-rheometer measurements. This was attributed to the improvement in fiber-matrix interfacial bonding between sisal fibers and matrix.

2.2.3 Mechanical properties

Mishra, Naik, and Patil (2000) studied the use of banana, hemp, and sisal fibers as fillers in phenol-formaldehyde (novolac) resin. The surface of these fibers was treated with MA. The modulus of the untreated fiber composites increased with an increase in the fiber content until 45% beyond this content, the modulus slightly decreased. For MA treated fiber composites, modulus was increased with an increase of fiber content until 50%. The tensile strength, impact strength and hardness of MA treated fiber composites were also higher than that of untreated fiber composites. The increase in mechanical properties of MA-treated fibers composites was caused from the enhancement of interfacial adhesion between fiber and matrix due to the esterification of MA and fibers surface.

Cantero, Arbelaiz, Ponte, and Mondragon (2003) treated flax fiber with MA, MAPP and vinyltris (2-methoxy-ethoxy) silane (VTMO). MAPP treatement was the only treatment that led to improve the strength of composites. MA treatment produced the highest modulus values. This fact could be related to the variations on the OH absorption bands in this treatment. A higher strength of MAPP treated fiber composites was possibly related to a better fiber-matrix interphase. This might be attributed to the surface energy of PP chains of the MAPP was similar to the PP matrix, helping to achieve a better wetting between fibers and PP matrix. VTMO treatment produced a slight improvement in the flexural strength. The decreasing in polarity due to VTMO treated fiber allowed a better miscible between cellulose and PP matrix, thereby led to a strong interphase than that of untreated fiber composites.

Arbelaiz et al. (2005) studied the effect of two different MAPP compatibilizers, Epolene E43 and G3003 on the mechanical properties of flax fiber-PP composites. Epolene E43 had a low molecular weight and acid number of 45. On the other hand, Epolene G3003 had a higher molecular weight but acid number lower than Epolene E43. 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 until maximum compatibilizer content. The maximum improvement in the tensile strength for E43 and G3003 were 42% and 58%, respectively. After adding only 1 wt% of the compatibilizers, the composites strength of both types of MAPP clearly increased. The maximum tensile strength for both MAPP modified composites was found at 5 and 10 wt%. The tensile strength of MAPP modified composites seemed to be more effective than the unmodified composites due to a better stress transfer from the matrix to the fiber. Modulus values slightly increased when MAPP was added. Nevertheless, at a high compatibilizer content (20 wt%) the modulus showed a small drop. The impact strength decreased drastically when the flax fiber was added for both unmodified and MAPP-modified composites. 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% MAPP, which could be attributed to the migration of a compatibilizer from the fibers to the matrix. This caused a self-entanglement between the compatibilizer chains rather than with the matrix affected in the slippage.

2.2.4 Morphological properties

Karnani, Krishnan, and Narayan (1997) investigated of the effect of modification of PP matrix by reacting with MA on the morphology of kenaf-PP composites. SEM micrograph of uncompatibilized composite revealed some fiber pull-out. The improvement in bonding between fiber and the matrix of the compatibilized composite was clearly seen. A few amount of polymer residue remained on the fiber surface.

Ichazo, Albano, Gonzalez, Perera, and Candal (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% vinyltris (2-methoxy-ethoxy) silane. MAPP was also used as a compatibilizer. A better polymer-filler adhesion was found in modified WF composites due to an increase in the thickness of interface between WF and polymer matrix.

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

Bos, Mussig, and van den Oever (2006) studied the surface morphology of flax fiber-PP composites. In case of unmodified flax fiber-PP composites, the fibers were clearly loosed in the sockets whereas the surface morphology of MAPP-modified composites presented fully coated with the PP matrix. Thus, it was concluded that the compatibilizer could be used to improve surface adhesion between fiber and PP.

Qiu, Endo, and Hirotsu (2006) studied the effect of MAPP on the morphological properties of fibrous cellulose reinforced polypropylene composite using a scanning electron microscope (SEM). The composites with a 30 wt% cellulose content were prepared by internal mixer at the temperature of 190ºC, rotor speed of 55 rpm for 20 min. The fracture surface of PP-cellulose composite clearly showed that there were large gaps and voids between PP matrices and cellulose fibers. This indicated the interfacial adhesion between cellulose and PP matrix was very poor. The fracture surfaces of MAPP compatibilized composites revealed a strong interfacial adhesion between MAPP and cellulose fibers. Since, the cellulose fibers were tightly connected with the matrix and they were broken and/or torn up.

2.2.5 Water absorption

Joseph, Rabello, Mattoso, Joseph, and Thomas (2002) studied the effect of MAPP on the water absorption of sisal-PP composites. PP-sisal composites were prepared by the melt mixing (Haake Rheocord) at temperature of 170ºC and rotor speed of 50 rpm for 10 min. The treated sisal-PP composite with 20 wt% fiber loading showed a decreased water absorption compared to untreated sisal-PP composite. The reduction of water absorption was caused from the improvement in fiber-matrix adhesion. The coupling agent built up chemical bonds and hydrogen bonds that reduced the water uptake caused from fiber-matrix debonding. This in turn reduced the extent of water absorption. The enhanced bonding of MAPP treated fiber composite 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.

Thwe and Liao (2003) studied moisture absorption of bamboo fiber reinforced polypropylene composite (BFRP). MAPP was used as compatibilizer. BFRP was prepared by melt mixing using torque rheometer at 190ºC and a rotor speed of 40 rpm for 8-10 min. BFRP samples were immersed in water at 25ºC for up to 6 months and at 70ºC for up to 3 months. Mass change of the samples was recorded using as electronic balance at regular time intervals. The moisture absorption level (about 1.2%) for BFRP samples was higher than that of PP samples. PP samples showed little moisture uptake after aging in water for 6 months at 25ºC. Use of PP-MAPP matrix further reduced water uptake for BFRP. This reduction was attributed to the improvement of interfacial adhesion that reduced water accumulation in the interfacial voids and prevented water from entering the bamboo fiber. A saturated moisture level at 75ºC had not been attained at the end of the 3 months aging period. Sorption rate during the initial stage was significantly higher compared to those aged at 25ºC. Moisture contents of about 3.6% were seen for BFRP samples after 3 months.

Arbelaiz et al. (2005) studied the effect of surface modification on water absorption of short flax fiber bundle-polypropylene composites. Two different MAPP compatibilizers, Epolene E43 and G3003 were used to investigate the effect of fiber surface modification. Epolene E43 had a low molecular weight and acid number of 45. On the other hand, Epolene G3003 had a higher molecular weight but acid number lower than Epolene E43. The composites were mixed using melt mixer (Haake Rheomix 600) at 180ºC, rotor speed of 40 rpm and mixing time of 5 min. A 30 wt% fiber bundle was used to compare the effect of amount and type of MAPP coupling agent. Five composite samples were immersed in distilled water at room temperature for 7 months to study water absorption. The composites with Epolene E43 presented a lower water uptake than G3003 modified composites since Epolene E43 had a higher acid number than Epolene G3003. Use of MAPP slightly reduced equilibrium water uptake of the composites. The decrease of water uptake might be attributed to some of fiber hydrophilic –OH groups reacted with MA to form ester linkages.

Yang, Kim, Park, Lee, and Hwang (2006) studied thickness swelling and water absorption of rice-husk flour (RHF) and wood flour (WF) reinforced polyolefin (polypropylene, high-density polyethylene, low-density polyethylene). MAPP (Epolene G-3003TM) and MAPE (maleated polyethylene, Polybond-3009TM) were used as compatibilizers. The amount of compatibilizer was 3 wt%. The matrices were blended with various loading of RHF and WF using a laboratory-size twin screw extruder. The thickness swelling and water absorption of the composites increased with increasing filler loading. The increase in water absorption was attributed to an increase in the number of micro voids caused by the larger amount of poor bonded area between the hydrophilic filler and the hydrophobic matrix polymer. Water was easily absorbed by the voids. The PP composite at 30 wt% RHF and 3 wt% MAPP exhibited significantly less thickness swelling than the PP-RHF composite, because the MAPP chemically bonded with the -OH groups in the lignocellulosic filler. This limited the water absorption. The composite containing MAPP and MAPE showed lower thickness swelling and water absorption than that of the composites without MAPP and MAPE. The strong interfacial bonding between the filler and polymer matrices caused by the compatibilizers limited the thickness swelling and water absorption of the composites.

CHAPTER III

EXPERIMENTAL

3.1 Materials

A commercial grade of isotactic polypropylene (PP, 700 J) was supplied by Thai Polypropylene Co., Ltd. Maleic anhydride grafted polypropylene (MAPP, Fusabond® P MZ 109D, DuPont, MFI 120 g/10 min) was used as a compatibilizer, and vinyltriethoxysilane (VTES, Aldrich) and octadecyltrimethoxysilane (OTMS, Aldrich) as coupling agents. The chemical structures of silane coupling agents are shown in Figure 3.1. Rossells fibers (Hibiscus sabdariffa) were obtained from NEP Realty and Industry Public Company Limited. Sisal fibers (Agave sisalana) were purchased from Sisal-Handicraft OTOP Group, Tambon Ban Kao, Amphur Dan Khun Thod, Nakhon Ratchasima, Thailand.

$$H_2C{=}CH{-}Si(OC_2H_5)_3 \qquad C_{18}H_{37}{-}Si(OCH_3)_3$$

Vinyltriethoxysilane Octadecyltrimethoxysilane

Figure 3.1 Chemical structure of vinyltriethoxysilane and octadecyltrimethoxysilane**.**

3.2 Experimental

3.2.1 Fiber preparation

3.2.1.1 Fiber cleaning

Rossells fibers were cut into an approximate length of 20 cm then soaked in water at a liquor ratio of 15:1 for a week. After that, the fibers were washed with water in order to remove small barks and dirt. The fibers were dried in an oven at 60ºC overnight, and then the fibers were carded to separate as fiber filaments. Sisal fibers were used as received. They were dried in an oven at 60ºC overnight. These fibers were called “nonpretreated fibers (NP)”.

The nonpretreated rossells and sisal fibers were cut into an approximate length of 2 mm. The short fibers were boiled with methanol and benzene mixture (1:1) for 3 hrs to eliminate waxes and low molecular weight species, and then dried in an oven at 60ºC overnight. After that, the fibers were cleaned with 2 wt% sodium hydroxide (NaOH) solution for 2 hrs to eliminate hemicelluloses. The fibers were washed with water several times and dried in an oven at 60ºC overnight. These fibers were called “cleaned fibers (CL)”.

3.2.1.2 Preparation of silane-treated fibers

The CL fibers were immersed in 2 wt% VTES solution and 2 wt% OTMS solution at a liquor ratio of 15:1 for 3 hrs and 24 hrs. The 2 wt% VTES solution was prepared by dissolving VTES in distilled water. In a case of OTMS solution, 2 wt% of OTMS was dissolved in ethanol and distilled water mixture (90:10 wt/wt). The pH of the solution was adjusted to 3.5 with acetic acid. The VTES treated fibers were washed with distilled water several times. For the OTMS treated fibers, they were washed with ethanol. The fibers were then dried in an oven at 60ºC overnight.

3.2.2 Preparation of composites

The PP composites were prepared using an internal mixer (Hakke Rheomix 3000P) at 170ºC with a rotor speed of 50 rpm. First, PP was added into the mixing chamber for 5 min, after that the CL or silane treated fibers were added. The total mixing time was 13 min. In a case of MAPP modified composites, PP and MAPP were firstly mixed for 5 min, and then the CL fibers were added. The total time of blending was 13 min as well. The composition and designation of materials used in this study is shown in Table 3.1.

Table 3.1 The composition for preparing PP composites.

Designation	**PP (wt%)**	**Cleaned fiber (wt%)**	**VTES treated fiber (wt%)**	**OTMS treated fiber (wt%)**	**MAPP (phr)**
PP	100	-	-	-	-
Unmodified	80	20	-	-	-
VTES_3hr	80	-	20	-	-
VTES_24hr	80	-	20	-	-
OTMS_3hr	80	-	-	20	-
OTMS_24hr	80	-	-	20	-
MAPP_1phr	80	20	-	-	1
MAPP_2phr	80	20	-	-	2
MAPP_4phr	80	20	-	-	4
MAPP_6phr	80	20	-	-	6
MAPP_8phr	80	20	-	-	8
MAPP_10phr	80	20	-	-	10

The test specimens were molded by a Chuan Lih Fa injection molding machine (model CLF 80T) with melting temperature at 175ºC, mold temperature at 25ºC, injection speed of 46 mm/sec, screw speed of 130 rpm, and holding pressure of 1,400 kg/cm^2.

3.2.3 Fiber characterization

3.2.3.1 Measurement of fiber dimension

The average lengths and diameters of NP and CL fibers were measured based on 100 samples using the Nikon polarize optical microscope (model Eclipes E600 POL).

3.2.3.2 Thermal properties

Thermal analysis of the fibers was determined using the TA thermogravimetric analyzer (TGA, model SDT 2960). TGA and DTGA curves of fibers were obtained by heating the samples under a nitrogen atmosphere at a heating rate of 20ºC/min.

3.2.3.3 Mechanical properties

Tensile properties of NP, CL, and silane-treated fibers were tested according to ASTM D3822 using the Instron universal testing machine (UTM, model 5569) with a load cell of 10 N, a crosshead speed of 0.5 mm/min, and a gauge length of 5 cm. The length of specimens was about 20 cm.

3.2.3.4 Morphological properties

Surface morphology of fibers were investigated using a scanning electron microscope (SEM, model JSM6400) at 10 keV. The samples were coated with gold before investigation.

3.2.4 Composite characterization

3.2.4.1 Thermal properties

The thermal degradation of PP and PP composites were determined using TGA. The melting temperature (T_m), crystallization temperature (T_c), and crystallinity were investigated using Perkin Elmer differential scanning calorimeter (DSC, model DSC-7). TGA and DTGA curves of PP composites were obtained by heating samples under 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 25ºC to 180ºC at a heating rate of 10ºC/min. Then the sample was annealed for 5 min to remove the thermal history. After that, the cooling scan was begun by cooling the sample to 25ºC at a cooling rate of 10ºC/min. Finally, the second heating scan was performed by heating the sample from 25ºC to 180ºC at a heating rate of 10ºC/min. The crystallinity of the PP composites was calculated by the following equation:

$$\text{Crystallinity (\%)} = (\Delta H_{sample} / \Delta H_f^o \, w) \times 100 \qquad (1)$$

Where ΔH_{sample} is the heat of fusion of sample (J/g) obtained from the second heating scan. ΔH_f^o is the heat of fusion of pure crystalline PP equal to 209 J/g (Arbelaiz, Fernandez, Ramos, and Mondragon, 2006). w is mass fraction of the PP in the composite.

Heat distortion temperature (HDT) of PP and PP composites were tested following ASTM D648 using a HDT testing machine (model HDV 1) at a heating rate of 2ºC/min at 455 kPa.

3.2.4.2 Rheological properties

Melt flow index (MFI) of the PP and PP composites were obtained using the Kayeness melt flow indexer (model 4004) at 180ºC and a load of 2.16 kg. Viscosity at various shear rates (shear rate ranges 10-1000 s^{-1}) was obtained using the Kayeness capillary rheometer (model D5052m) at 180ºC.

3.2.4.3 Mechanical properties

Tensile properties of PP and PP composites were tested by following ASTM D638 using the Instron universal testing machine (UTM, model 5565) with a load cell of 5 kN, a crosshead speed of 10 mm/min, and a gauge length of 80 mm. The tensile strength of PP was obtained using a test speed of 50 mm/min. This was because PP specimen did not break at a speed of 10 mm/min.

Flexural properties of the PP and PP composites were examined according to ASTM D5943 using the Instron universal testing machine (UTM, model 5565) with a load cell of 5 kN, a crosshead speed of 15 mm/min, and a span length of 56 mm.

Unnotch Izod impact strength of PP and PP composites were performed according to ASTM D256 using an Atlas testing machine (model BPI).

3.2.4.4 Morphological properties

Morphology of the fracture surface of PP composites was examined using a scanning electron microscope (SEM, model JSM6400) at 10 keV. The samples were coated with gold before analysis.

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3.2.4.5 Water absorption

Water absorption of PP composites was performed by following ASTM D570. The test specimens were immersed in distilled water at room temperature for 3 months. The water absorption was calculated by the following equation:

$$\text{Water absorption (\%)} = [(\text{wet weight} - \text{dried weight})/\text{dried weight}] \times 100 \qquad (3)$$

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of surface modification on properties of rossells fibers

4.1.1 Measurement of fiber dimension

The fiber length, diameter, and aspect ratio (L/D) of NP, CL, and silane-treated rossells fibers are shown in Table 4.1. The fibers after cleaning with mixed solvent and alkalization (CL fibers) were destructed of the mesh structure and separated into fiber bundles (Ray, Basak, and Bose, 2002). Thus, the average diameter of CL fibers was lower than the NP fibers, VTES_3hr and OTMS_3hr treated fibers. However, the average diameter of VTES and OTMS treated fibers at 24 hrs slightly lower than 3 hrs. This might be caused from the splitting into fiber bundles of the fibers by the mechanical breaking during a long time stirring for 24 hrs treatments. The difference of aspect ratio might be caused from the variation of fiber. Silane treatment showed no remarkable effect on average length of the fibers.

4.1.2 Thermal properties

TGA and DTGA thermograms of NP, CL, and silane-treated rossells fibers at treatment time of 3 and 24 hrs are shown in Figure 4.1. Decomposition temperatures of NP, CL, VTES, and OTMS treated rossells fibers are listed in Table 4.2. The first decomposition temperature below 100ºC corresponded to the evaporation of moisture. The CL fibers presented a slightly lower in moisture content than that of the NP fibers. The moisture content about 6% was observed. The second decomposition temperature of NP fibers around 207ºC indicated the loss of impurities and low molecular weight species. The third decomposition temperature was the decomposition temperature of hemicellulose and lignin. The beginning of this decomposition temperature was observed around 250ºC. The thermal decomposition temperature of hemicelluloses and lignin were in the ranges of 220-280ºC and 280-300ºC, respectively (Saheb and Jog, 1999). In the case of CL fibers, the second decomposition temperature was absent, and the third decomposition changed into the shoulder. This indicated that the cleaning with mixed solvent and alkalization were able to remove impurities, low molecular weight species, and some hemicelluloses and lignin from the fiber surface. The fourth decomposition temperature was the decomposition of cellulose as observed in the range of 350-400ºC. The decomposition temperature of cellulose slightly reduced when the fibers were cleaned. This might be attributed to the absence of lignin affected on thermal resistance of the fibers. However, the decomposition temperatures of cellulose of VTES and OTMS treated fibers showed no remarkable different compared to the CL fibers. This might be caused from the reaction between fibers and silane coupling agent as illustrated in Figure 4.2. Silane treatment insignificantly affected on the decomposition temperature of cellulose of the fibers.

4.1.3 Mechanical properties

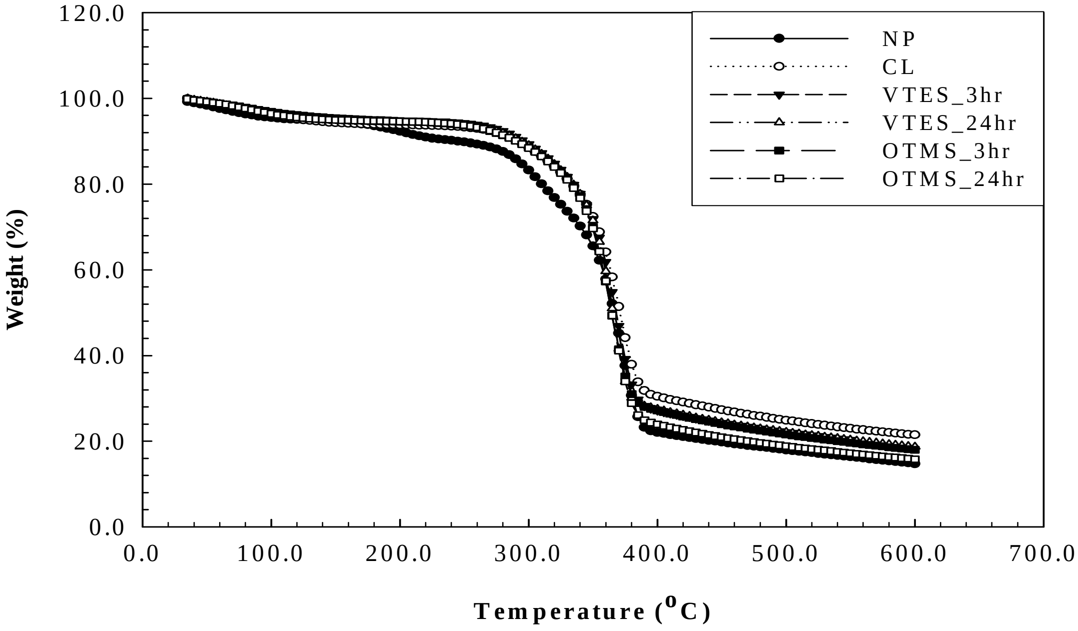
Tensile properties of single fiber are shown in Table 4.3. Tensile strength of CL and silane treated fibers were lower than that of NP fibers. This was due to the removal of hemicelluloses and lignin that held fiber bundles together. The efficiency of stress transfer between fiber bundles was reduced. No remarkable difference in Young’s modulus of NP, CL, and silane treated fibers was found except OTMS treated fiber at treatment time of 24 hr.

Table 4.1 Fiber length, diameter and aspect ratio of NP, CL, VTES, and OTMS treated rossells fibers.

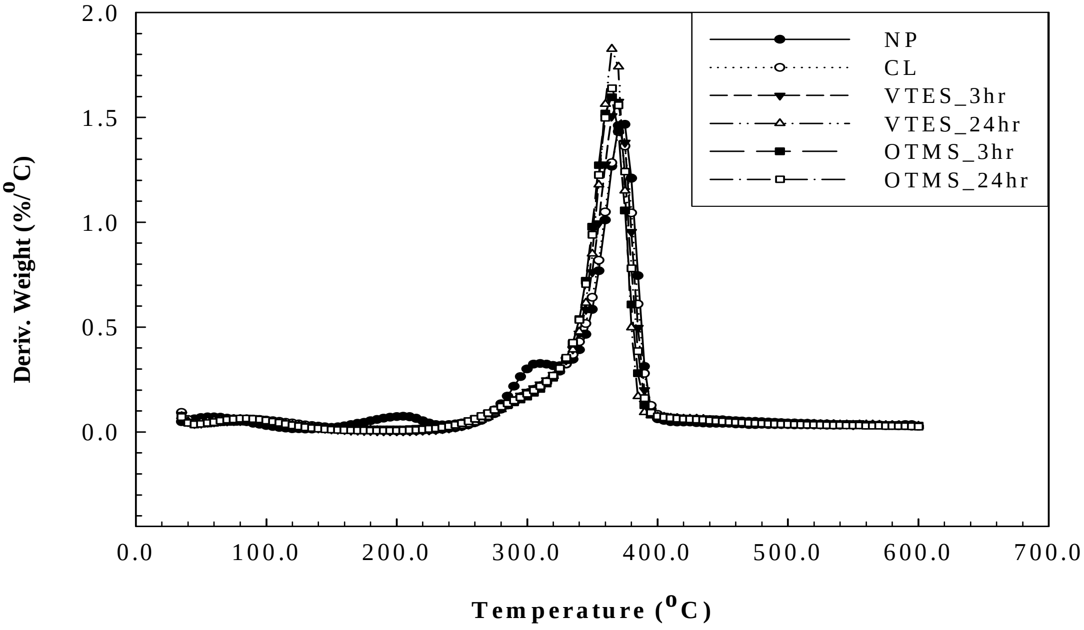
Type of fibers	Length (mm)		Diameter (µm)		L/D
	range	average	range	average	
NP	0.71-3.92	1.86±0.71	27.2-166.0	71.6±27.2	26.6
CL	0.60-2.54	1.26±0.60	30.5-190.0	55.1±30.3	27.9
VTES_3hr	0.44-2.34	1.33±0.52	20.0-190.0	61.7±33.0	26.8
VTES_24hr	0.38-2.34	1.40±0.43	20.0-150.0	56.7±23.6	27.7
OTMS_3hr	0.36-2.64	1.49±0.51	20.0-170.0	66.2±34.5	28.4
OTMS_24hr	0.40-2.80	1.52±0.55	20.0-160.0	59.2±21.2	29.2

Table 4.2 Decomposition temperature of NP, CL, VTES, and OTMS treated rossells fibers.

Type of fibers	Decomposition temperature (°C)			
	1st	2nd	3rd	4th
NP	78.1	206.8	309.1	373.2
CL	72.9	-	-	365.9
VTES_3hr	81.2	-	-	369.1
VTES_24hr	81.5	-	-	367.4
OTMS_3hr	82.4	-	-	367.3
OTMS_24hr	83.7	-	-	366.8



(a)



(b)

Figure 4.1 TGA (a) and DTGA (b) thermograms of NP, CL, VTES, and OTMS treated rossells fibers.

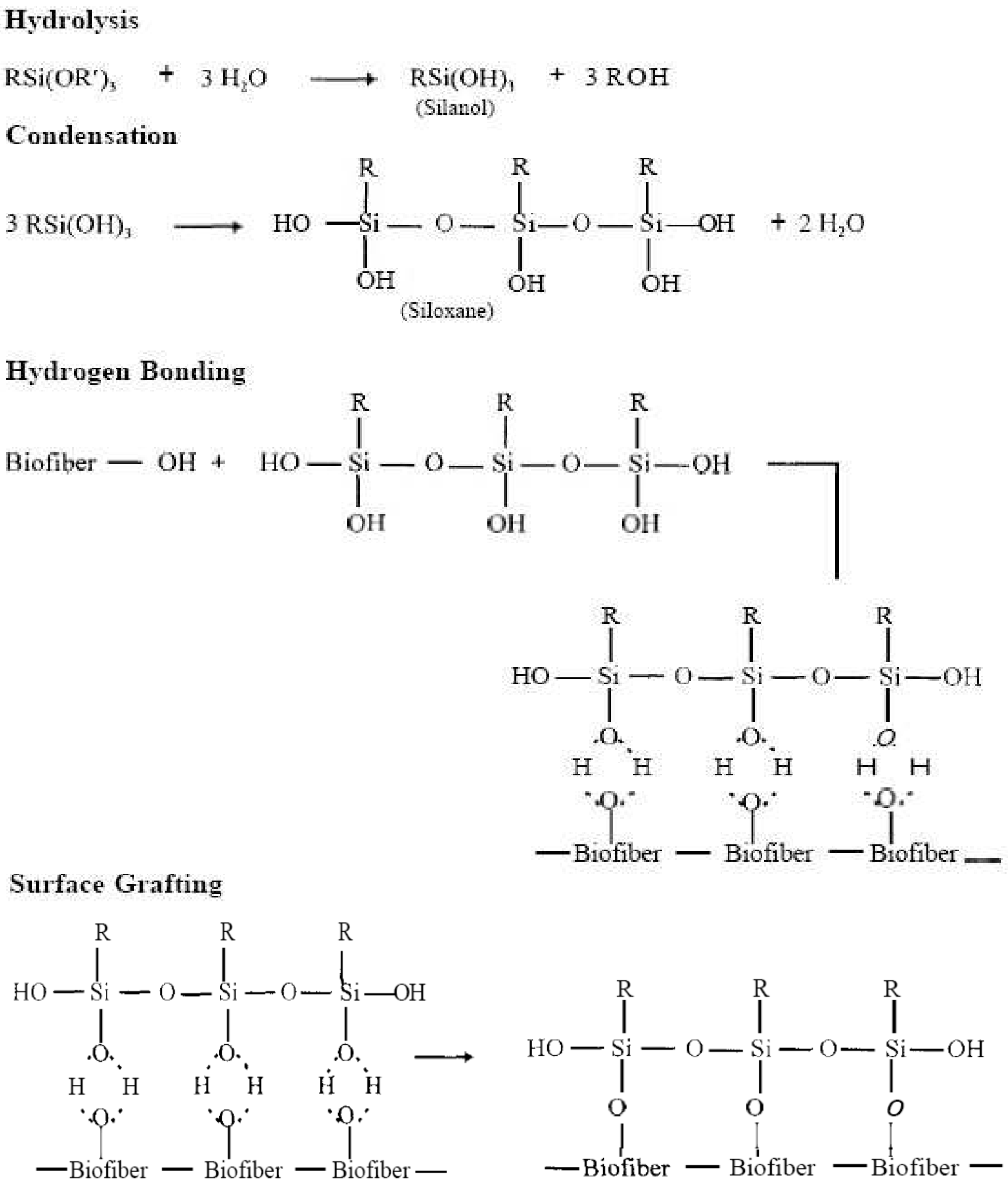


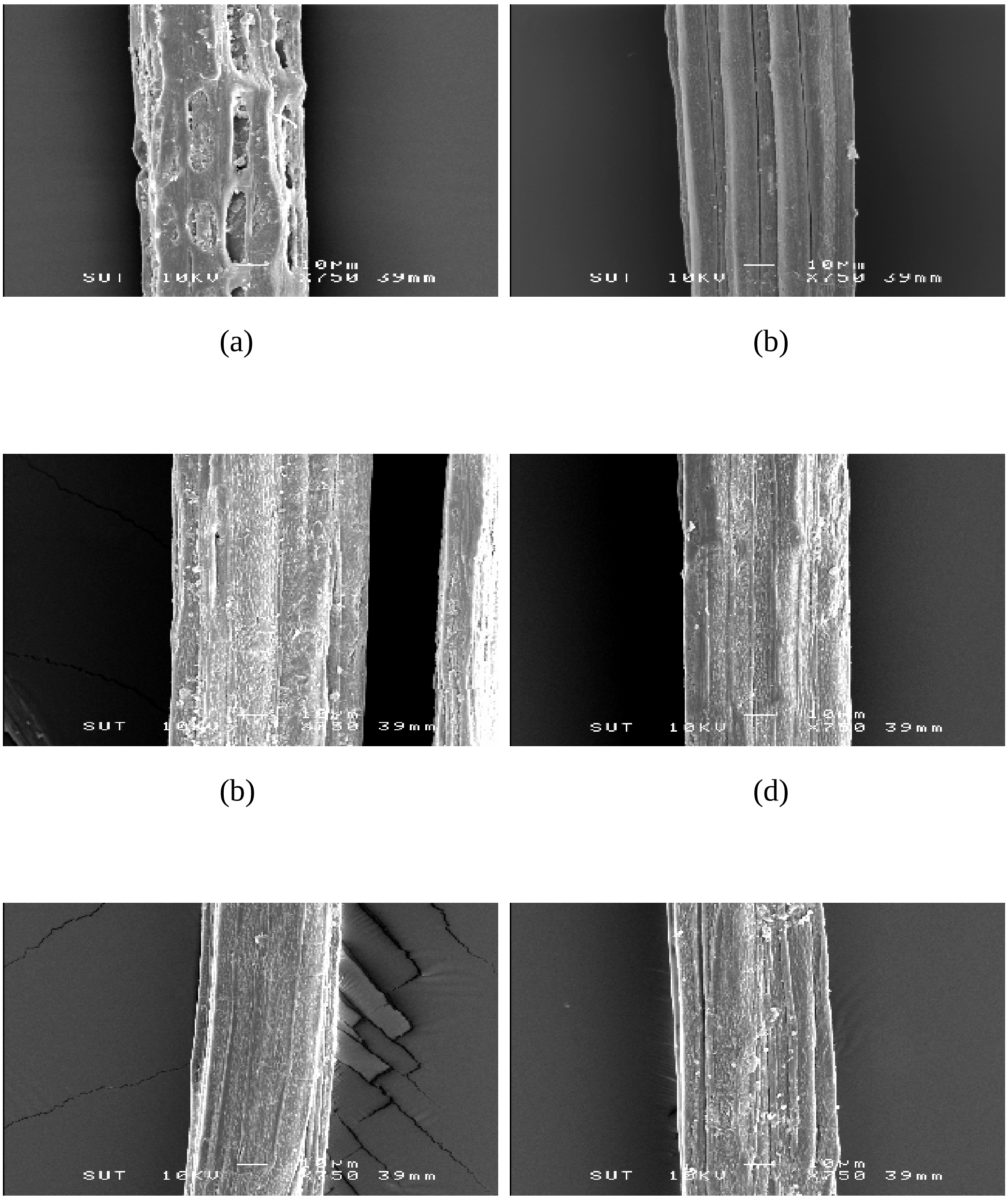
Figure 4.2 Schematic illustration of silane treated natural fibers (Kanani, Krishnan, and Narayan, 1997).

Table 4.3 Tensile strength and Young’s modulus of NP, CL, VTES, and OTMS treated rossells fibers.

Type of fibers	Tensile strength (MPa)		Young's modulus (GPa)	
	range	average	range	average
NP	317.0-853.0	473.4±120.2	28.2-62.0	40.6±9.9
CL	153.0-715.5	434.7±164.4	20.1-69.0	41.7±12.5
VTES_3hr	151.0-942.0	335.0±183.5	18.8-92.5	38.0±16.0
VTES_24hr	136.0-652.0	353.6±147.0	15.3-120.0	39.5±22.2
OTMS_3hr	154.0-471.0	287.3±93.2	20.1-55.5	35.4±12.0
OTMS_24hr	116.0-638.0	295.7±139.6	11.0-47.4	25.4±9.3

4.1.4 Morphological properties

SEM micrographs of NP, CL, and silane treated rossells fibers are shown in Figure 4.3. The impurities were observed on the surface of the NP fibers as shown in Figure 4.3 (a). Natural waxy substances on the fiber surface contribute to ineffective fiber-matrix bonding and poor surface wet-out (Mohanty et. al., 2003). Cleaning fibers with mixed solvent and alkalization were able to remove low molecular weight species, hemicelluloses, and lignin from the fiber surface as confirmed by thermal analysis. It indicated that cleaning fibers with mixed solvent and alkalization were sufficient to remove the impurities from the fiber surface. After cleaning (Figure 4.3 (b), the binding components (e.g. hemicelluloses and lignin) between fiber bundles were further partly removed as more separation of individual fiber bundles as agree with the reduction of average fiber diameter. Thus, the fine structure and clean surface of the fibers were obtained (Mwaikambo and Ansell, 2002). When the CL fibers were treated with VTES and OTMS solution, their surfaces appeared rougher than that of CL fibers as shown in the Figure 4.3 (c-f).



(a) (b)

(b) (d)

(e) (f)

Figure 4.3 SEM micrographs at 750x magnification of rossells fibers; (a) NP, (b) CL, (c) VTES_3hr, (d) VTES_24hr, (e) OTMS_3hr, (f) OTMS_24hr.

4.2 Effect of compatibilizer on properties of rossells-PP composites

4.2.1 Thermal properties

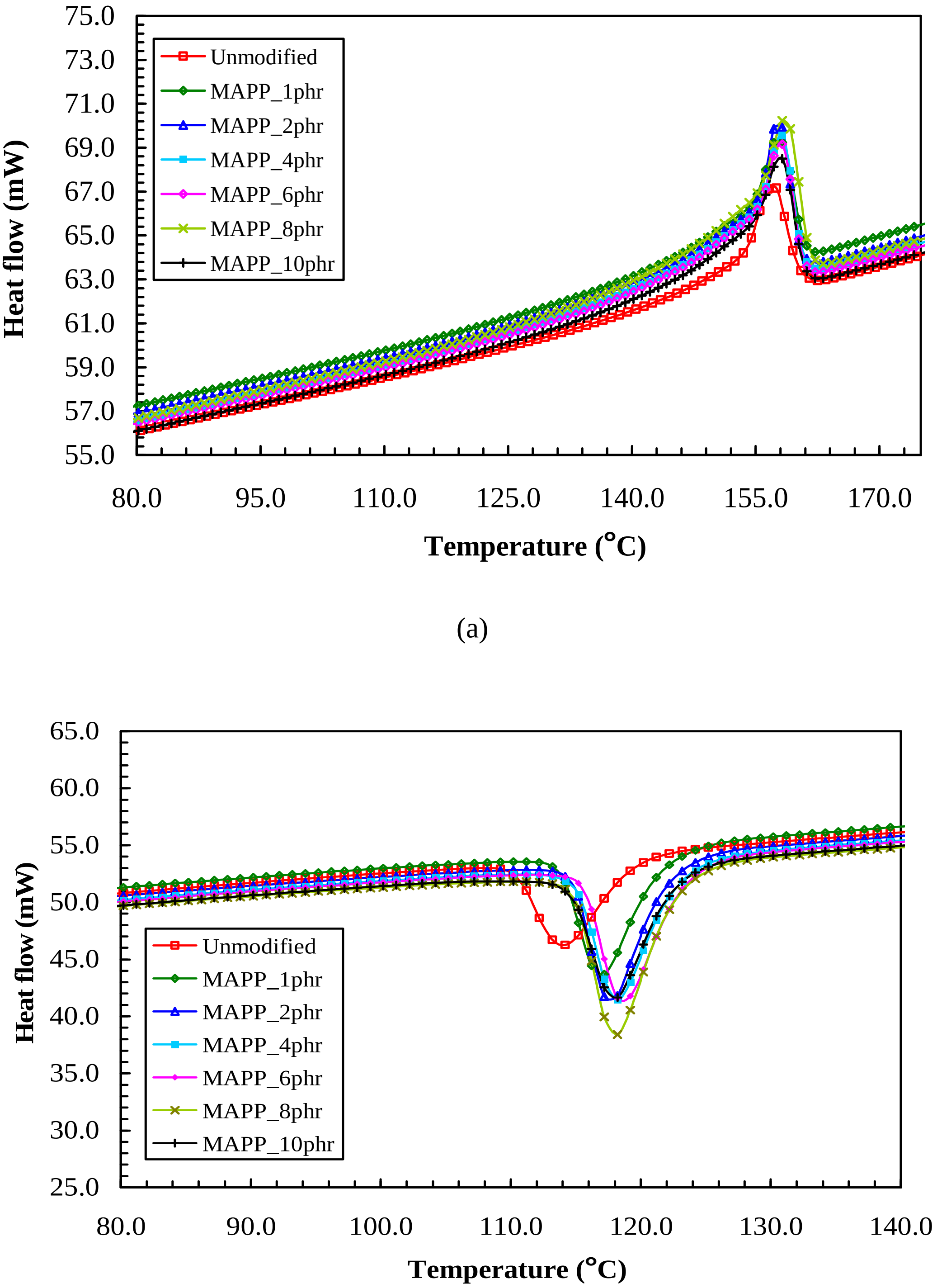
The results of DSC analysis of PP and rossells-PP composites with various MAPP contents are shown in Table 4.4 and Figure 4.4. Melting temperature of PP did not change with the addition of the fibers whereas crystallization temperature increased. Manchado et al. (2000) reported that sisal fibers had no effect on the melting temperature of PP composites. The increase in crystallization temperature might be attributed to the induced crystallization effect of the fibers affected on a fast crystallization. Similarly, Amash and Zugenmaier (2000) and Quillin et al. (1994) 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. The 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, Suppakarn, Sutapun, and Thomthong, 2007). The incorporation of MAPP insignificantly changed both melting and crystallization temperature of the composites. An increase in crystallinity of the MAPP modified rossells-PP composites might be caused from the reduction of micro voids or gap due to the improvement in surface adhesion between fibers and PP matrix with the addition of MAPP (Qiu, Endo, and Hirotsu, 2006).

TGA and DTGA curves of PP, unmodified and MAPP modified rossells-PP composites are shown Figure 4.5. Decomposition temperatures of cellulose and PP of unmodified and MAPP modified rossells-PP composites are listed in Table 4.5. The first peak at about 370ºC was a decomposition temperature of cellulose related to the results of thermogravimetric analysis of fibers, and the second peak at 460ºC was a decomposition temperature of PP. The decomposition temperature of cellulose insignificantly changed with the addition of MAPP and the increasing of MAPP content while the decomposition temperature of PP slightly increased.

HDTs of PP and rossells-PP composites are shown in Table 4.6. HDT of PP was improved with adding the fibers. When the MAPP was added the HDT of composites increased. It might be due to the improvement of the fibers-matrix interface. However, no significant difference on HDT of the composites with an increase of MAPP content was found.

Table 4.4 Melting temperature, crystallization temperature, and crystallinity of PP and rossells-PP composites with different MAPP contents.

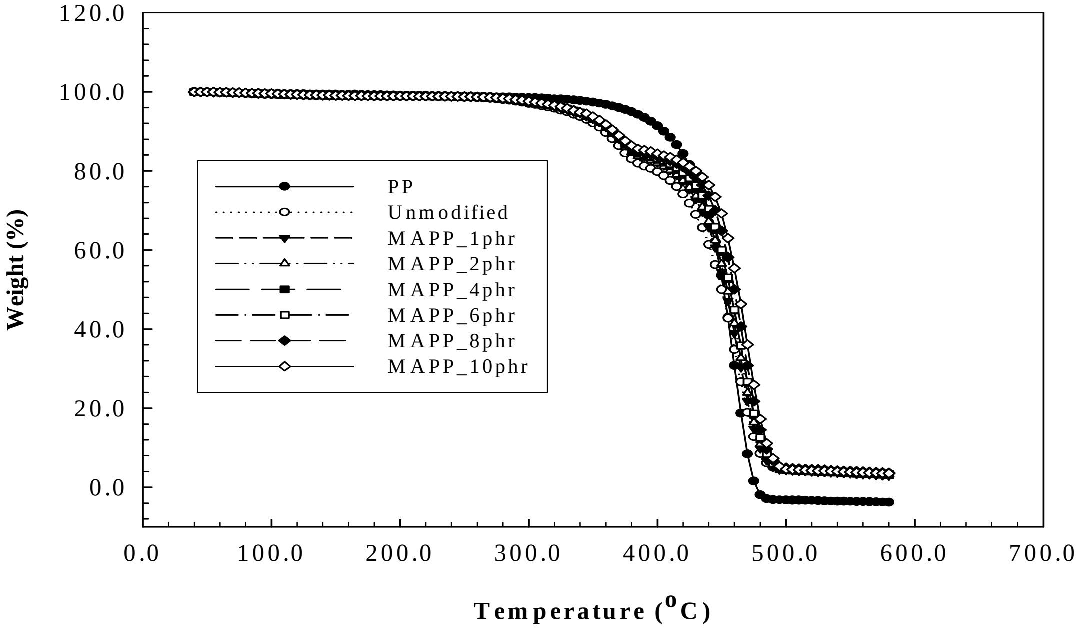
Materials	**T_m (ºC)**	**T_C (ºC)**	**Crystallinity (%)**
PP	157.2	108.4	51.09
Unmodified	156.9	114.0	42.47
MAPP_1phr	157.7	116.9	42.79
MAPP_2phr	157.7	117.7	43.45
MAPP_4phr	158.1	118.2	43.81
MAPP_6phr	158.0	118.7	42.33
MAPP_8phr	158.5	118.1	43.96
MAPP_10phr	157.9	118.0	41.69



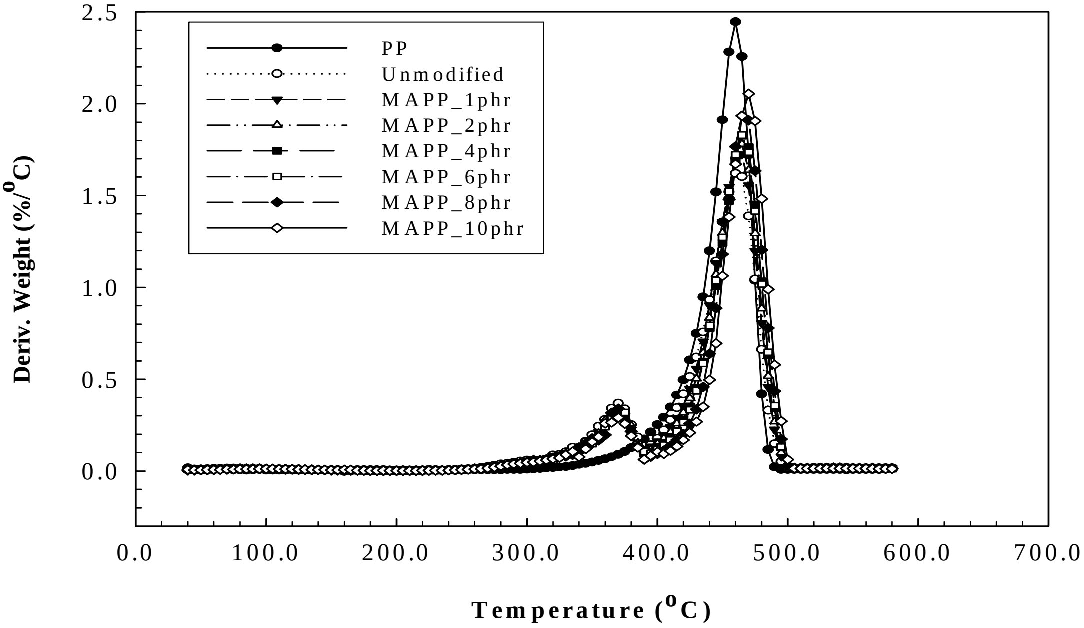
(a)

(b)

Figure 4.4 DSC thermograms of rossells-PP composites with different MAPP contents; (a) heating scan, (b) cooling scan.



(a)



(b)

Figure 4.5 TGA (a) and DTGA (b) thermograms of PP and rossells-PP composites with different MAPP contents.

Table 4.5 Decomposition temperature of fibers and PP of rossells-PP composites with different MAPP contents.

Materials	**Cellulose decomposition temperature (ºC)**	**PP decomposition temperature (ºC)**
Unmodified	369.6	461.7
MAPP_1phr	370.7	463.7
MAPP_2phr	371.2	465.1
MAPP_4phr	370.5	466.2
MAPP_6phr	372.2	465.8
MAPP_8phr	373.4	466.9
MAPP_10phr	374.2	470.0

Table 4.6 Heat distortion temperature of PP and rossells-PP composites with different MAPP contents.

Materials	**HDT (ºC)**
PP	79.4±2.5
Unmodified	128.0±1.0
MAPP_1phr	139.2±1.0
MAPP_2phr	142.2±2.4
MAPP_4phr	141.2±2.0
MAPP_6phr	139.7±2.1
MAPP_8phr	140.5±2.4
MAPP_10phr	139.5±3.5

4.2.2 Rheological properties

Melt flow index (MFI) of PP decreased with adding fibers as shown in Table 4.7. The rossells-PP composites exhibited higher viscosity than that of PP as shown in Figure 4.6. This was attributed to the fibers perturbed the flow of polymer and hindered the mobility of chain segments in melt flow. However, adding MAPP to the rossells-PP composites showed no remarkable difference in MFI and viscosity. These results were similar to the study of Schemenauer, Osswald, Sanadi, and Caulfield (2000). They reported that no significant effect of MAPP on viscosity of jute-reinforced polypropylene composites.

Table 4.7 Melt flow index of PP and rossells-PP composites with different MAPP contents.

Materials	**MFI (g/10min)**
PP	4.16±0.06
Unmodified	2.57±0.01
MAPP_1phr	2.37±0.04
MAPP_2phr	2.37±0.02
MAPP_4phr	2.19±0.03
MAPP_6phr	2.19±0.04
MAPP_8phr	2.10±0.05
MAPP_10phr	2.03±0.07

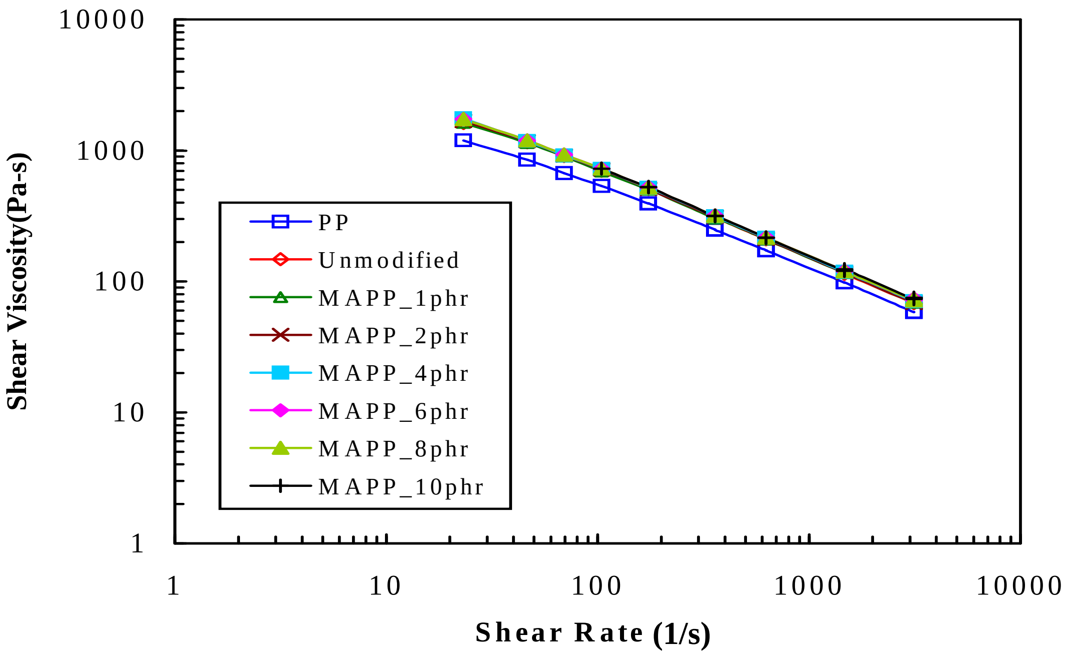


Figure 4.6 Flow curves of PP and rossells-PP composites with different MAPP contents.

4.2.3 Mechanical properties

Tensile, flexural, and impact strength of PP and rossells-PP composites with and without the addition of compatibilizer (MAPP) are shown in Table 4.8. Tensile strength, impact strength, and Young's modulus of PP were increased with adding the fibers but tensile strain at break of PP decreased. Tensile strength and impact strength of MAPP modified rossells-PP composites were higher than that of unmodified rossells-PP composite and slightly increased with increasing MAPP content as shown in Figure 4.8. Tensile strength of rossells-PP composites increased with increasing MAPP until 2 phr. Higher contents of MAPP did not give rise to further tensile strength. However, no significant difference of Young's modulus was found when the MAPP was added. Tensile strain at break slightly increased with increasing MAPP content as shown in Figure 4.9. MAPP affected on the improvement in surface adhesion between non polar PP and polar rossells fibers. The increase in mechanical properties of MAPP modified rossells-PP composites was attributed to the linkage between the hydrophilic hydroxyl groups of fibers and the carboxyl groups of the compatibilizer (Rana et al., 1998). A hypothetical model of hydroxyl groups of fibers and MAPP at the interface as shown in Figure 4.7 illustrated that 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).

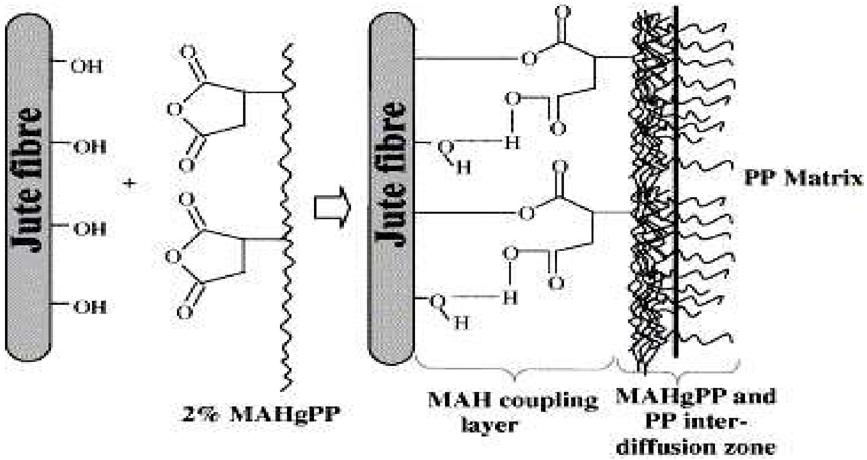


Figure 4.7 Hypothetical structure of maleic anhydride graft polypropylene (MAHgPP or MAPP) and jute fibers at the interface (Doan et al., 2005).

Table 4.8 Mechanical properties of PP and rossells-PP composites with different MAPP contents.

Materials	Tensile Strength (MPa)	Impact Strength (kJ/m^2)	Young’s Modulus (GPa)	Tensile strain at break (%)	Flexural Strength (MPa)	Flexural modulus (GPa)
PP	13.9±2.0	85.8±1.1	1.08±0.03	248.8±56.4	46.4±1.5	1.43±0.04
Unmodified	22.9±0.8	19.0±0.8	1.71±0.07	8.8±1.5	50.9±0.2	2.67±0.00
MAPP_1phr	28.1±0.9	19.5±1.8	2.02±0.03	5.2±0.4	58.6±0.4	3.23±0.06
MAPP_2phr	30.3±0.3	19.6±1.4	2.01±0.05	5.2±0.3	59.5±0.3	3.24±0.08
MAPP_4phr	30.7±1.1	21.0±1.8	2.01±0.04	5.6±0.4	61.6±0.3	3.23±0.05
MAPP_6phr	31.6±0.5	22.2±1.6	1.97±0.03	5.5±0.2	62.7±0.4	3.24±0.02
MAPP_8phr	31.5±1.2	23.1±2.8	1.94±0.03	5.9±0.3	63.9±0.4	3.15±0.02
MAPP_10phr	31.9±0.5	22.7±2.2	1.94±0.04	6.0±0.2	63.6±0.4	3.07±0.03

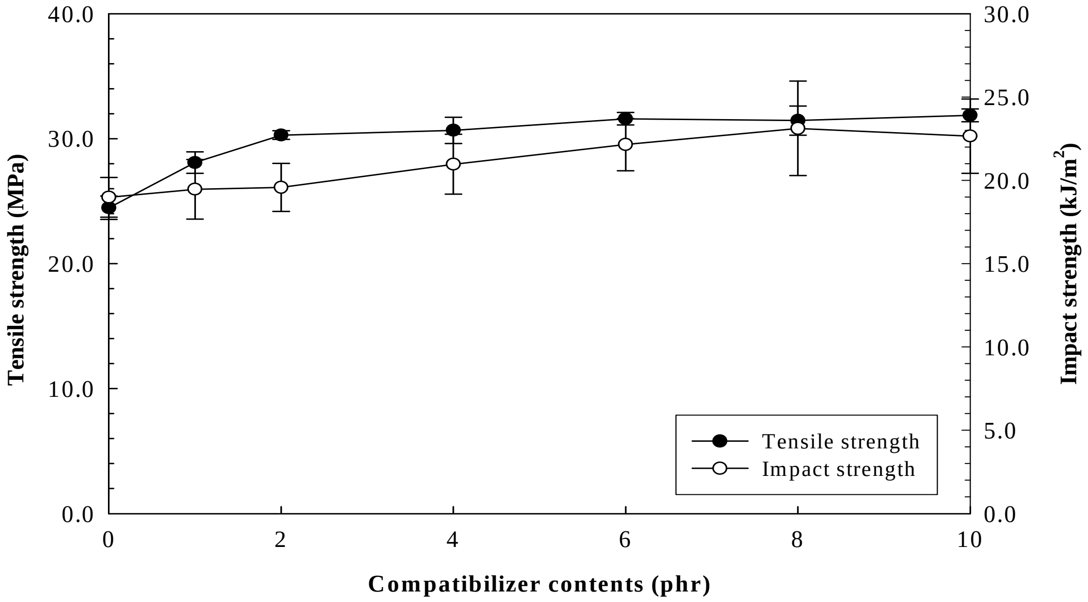


Figure 4.8 Tensile and impact strength of rossells-PP composites with different MAPP contents.

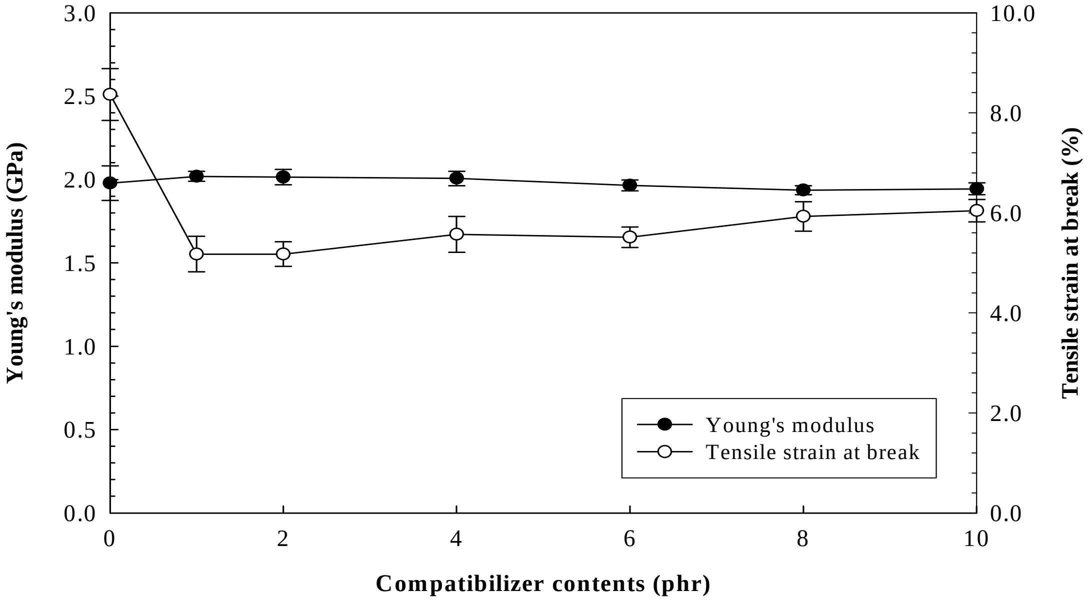


Figure 4.9 Young’s modulus and tensile strain at break of rossells-PP composites with different MAPP contents.

Flexural strength and modulus of PP increased with adding the fibers are shown in Table 4.8. The flexural properties of MAPP modified rossells-PP composites are shown in Figure 4.10. Flexural strength of MAPP modified rossells-PP composites was higher than the unmodified rossells-PP composite and slightly increased with increasing MAPP content. Flexural modulus of MAPP modified rossells-PP composites was also higher than unmodified rossells-PP composite but no significant change with increasing MAPP contents. It had been explained that the surface adhesion between fibers and PP was improved due to the esterification of the hydroxyl groups of fibers by maleic anhydride parts of MAPP. Thus, it led to a strong interfacial adhesion in the MAPP modified rossells-PP composites (Cantero, Arbeliaiz, Llano-Ponte, and Mondragon, 2003).

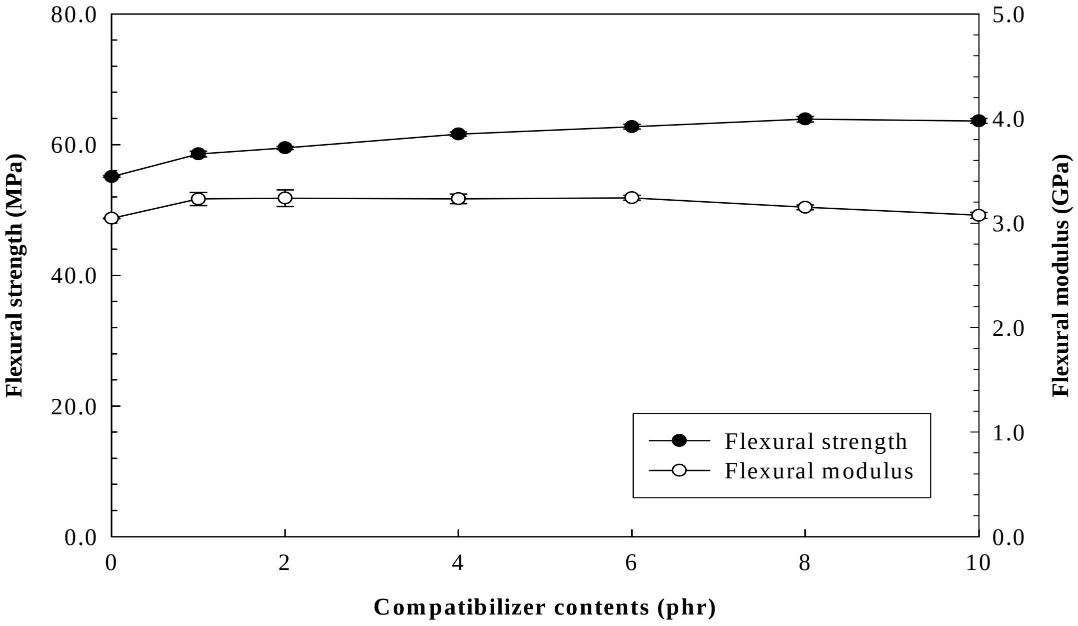


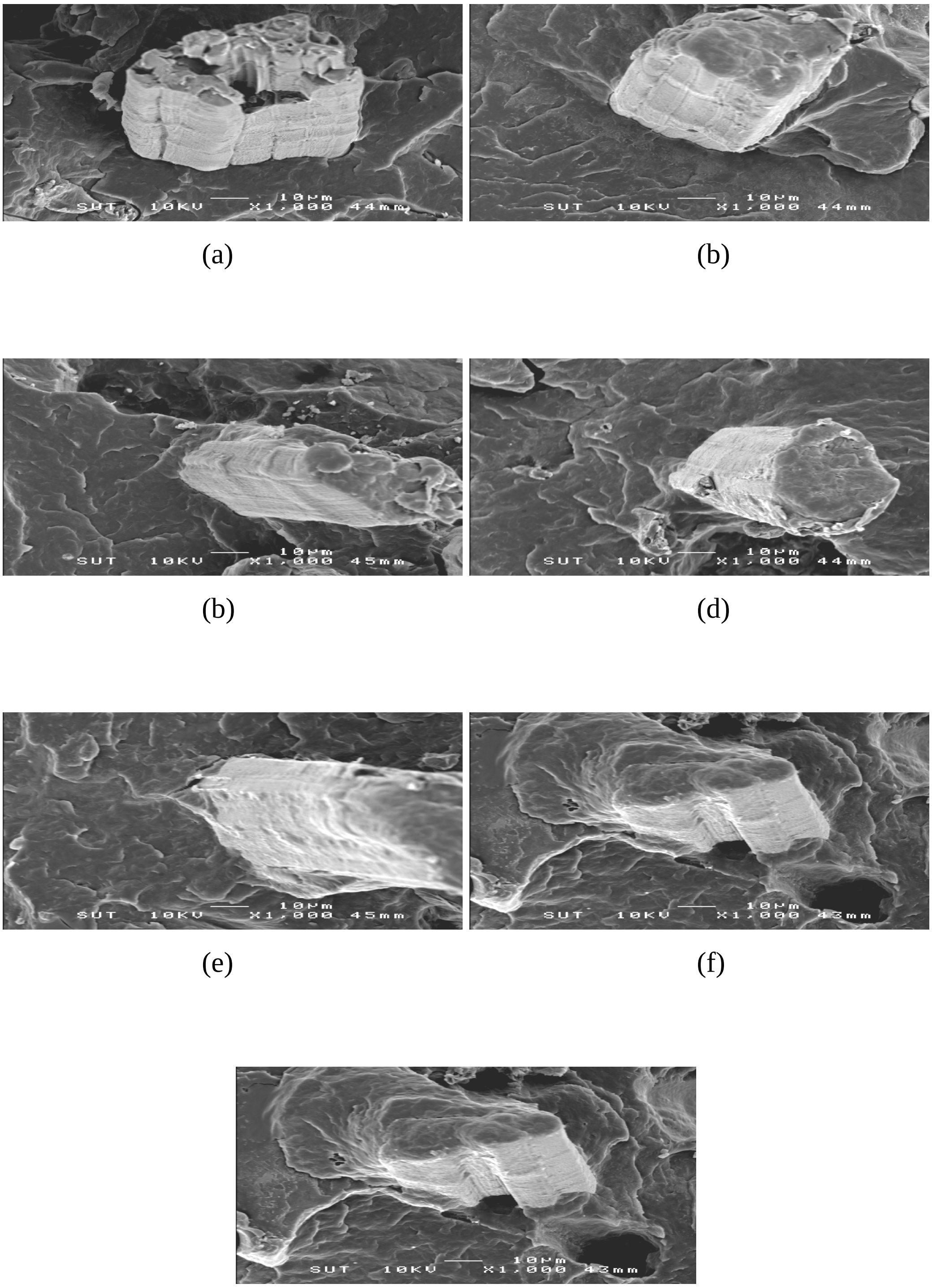
Figure 4.10 Flexural strength and flexural modulus of rossells-PP composites with different MAPP contents.

4.2.4 Morphological properties

Surface morphologies of rossells-PP composites are shown in Figure 4.11. The fracture surface of unmodified composite in Figure 4.11 (a) presented the surface of fiber pull-out fairly cleaned. Whereas, the MAPP modified rossells-PP composites had a fair amount of polymer residue remained on the fibers. The improvement of surface adhesion between the fiber and matrix was seen (Karnani, Krishnan, and Narayan, 1997). However, no significant difference in the fracture surface of MAPP modified rossells-PP composites with increasing MAPP contents was observed.

4.2.5 Water absorption

The water absorption of unmodified rossells-PP composite was higher than that of the MAPP modified rossells-PP composites as shown in Figure 4.12. This indicated that the MAPP was able to reduce the water absorption of rossells-PP composites 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.



(a) (b)

(b) (d)

(e) (f)

(g)

Figure 4.11 SEM micrographs at 1,000x magnification of rossells-PP composites; (a) Unmodified, (b) MAPP_1phr, (c) MAPP_2phr, (d) MAPP_4phr, (e) MAPP_6phr, (f) MAPP_8phr, and (g) MAPP_10phr.

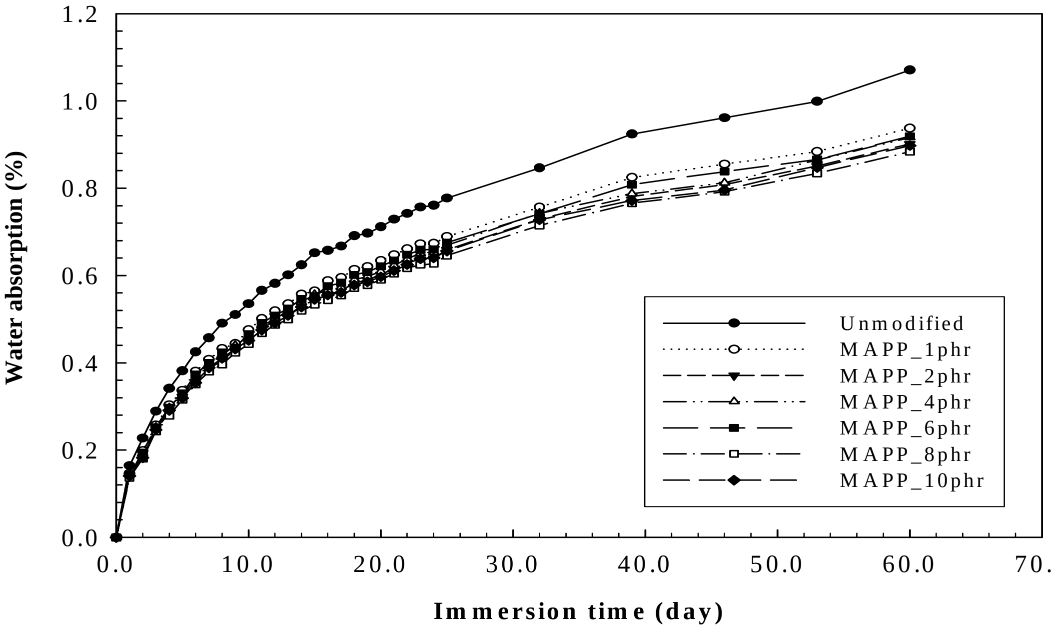


Figure 4.12 Water absorption of rossells-PP composites with different MAPP contents.

4.3 Effect of silane coupling agents on properties of rossells-PP composites

4.3.1 Thermal properties

DSC thermograms as shown in Figure 4.13 revealed that no difference in melting temperature of PP and unmodified rossells-PP composites was observed. However, the addition of rossells fibers increased crystallization temperature of PP. The crystallinity of unmodified rossells-PP composites was reduced due to the restriction of fibers and micro voids between fiber surface and PP. In case of silane treated rossells-PP composites, melting temperature and crystallization temperature did not change but crystallinity was increased. An increase in crystallinity of silane treated rossells-PP composites might be caused from the reduction of micro voids due to the improvement in surface adhesion between fibers and matrix. No significant difference in melting temperature, crystallization temperature and crystallinity of the composites was found when the fibers were treated with VTES and OTMS.

TGA thermograms of PP, unmodified, and silane treated rossells-PP composites showed that the decomposition temperature of fibers for both VTES and OTMS treated rossells-PP composites was decreased. However, the decomposition temperature of PP was slightly higher than unmodified rossells-PP composite as shown in Figure 4.14 and Table 4.10. This indicated that VTES and OTMS treatments influenced on the thermal stability of PP. Treatment times showed no significant effect on PP decomposition temperature.

Table 4.9 Melting temperature, crystallization temperature, and crystallinity of PP, unmodified, and silane treated rossells-PP composites.

Materials	T_m (°C)	T_c (°C)	Crystallinity (%)
PP	157.2	108.4	51.09
Unmodified	156.9	114.0	42.47
VTES_3hr	156.6	112.8	53.57
VTES_24hr	156.6	112.8	51.44
OTMS_3hr	156.6	112.8	57.35
OTMS_24hr	156.6	112.8	52.67

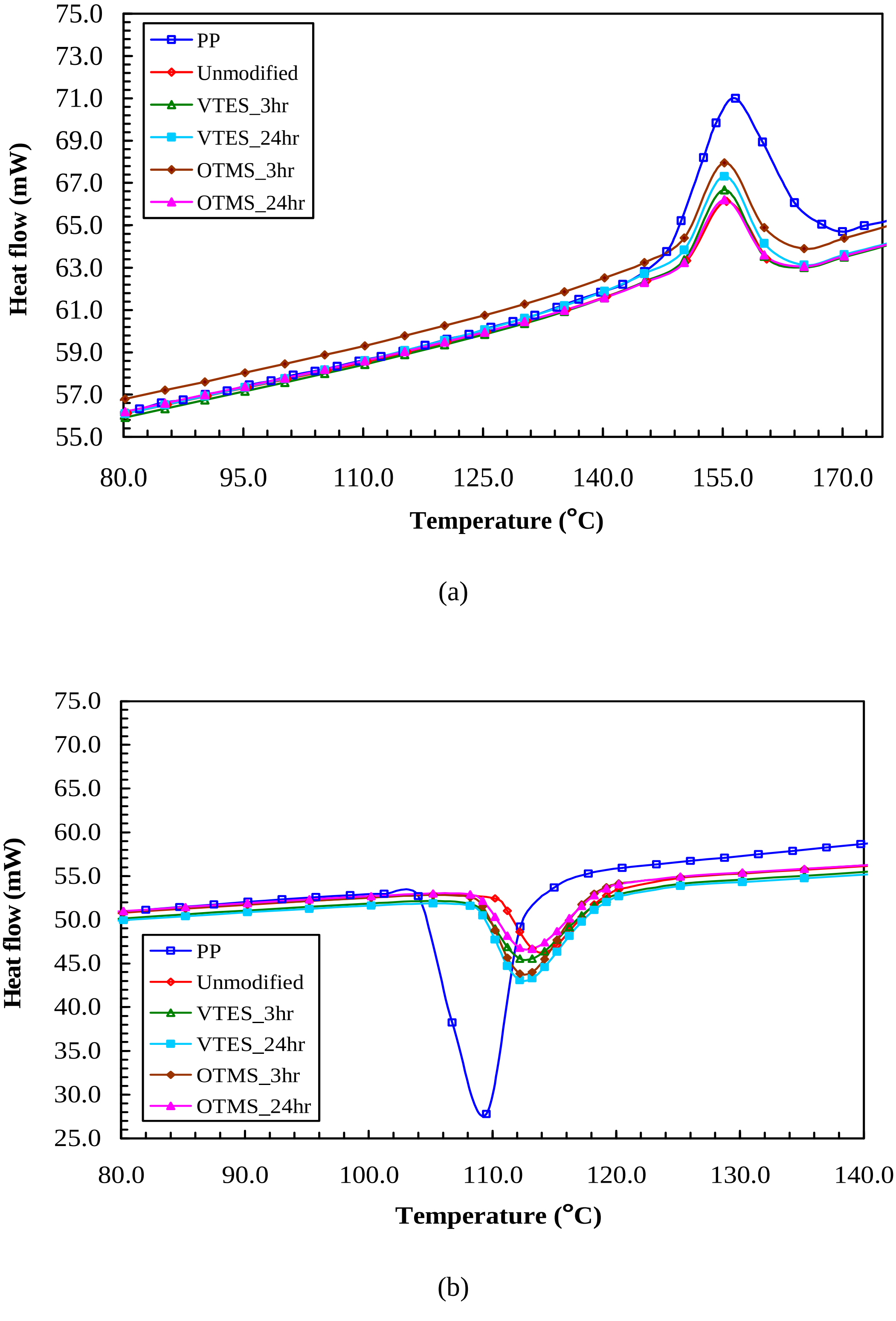
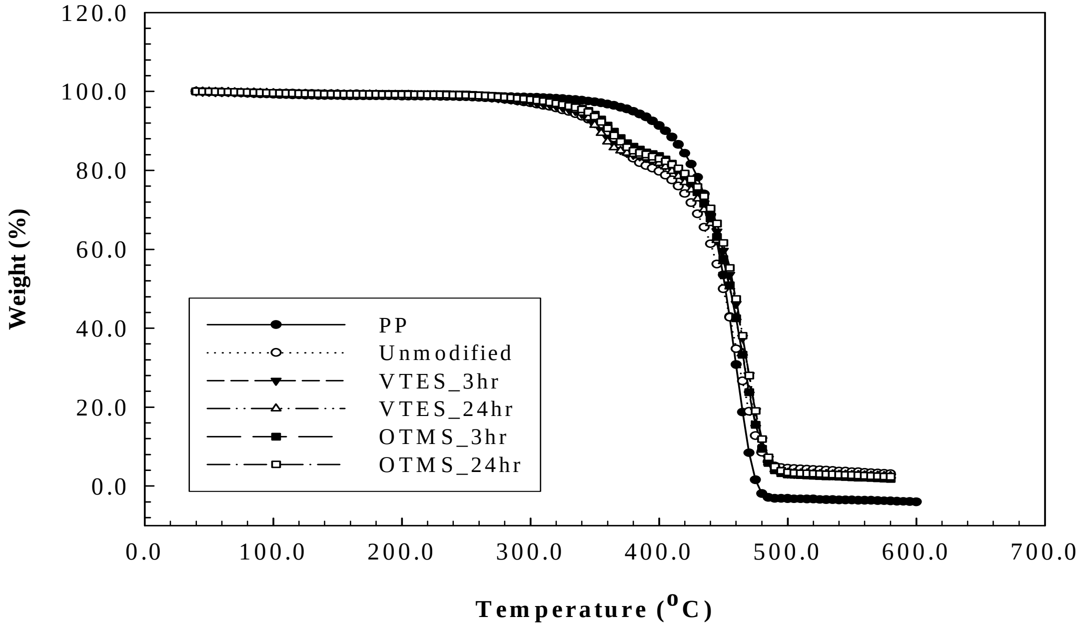
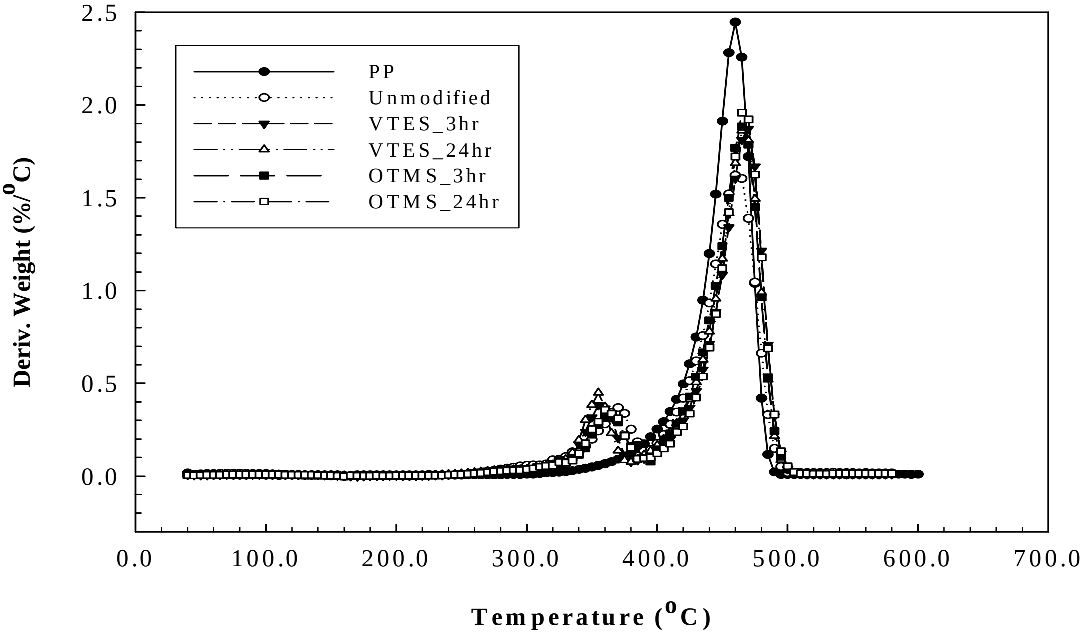


Figure 4.13 DSC thermograms of PP, unmodified, and silane treated rossells-PP composites; (a) heating scan, (b) cooling scan.



(a)



(b)

Figure 4.14 TGA (a) and DTGA (b) thermograms of PP, unmodified, and silane treated rossells-PP composites.

Table 4.10 The decomposition temperature of fibers and PP of unmodified, and silane treated rossells-PP composites.

Materials	**Cellulose decomposition temperature (ºC)**	**PP decomposition temperature (ºC)**
Unmodified	369.6	461.7
VTES_3hr	356.6	468.6
VTES_24hr	355.3	466.5
OTMS_3hr	362.9	464.8
OTMS_24hr	363.3	466.9

HDT of PP and rossells-PP composites are shown in Table 4.11. As expected, incorporating rossells fibers in to PP improved the HDT. There was no remarkable difference in HDT of VTES, OTMS treated rossells-PP composites and the unmodified rossells-PP composite.

Table 4.11 Heat distortion temperature of PP, unmodified, and silane treated rossells-PP composites.

Materials	**HDT (ºC)**
PP	79.4±2.5
Unmodified	128.0±1.0
VTES_3hr	126.6±1.0
VTES_24hr	128.0±1.0
OTMS_3hr	126.3±1.0
OTMS_24hr	127.0±0.8

4.3.2 Rheological properties

MFI of PP, unmodified and silane treated rossells-PP composites are shown in Table 4.12. MFI of PP decreased when the fibers was added. Silane treatment showed no significant effect on MFI of rossells-PP composites. This is also shown in flow curves as shown in Figure 4.15. Viscosity of PP increased with adding fiber but no remarkable difference between the viscosity of unmodified and silane treated rossells-PP composites was observed.

Table 4.12 Melt flow index of PP, unmodified, and silane treated rossells-PP composites.

Materials	**MFI (g/10min)**
PP	4.16±0.06
Unmodified	2.57±0.01
VTES_3hr	2.80±0.01
VTES_24hr	2.86±0.04
OTMS_3hr	2.89±0.05
OTMS_24hr	2.85±0.02

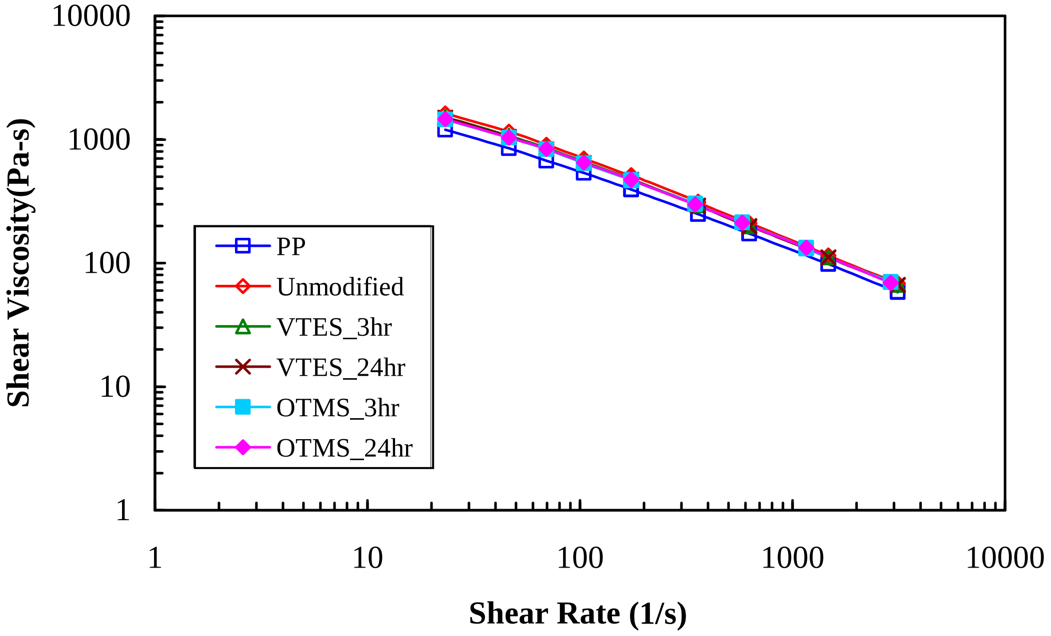


Figure 4.15 Flow curves of PP, unmodified, and silane treated rossells-PP composites.

4.3.3 Mechanical properties

Tensile strength and Young's modulus of PP, unmodified, and silane treated rossells-PP composites are shown in Table 4.13, Figure 4.16, and 4.17. Tensile strength and Young's modulus of PP were improved with the addition of the fibers. In the case of VTES treated rossells-PP composites, both tensile strength and Young's modulus increased but OTMS treated rossells-PP composites decreased. The improvement in tensile strength and Young's modulus of VTES treated rossells-PP composites was caused from the interaction between the siloxane and –OH group of fibers, and vinyl groups of VTES silane reacted with PP. The resulting reaction gave rise to chemical bonding between the fibers and the matrix which enhanced the interfacial adhesion. Figure 4.16 depicts possible reactions between silane treated fibers and polymer matrix (Abdelmouleh, Boufi, Belgacem, and Dufresne, 2007).

The reduction in tensile strength and Young's modulus of OTMS treated rossells-PP composites was due to the long flexible octadecyl group of OTMS. On the contrary, Valadez-Gonzalez, Cervantes-Uc, Olayo, and Herrera-Franco (1999) reported that the tensile strength of vinyltris (2-methoxy-ethoxy) silane treated henequen-HDPE composites increased because the interaction between silane-treated fibers and polymer matrix seem to be stronger than that of the untreated fibers. Treatment times did not influence on both tensile strength and Young's modulus of VTES and OTMS treated rossells-PP composites. From the mechanical properties investigated, it can be concluded that VTES treatment provided rossells-PP composites higher tensile strength and Young's modulus than the OTMS treatment. This might be due to VTES was lower flexible vinyl groups than that of octadecyl groups of OTMS as evident from the molecular structure.

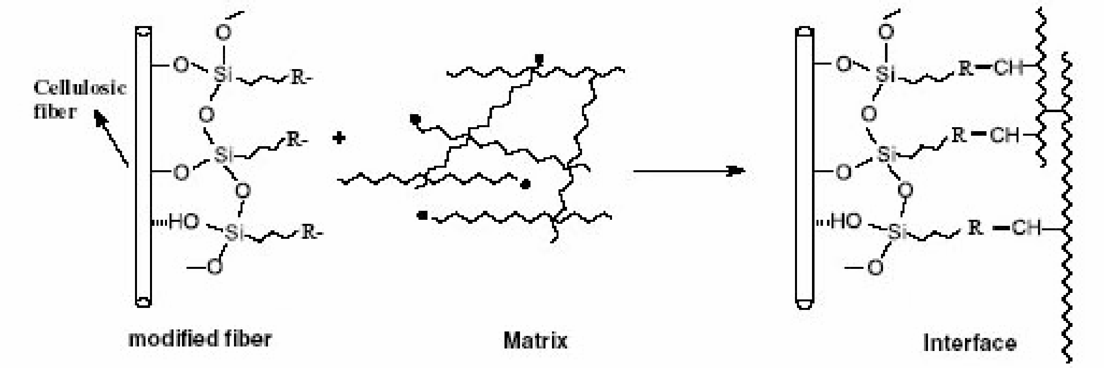


Figure 4.16 Schematic illustration of the interfacial zone in Polymer-based composites containing silane treated cellulose fibers (Abdelmouleh, Boufi, Belgacem, and Dufresne, 2006).

Table 4.13 Mechanical properties of PP, unmodified and silane treated rossells-PP composites.

Materials	Tensile Strength (MPa)	Impact strength (kJ/m^2)	Young's Modulus (GPa)	Tensile strain at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)
PP	13.9±2.0	85.8±1.1	1.08±0.03	248.8±56.4	46.4±1.5	1.43±0.04
Unmodified	22.9±0.8	19.0±0.8	1.71 ±0.07	8.8±1.5	50.9±0.2	2.67±0.01
VTES_3hr	24.4±0.8	18.2±1.9	1.80±0.09	7.0±0.4	50.8±0.4	2.81±0.04
VTES_24hr	23.8±0.6	20.4±1.2	1.77±0.05	6.9±0.9	50.5±0.2	2.77±0.01
OTMS_3hr	20.7±0.5	23.8±0.6	1.66±0.05	11.9±1.2	57.0±0.8	3.19±0.15
OTMS_24hr	21.1±0.4	23.3±1.1	1.67±0.03	11.1±2.0	57.6±0.7	3.33±0.07

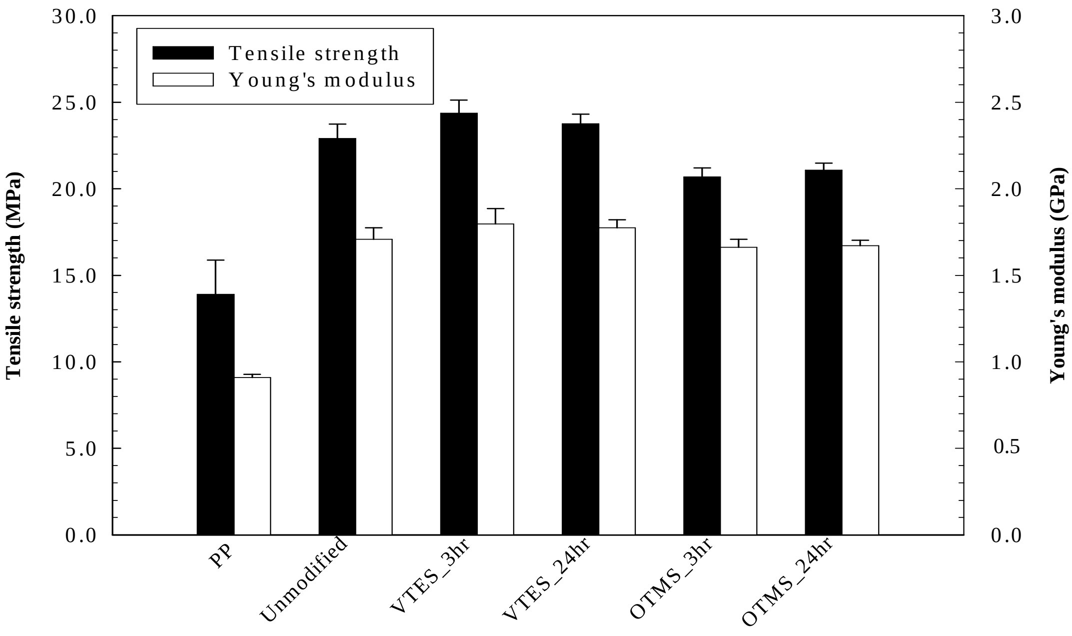


Figure 4.17 Tensile and impact strength of PP, unmodified, and silane treated rossells-PP composites.

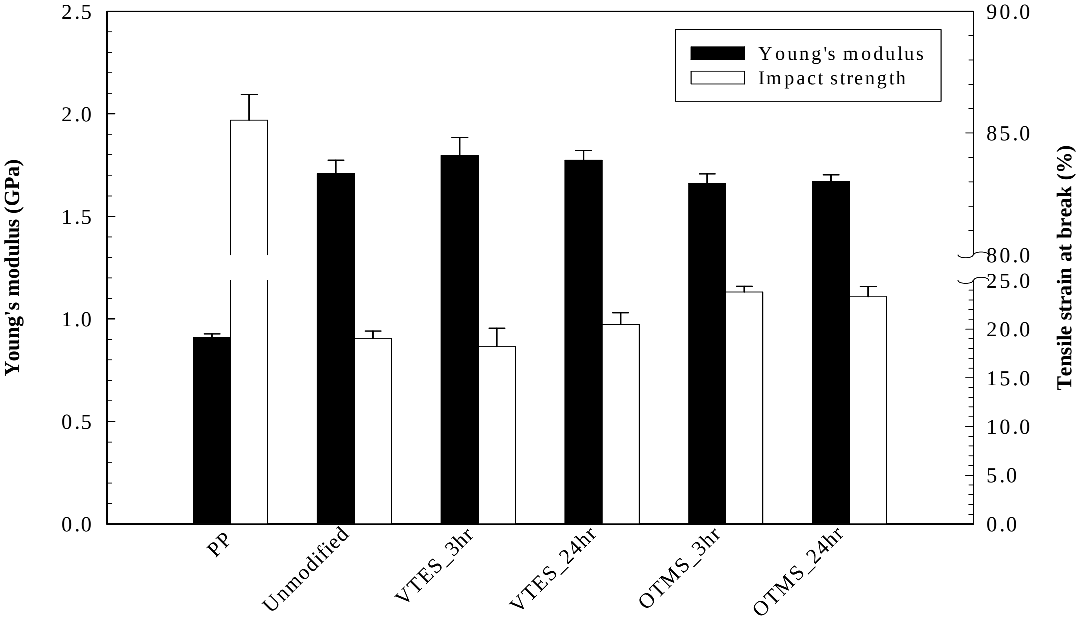


Figure 4.18 Young’s modulus and tensile strain at break of PP, unmodified, and silane treated rossells-PP composites.

The addition of fibers affected on the reduction of tensile strain at break and impact strength of PP as shown in Figure 4.17 and 4.18. Tensile strain at break and impact strength of silane treated rossells-PP composites were slightly higher than the unmodified rossells-PP composites. In case of OTMS treated rossells-PP composites, tensile strain at break and impact strength showed a higher than that of the VTES treated rossells-PP composites. This was attributed to the OTMS treated rossells-PP composites were tougher than the VTES treated rossells-PP composites due to the long and flexible octadecyl group of OTMS.

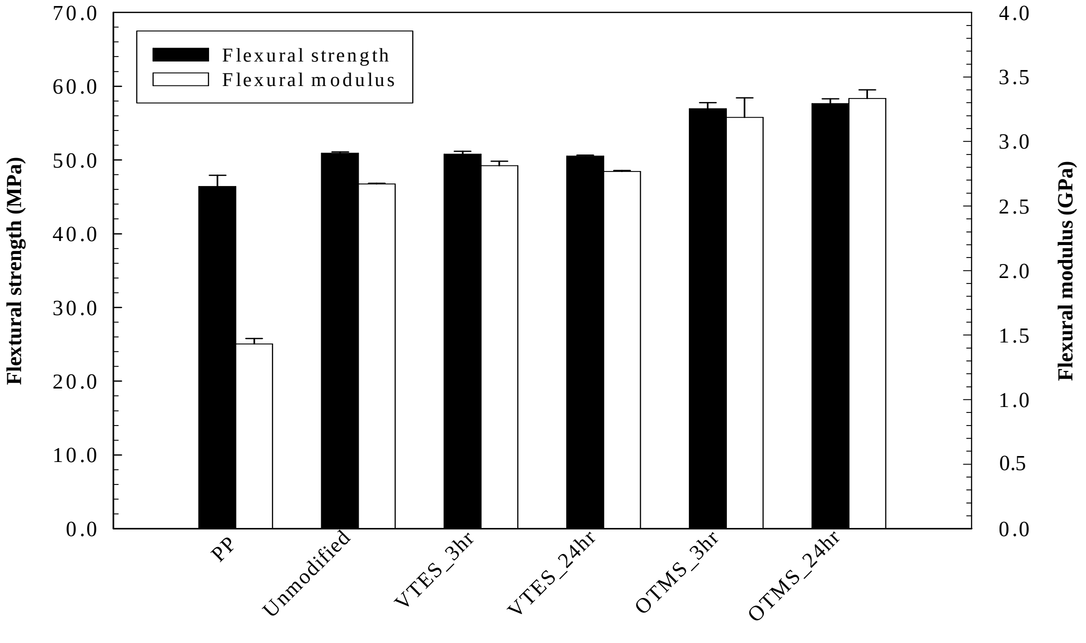


Figure 4.19 Flexural strength and flexural modulus of PP, unmodified, and silane treated rossells-PP composites.

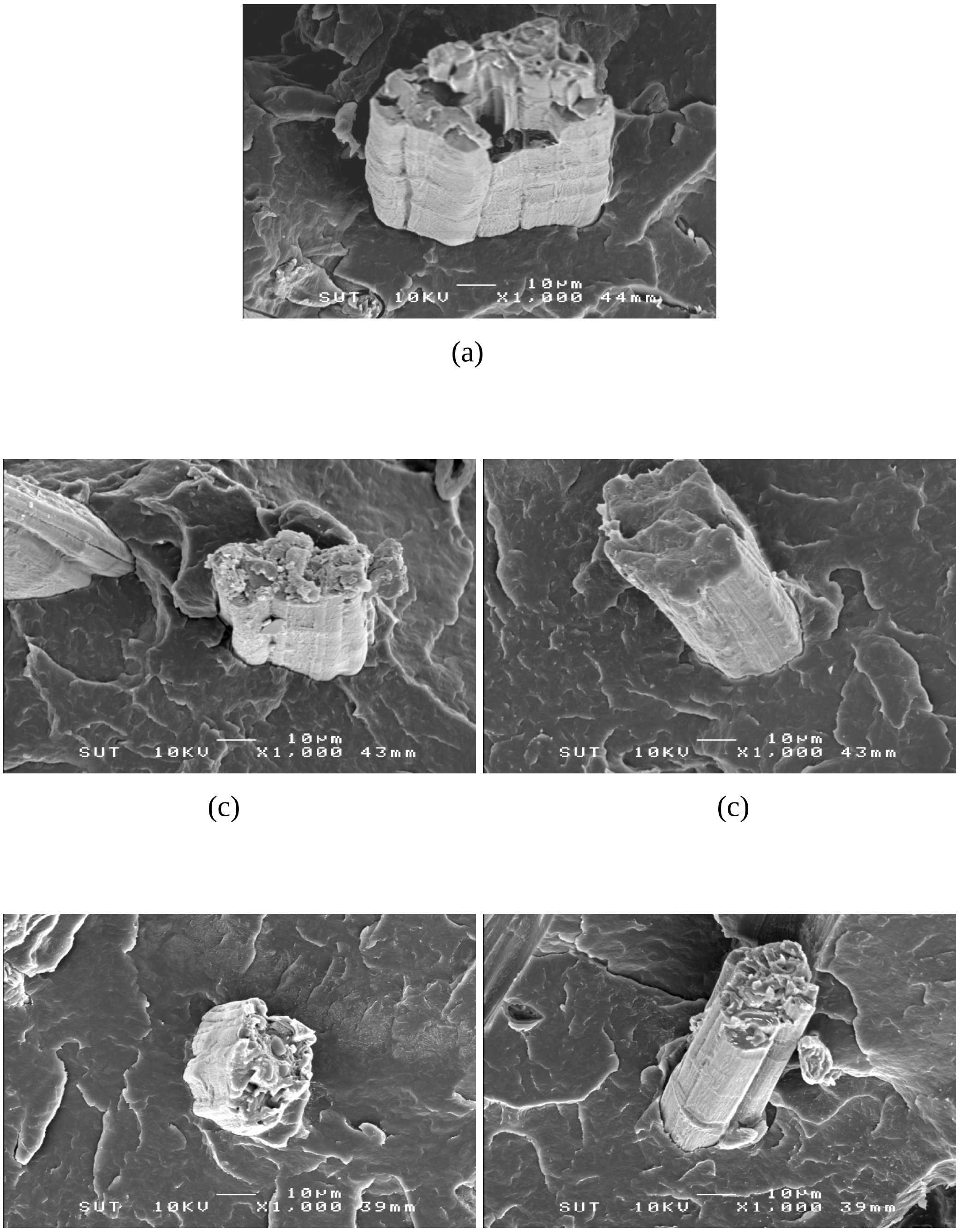
Flexural properties of PP and rossells-PP composites are shown in Table 4.13 and Figure 4.19. Flexural strength and modulus of PP were enhanced with the addition of the fibers. For the VTES treated rossells-PP composites, flexural strength and modulus insignificantly changed comparing with the unmodified rossells-PP composites but the OTMS treated rossells-PP composites was increased. This was attributed to the long octadecyl groups which contributed to the toughness of the rossells-PP composites. However, treatment time did not affect on both flexural strength and modulus of the VTES and OTMS treated rossells-PP composites.

4.3.4 Morphological properties

SEM micrographs of the fracture surface of unmodified and silane treated rossells-PP composites as shown in Figure 4.20 (a)-(b) illustrate that the gap between fiber surface and PP of both VTES and OTMS treated rossells-PP composites was reduced. This indicated that both VTES and OTMS treatment contributed to the improvement in surface adhesion between rossells fibers and PP. In addition, silane coupling agents could improve a fiber dispersion of the composite (Herrera-Franco and Aguilar-Vega; 1997).

4.3.5 Water absorption

The relationship between water absorption and immersion time of VTES and OTMS treated rossells-PP composites is shown in Figure 4.21. Water absorption of the unmodified rossells-PP composite was higher than that of VTES and OTMS treated rossells-PP composites. A decrease in water absorption of the silane treated rossells-PP composites indicated that both VTES and OTMS treatment could be used to reduce the hydrophilicity of rossells-PP composites (Varma, Krishnan, and Krishnamoorthy; 1987). The treatment times showed no influence on the water absorption of VTES and OTMS treated rossells-PP composites.



(a)

(c) (c)

(d) (e)

Figure 4.20 SEM micrographs at 1,000x magnification of rossells-PP composites; (a) Unmodified, (b) VTES_3hr, (c) VTES_24hr, (d) OTMS_3hr, (e) OTMS_24hr.

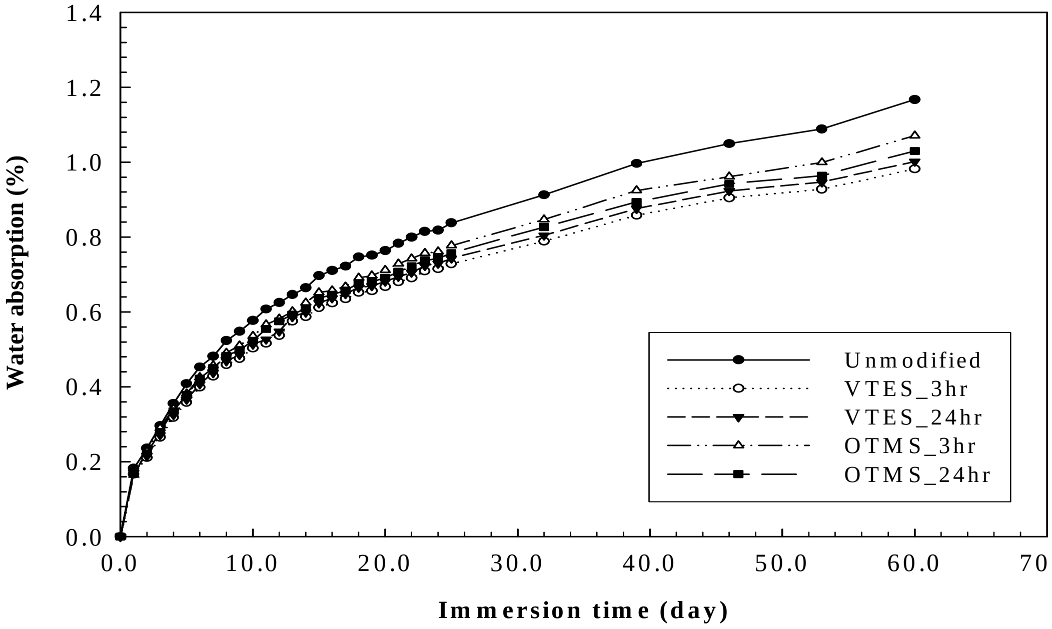


Figure 4.21 Water absorption of unmodified and silane treated rossells-PP composites.

4.4 Effect of surface modification on properties of sisal fibers

4.4.1 Measurement of fiber dimensions

The average fiber diameter of CL and silane treated fibers was slightly lower than NP fibers. This indicated that the diameter of fibers was reduced after the treatment due to removal of binding components (e.g. hemicelluloses and lignin) from the fibers. The reduction of fiber diameter affected on the increase of aspect ratio as shown in Table 4.14.

4.4.2 Thermal properties

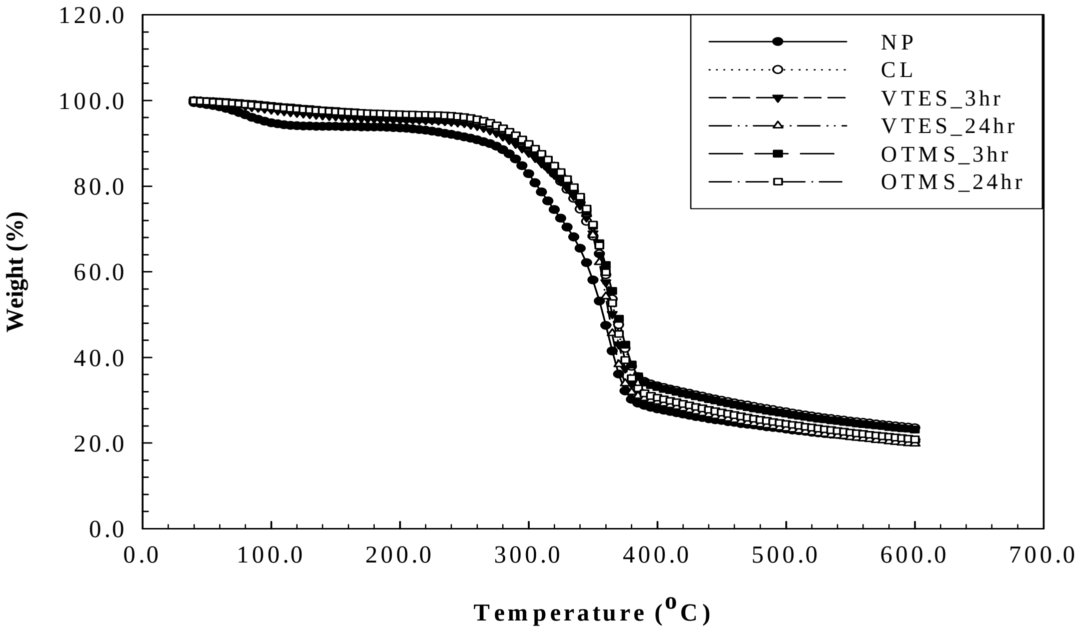
TGA and DTGA thermograms NP, CL, and silane treated sisal fibers are shown in Figure 4.22. From the results, NP fibers were clearly higher in moisture content than the CL fibers. This indicated that the cleaning with mixed solvent and alkalization could be removed hydrophilic component (e. g. pectin, hemicelluloses, and lignin) from the fibers leading to the reduction of fiber diameter. In the case of CL fibers, the absence of the second and third decomposition temperature indicated the removal of hemicelluloses and lignin, respectively. The decomposition temperature of cellulose of CL and silane treated fibers were not significant difference. This presented that the silane treatment did not affect on the decomposition temperature of cellulose. In addition, treatment times showed no influence on the decomposition temperature of fibers.

4.4.3 Mechanical properties

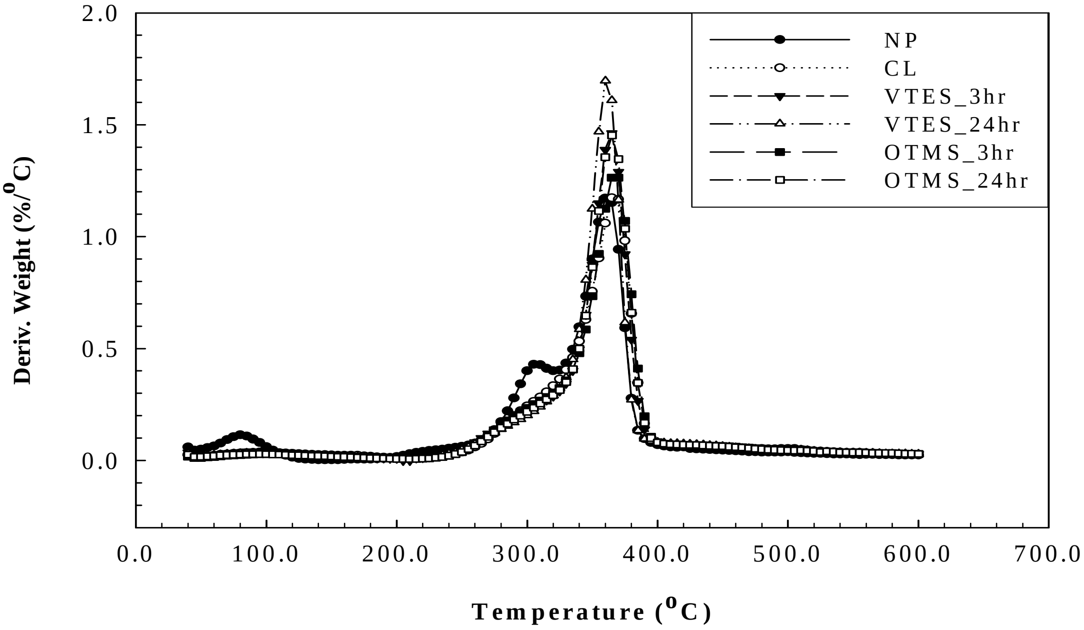
Tensile strength and Young's modulus of CL fibers were lower than that of NP fibers as shown in Table 4.16. This was due to the separation of fiber bundles affecting the decrease of stress transfer between the fiber bundles. For the VTES and OTMS treated fibers, tensile strength was lower than the CL fibers. However, there was no significant difference in Young's modulus between CL and silane treated fibers.

Table 4.14 Fiber length and diameter of NP, CL, VTES, and OTMS treated sisal fibers.

Type of fibers	Length (mm)		Diameter (μm)		L/D
	range	average	range	average	
NP	0.97-8.00	2.56±0.97	100.5-518.0	231.0±100.5	12.3
CL	0.92-6.68	2.77±0.92	90.0-498.0	227.9±90.0	14.3
VTES_3hr	1.69-7.22	2.97±0.97	100.0-300.0	181.0±46.9	17.1
VTES_24hr	2.31-5.57	3.53±0.67	120.0-540.0	229.9±68.0	16.6
OTMS_3hr	1.78-7.60	3.13±1.03	100.0-350.0	192.3±55.8	17.3
OTMS_24hr	2.2-5.30	3.36±0.64	120.0-360.0	212.0±56.2	17.0



(a)



(b)

Figure 4.22 TGA (a) and DTGA (b) thermograms of NP, CL, VTES, and OTMS treated sisal fibers.

Table 4.15 Decomposition temperature of NP, CL, VTES, and OTMS treated sisal fibers.

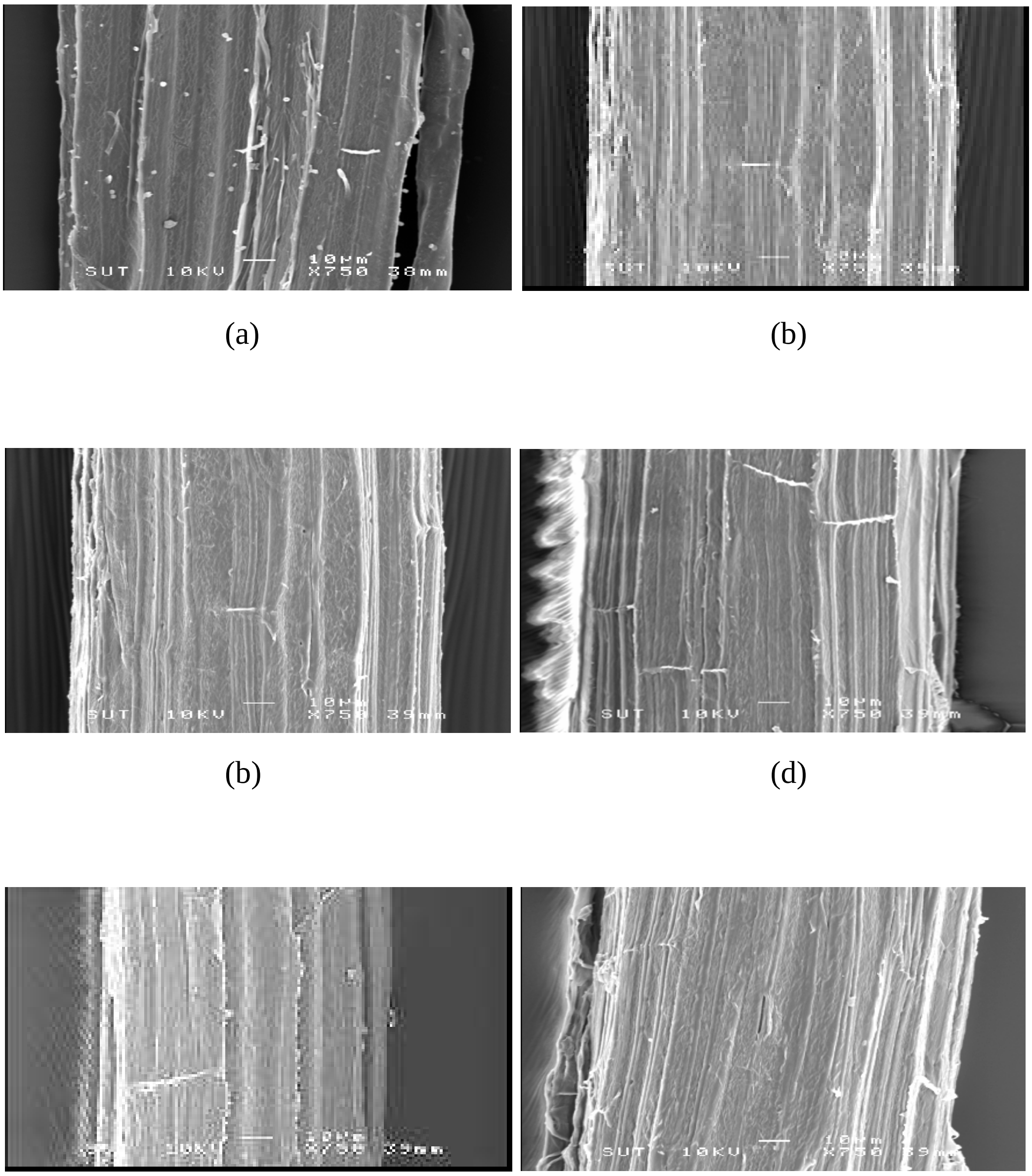
Type of fibers	**Decomposition temperature (°C)**			
	1st	**2nd**	**3rd**	**4th**
NP	80.2	220.7	307.2	362.8
CL	97.4	-	-	368.1
VTES_3hr	96.1	-	-	364.6
VTES_24hr	97.3	-	-	363.7
OTMS_3hr	96.6	-	-	368.6
OTMS_24hr	98.2	-	-	365.9

Table 4.16 Tensile strength and Young's modulus of NP, CL, VTES, and OTMS treated sisal fibers.

Type of fibers	**Tensile strength (MPa)**		**Young's modulus (GPa)**	
	range	**average**	**range**	**average**
NP	130.0-750.0	385.5±175.7	10.4-69.2	33.7±17.3
CL	111.0-730.0	377.8±140.4	7.5-35.1	19.6±7.6
VTES_3hr	105.0-833.0	333.2±158.9	9.3-48.3	24.2±9.5
VTES_24hr	112.0-886.0	311.0±163.2	12.7-46.3	26.0±10.1
OTMS_3hr	144.0-865.0	340.6±159.0	9.9-49.6	19.9±8.9
OTMS_24hr	130.0-608.0	327.8±129.9	11.3-51.4	24.0±11.7

4.4.4 Morphological properties

SEM micrographs of NP, CL, VTES and OTMS treated fibers are shown in Figure 4.23 (a)-(f). By cleaning fibers with mixed solvent and alkalization, some components such as surface impurities, low molecular weight species, hemicelluloses, and lignin were removed from the fiber surface. From the SEM micrograph, it was observed that the surface of CL fibers was more cleaned than the NP fibers (Valadez-Gonzalez, Cervantes-Uc, and Herrera-Franco, 1999). The surface morphology of silane treated fibers was not different from that of CL fiber.



(a) (b)

(b) (d)

(e) (f)

Figure 4.23 SEM micrographs at 750x magnification of sisal fibers; (a) NP, (b) CL, (c) VTES_3hr, (d) VTES_24hr, (e) OTMS_3hr, (f) OTMS_24hr.

4.5 Effect of compatibilizer on properties of sisal-PP composites

4.5.1 Thermal properties

DSC results of PP and sisal-PP composites are presented in Table 4.17 and Figure 4.24. Melting temperature of PP did not change when the fibers were added but crystallization temperature was increased. The crystallinity of PP slightly reduced with adding fibers. The addition of fibers was influenced on the increase in crystallization temperature due to the induce crystallization effect by the fibers. However, the fibers restricted the nucleation growth of PP so the crystallinity was decreased. The addition of MAPP did not affect on both melting temperature and crystallization temperature but crystallinity increased. The increasing of crystallinity was attributed to the reduction of micro voids due to the improvement of surface adhesion. However, the crystallinity slightly decreased with the MAPP content.

The results of thermogravimetric analysis of PP, unmodified and MAPP modified sisal-PP composites are shown in Table 4.18 and Figure 4.25. The decomposition temperature of fibers at about 370ºC did not change with adding fibers and MAPP while the decomposition of PP slightly increased when the fibers were added. The addition of MAPP affected on the increase of PP decomposition temperature. However, MAPP content did not influence in the decomposition temperature of PP.

HDT of PP was enhanced with the addition of fibers as shown in Table 4.19. When the MAPP was added the HDT of the MAPP modified sisal-PP composites was higher than the unmodified sisal-PP composites. This might be due to the improvement in the fiber-matrix interfacial adhesion. However, no significant difference on HDT of the MAPP modified sisal-PP composites was observed when the

MAPP content was increased.

Table 4.17 Melting temperature, crystallization temperature, and crystallinity of PP and sisal-PP composites with different MAPP contents.

Materials	**T_m (ºC)**	**T_C (ºC)**	**Crystallinity (%)**
PP	157.2	108.4	51.09
Unmodified	159.1	114.0	42.04
MAPP_1phr	159.0	116.4	58.73
MAPP_2phr	158.4	117.6	55.00
MAPP_4phr	159.0	118.8	50.93
MAPP_6phr	158.4	118.2	48.15
MAPP_8phr	159.0	118.8	44.26
MAPP_10phr	159.0	120.0	43.68

Table 4.18 Decomposition temperature of fibers and PP of sisal-PP composites with different MAPP contents.

Materials	**Cellulose decomposition temperature (ºC)**	**PP decomposition temperature (ºC)**
Unmodified	370.7	462.1
MAPP_1phr	370.4	464.9
MAPP_2phr	370.0	465.1
MAPP_4phr	371.9	466.2
MAPP_6phr	373.3	465.8
MAPP_8phr	369.2	467.0
MAPP_10phr	370.1	469.9

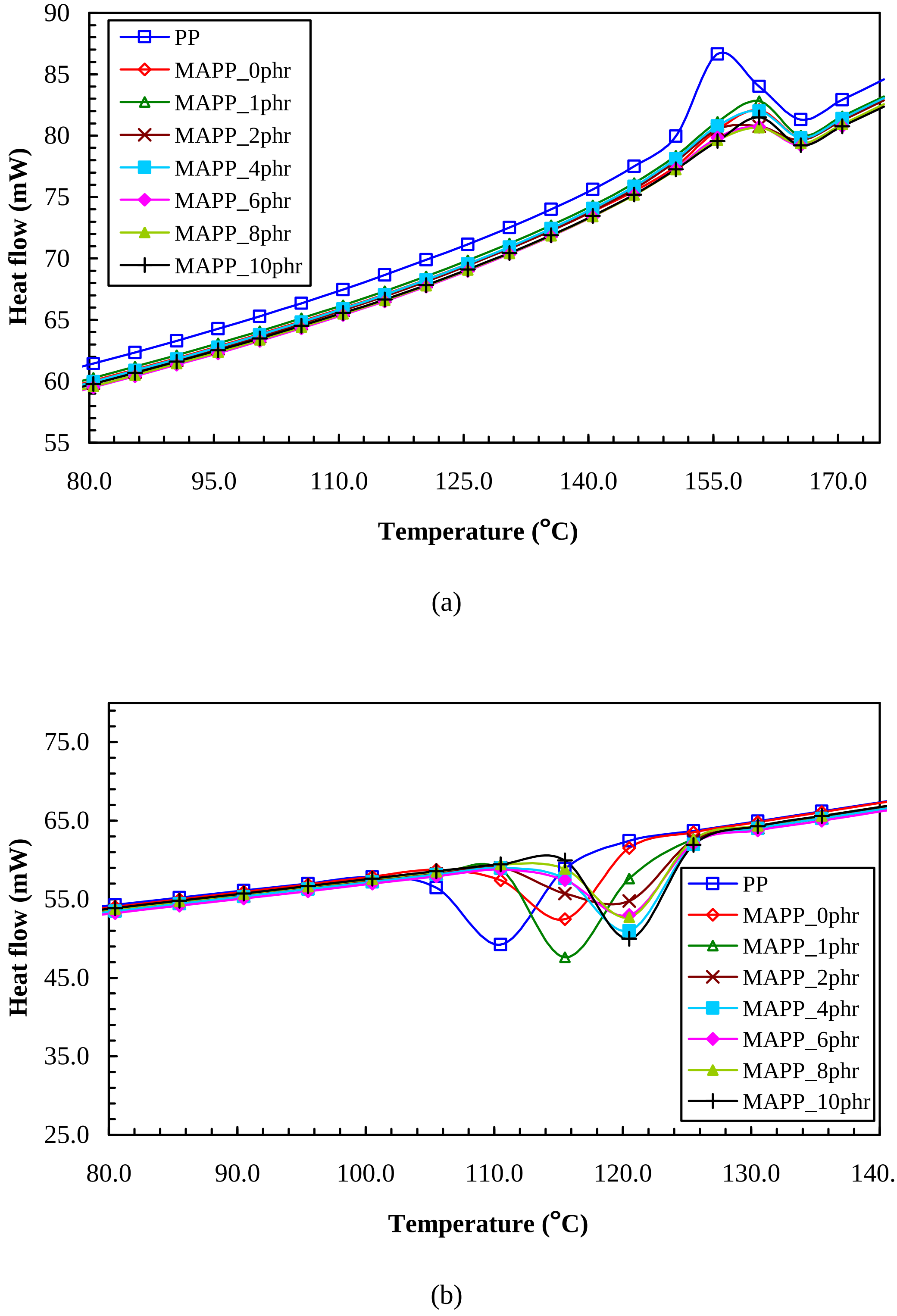
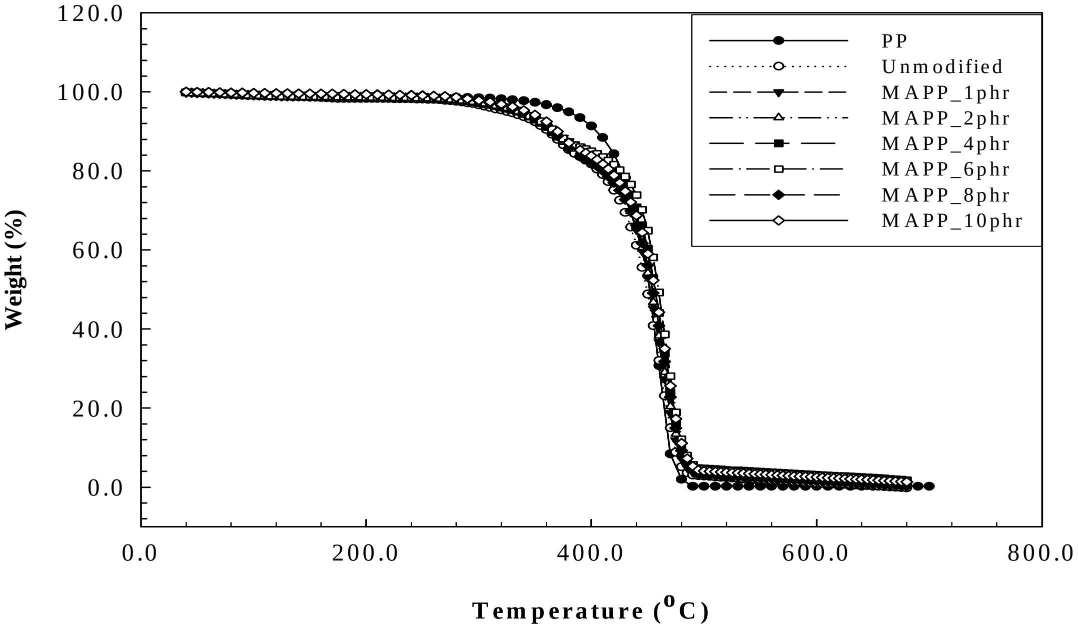
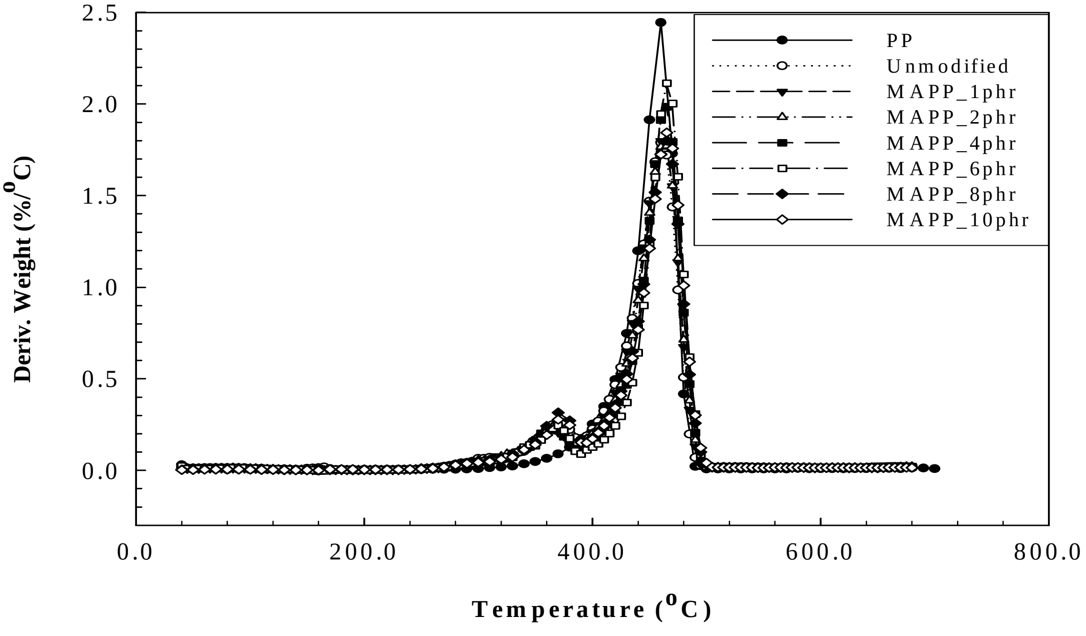


Figure 4.24 DSC thermograms of PP and sisal-PP composites with different MAPP contents; (a) heating scan, (b) cooling scan.



(a)



(b)

Figure 4.25 TGA (a) and DTGA (b) thermograms of PP and sisal-PP composites with different MAPP contents.

Table 4.19 Heat distortion temperature of PP and sisal-PP composites with different MAPP contents.

Materials	**HDT (ºC)**
PP	79.4±2.5
Unmodified	133.0±1.3
MAPP_1phr	134.7±1.2
MAPP_2phr	135.0±2.5
MAPP_4phr	137.0±2.5
MAPP_6phr	136.0±1.5
MAPP_8phr	134.0±1.0
MAPP_10phr	135.0±1.0

4.5.2 Rheological properties

MFI and flow curves of PP, unmodified and MAPP modified sisal-PP composites as shown in Table 4.20 and Figure 4.26 indicated that the viscosity of PP increased with the addition of fibers. The viscosity of MAPP modified sisal-PP composites insignificantly changed with adding MAPP and increasing MAPP content. However, Fung, Li, and Tjong (2002) reported the viscosity of MAPP modified sisal-PP composites was increased due to the improvement in fiber-matrix interfacial bonding between sisal fibers and matrix.

Table 4.20 Melt flow index of PP and sisal-PP composites with different MAPP contents.

Materials	MFI (g/10min)
PP	4.16±0.06
Unmodified	2.22±0.02
MAPP_1phr	2.21±0.01
MAPP_2phr	1.93±0.03
MAPP_4phr	1.88±0.03
MAPP_6phr	1.83±0.01
MAPP_8phr	1.74±0.04
MAPP_10phr	1.72±0.03

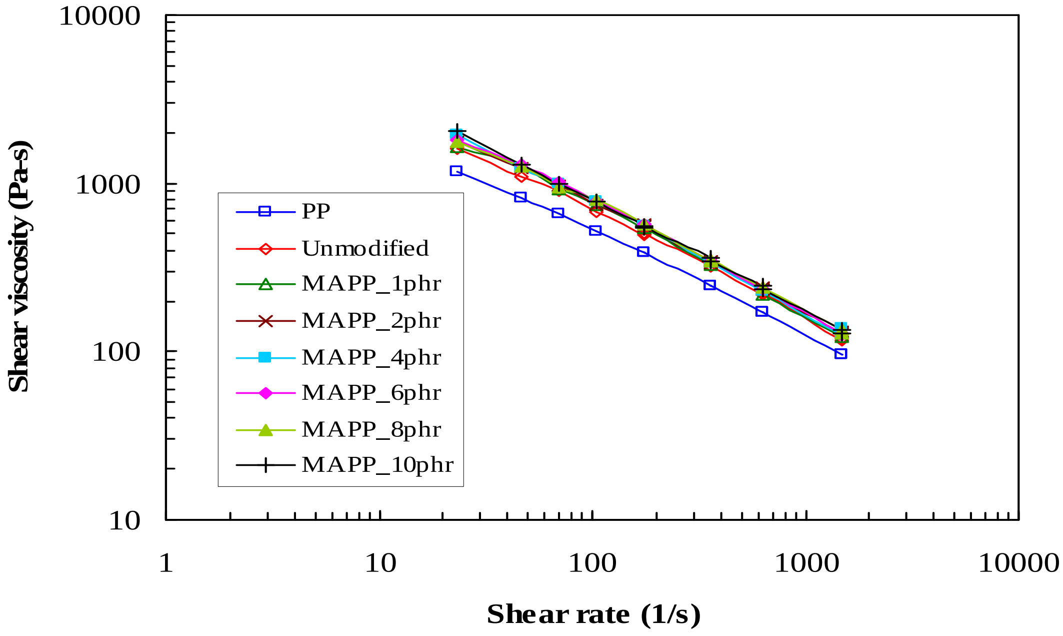


Figure 4.26 Flow curves of PP and sisal-PP composites with different MAPP contents.

4.5.3 Mechanical properties

Tensile strength and Young’s modulus of PP were improved when the fibers was added. With incorporating MAPP, tensile strength and Young’s modulus of sisal-PP composites were enhanced. Tensile strength was increased with MAPP content but Young’s modulus insignificantly changed. These results are shown in Table 4.21 and Figure 4.27 and 4.28. Tensile strain at break and impact strength of PP were reduced with adding fibers as shown in Figure 4.27 and 4.28, respectively. When MAPP was added, tensile strain at break and impact strength slightly decreased. However, the impact strength and tensile strain at break were no remarkable change with increasing MAPP contents.

The flexural strength and modulus of PP were increased with adding the fiber as shown in Table 4.21 and Figure 4.29. The flexural strength and modulus of sisal-PP composites were improved with the addition of MAPP. Tensile strength of MAPP modified sisal-PP composites slightly increased with the MAPP contents but flexural modulus insignificantly changed. Flexural strength increased with increasing MAPP contents until 4 phr beyond this content, the result showed insignificant in crease. It had been explained that the surface adhesion between fibers and PP was improved by the esterification of hydroxyl groups of fibers and anhydride part of MAPP. Thus, it led to more strong interfacial adhesion in the MAPP modified sisal-PP composites than the unmodified sisal-PP composite (Cantero, Arbeliaiz, Llano-Ponte, and Mondragon, 2003).

Table 4.21 Mechanical properties of sisal-PP composites with difference MAPP contents.

Materials	Tensile strength (MPa)	Impact strength (kJ/m^2)	Young's modulus (GPa)	Tensile strain at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)
PP	13.9±2.0	85.8±1.1	1.08±0.03	248.8±56.4	46.4±1.5	1.43±0.04
Unmodified	24.8±0.7	17.6±1.2	1.86±0.06	7.2±0.6	58.7±0.5	3.21±0.06
MAPP_1phr	27.6±0.5	14.9±1.3	1.99±0.04	5.9±0.5	63.3±0.3	3.51±0.08
MAPP_2phr	28.6±0.3	14.8±1.5	2.00±0.04	4.9±0.2	64.1±0.6	3.54±0.07
MAPP_4phr	29.7±0.6	14.5±1.6	2.01±0.05	5.0±0.3	67.3±0.4	3.70±0.05
MAPP_6phr	29.9±0.9	14.3±1.7	2.00±0.03	5.3±0.3	67.6±0.7	3.71±0.10
MAPP_8phr	30.5±0.7	14.2±1.7	1.96±0.03	5.1±0.4	68.3±0.6	3.61±0.08
MAPP_10phr	32.0±0.6	14.4±1.2	1.96±0.02	5.0±0.3	68.4±0.4	3.50±0.08

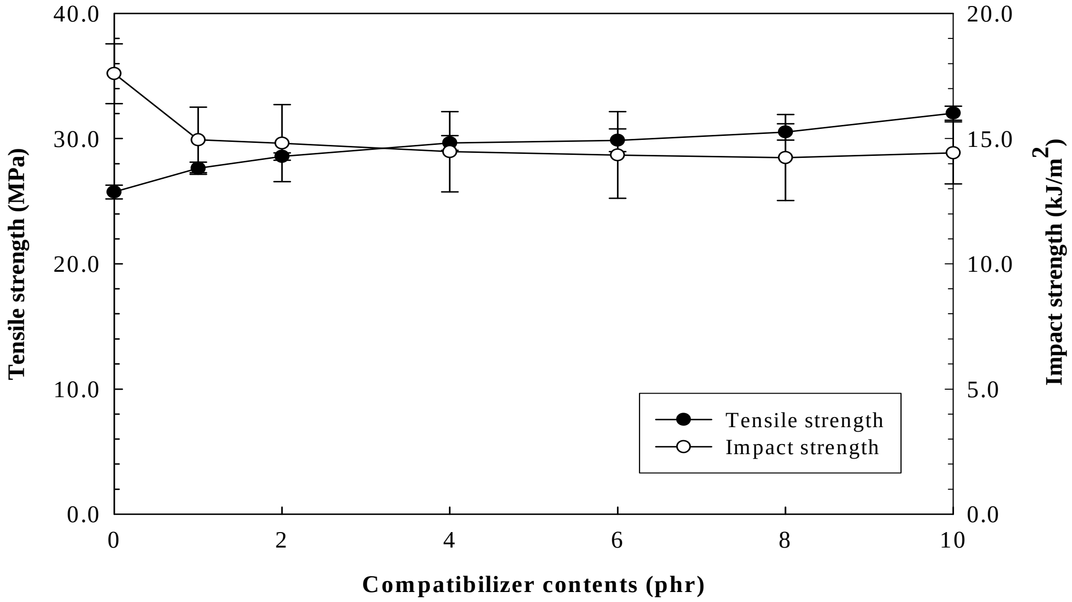


Figure 4.27 Tensile and impact strength of sisal-PP composites with different MAPP contents.

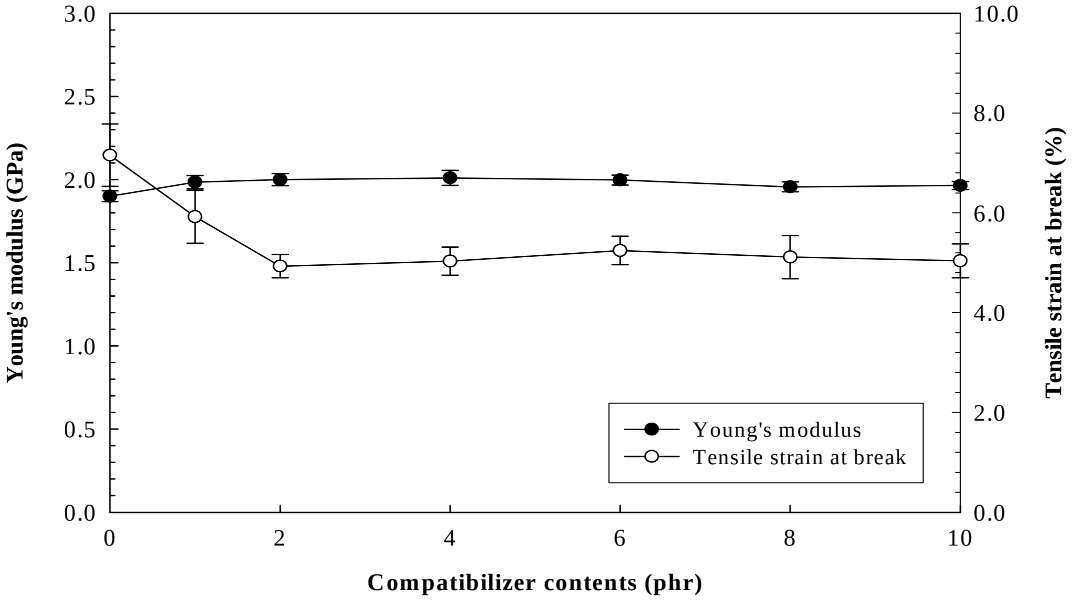


Figure 4.28 Young’s modulus and tensile strain at break of sisal-PP composites with different MAPP contents.

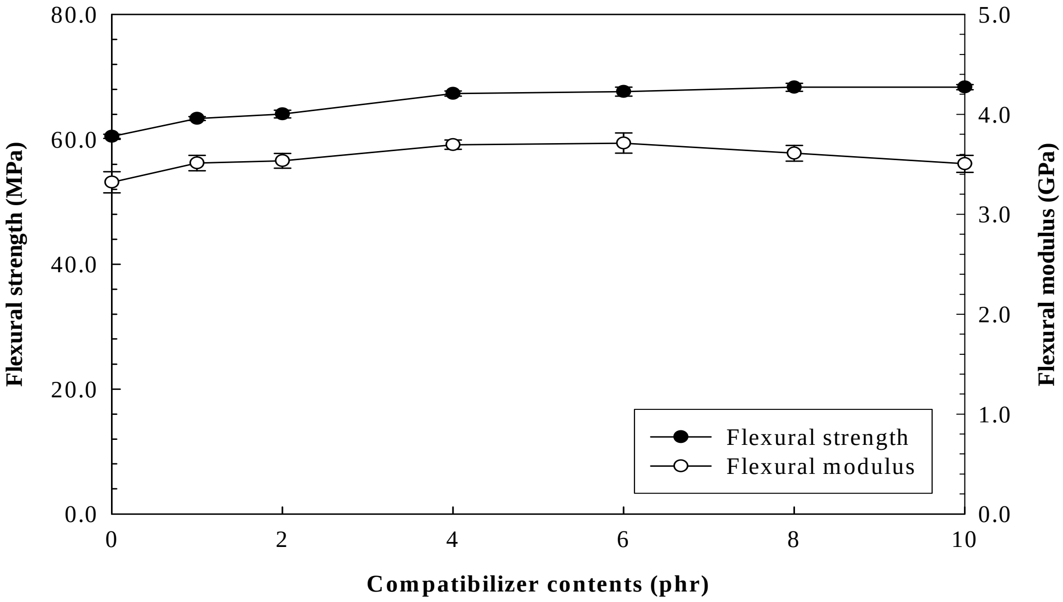
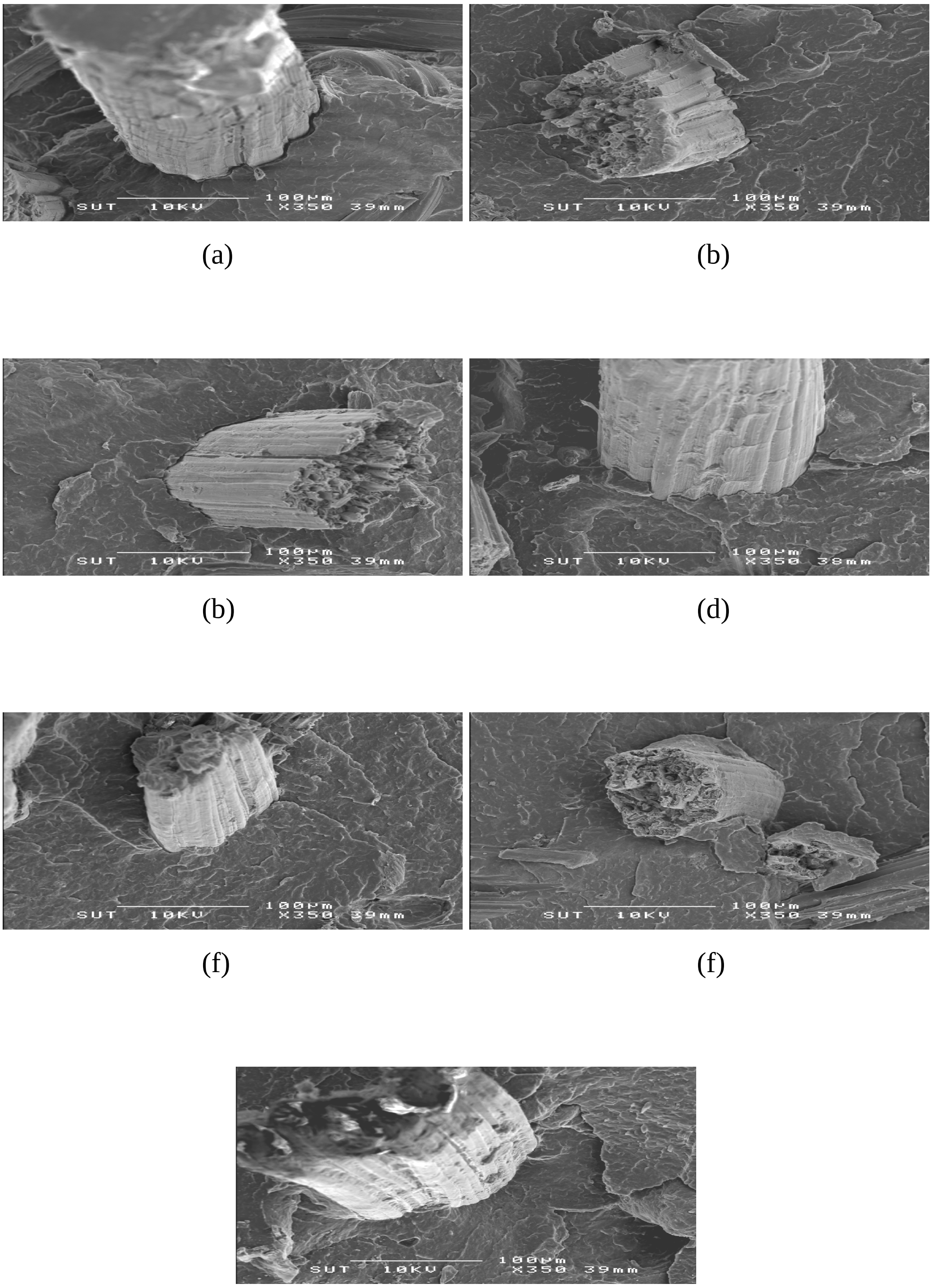


Figure 4.29 Flexural strength and flexural modulus of sisal-PP composites with different MAPP contents.

4.5.4 Morphological properties

Fracture surface of sisal-PP composites is shown in Figure 4.30. The fiber surface of unmodified sisal-PP composite in Figure 4.30 (a) presented that the fiber surface seem to be cleaned. Whereas, the MAPP modified sisal-PP composites had a fair amount of polymer residue remained on the fiber surface. This indicated the surface adhesion between fibers and PP matrix was improved (Karnani, Krishnan, and Narayan, 1997).



(a) (b)

(b) (d)

(f) (f)

(g)

Figure 4.30 SEM micrographs at 350x magnification of sisal-PP composites; (a) Unmodified, (b) MAPP_1phr, (c) MAPP_2phr, (d) MAPP_4phr, (e) MAPP_6phr, (f) MAPP_8phr, and (g) MAPP_10phr.

4.5.5 Water absorption

The water absorption of MAPP modified sisal-PP composite was lower than the unmodified sisal-PP composite as shown in Figure 4.31. The reduction of water absorption was caused from the decreasing of the hydrophilicity of sisal fibers. The enhancement of surface adhesion of MAPP modified sisal-PP composite was attributed to the esterification reaction between hydroxyl groups of sisal fibers and anhydride part of MAPP, which caused a reduction in interfacial tension and an increase in interfacial adhesion between PP and the fibers (Joseph, Rabello, Mattoso, Joseph, and Thomas; 2002, Arbelaiz et al.; 2005).

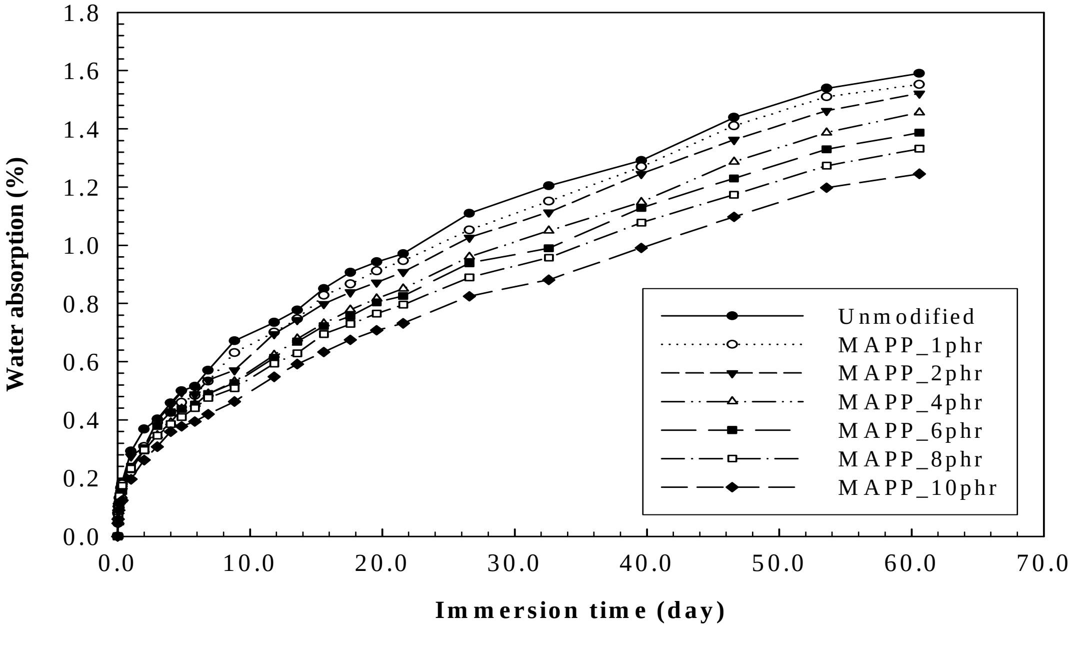


Figure 4.31 Water absorption of sisal-PP composites with different MAPP contents.

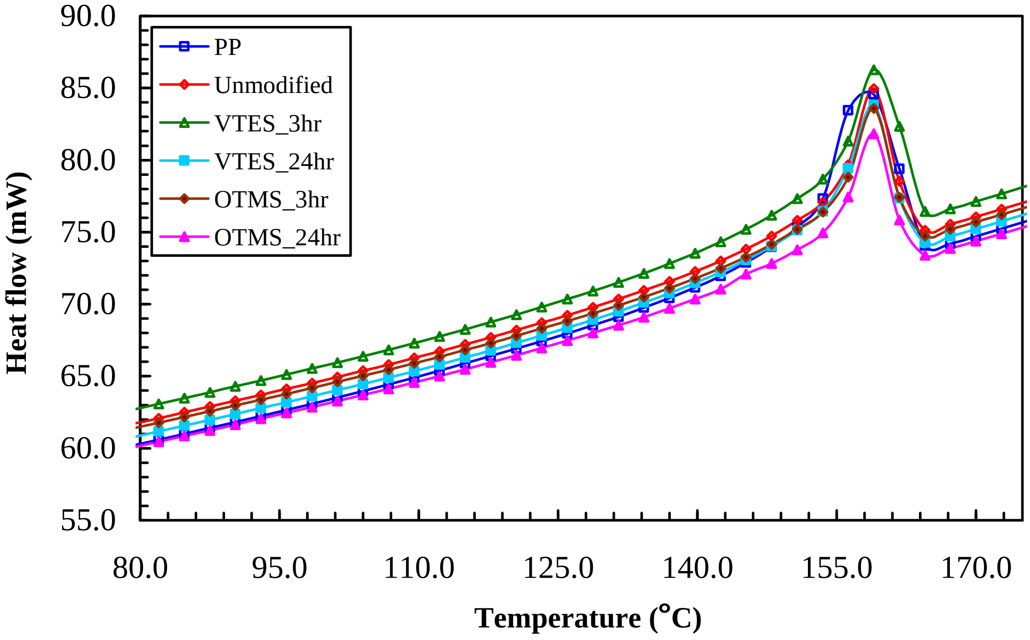
4.6 Effect of silane coupling agents on properties of sisal-PP composites

4.6.1 Thermal properties

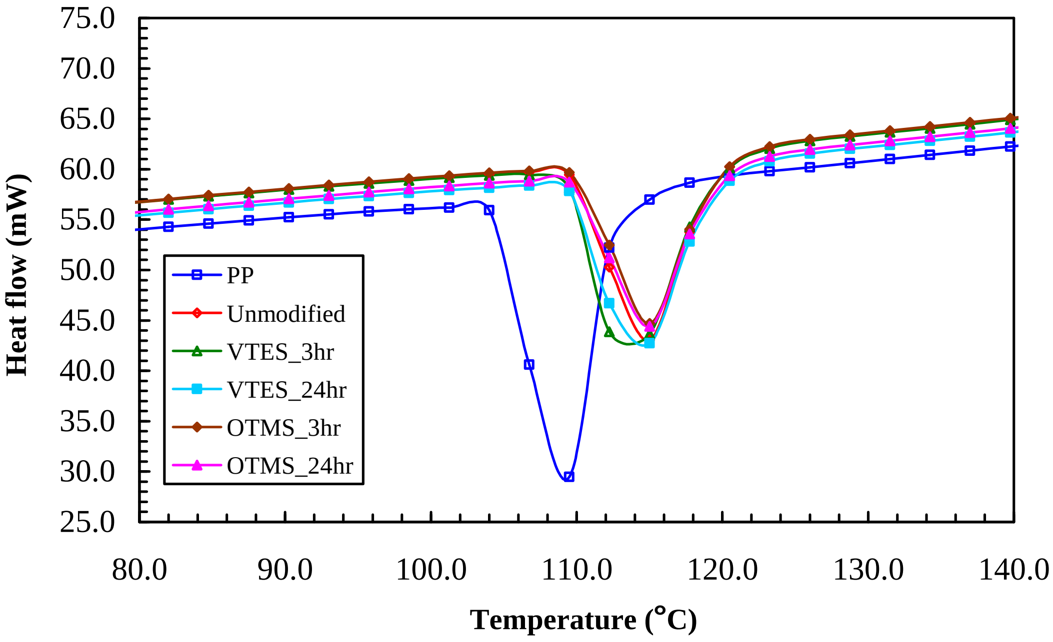
DSC thermograms of PP and sisal-PP composites as shown in Figure 4.32 presented no remarkable difference in melting temperature of PP and unmodified sisal-PP composites but crystallization temperature was slightly higher than that of PP. On the contrary, the crystallinity was decreased as shown in Table 4.22. An increase in crystallization temperature was due to the restriction of fibers on the molecular mobility of PP chains and the induce crystallization effect of the fibers. Moreover, the restriction of molecular mobility resulted in a low crystallinity of sisal-PP composites because of the low relaxation time of PP chains. No significant change of melting temperature, crystallization temperature, and crystallinity of unmodified, and silane treated sisal-PP composites was observed.

Table 4.22 Melting temperature, crystallization temperature, and crystallinity of PP, unmodified, and silane treated sisal-PP composites.

Materials	**T_m (°C)**	**T_c (°C)**	**Crystallinity (%)**
PP	157.2	108.4	51.09
Unmodified	159.1	114.0	42.04
VTES_3hr	159.8	113.5	42.89
VTES_24hr	159.3	114.1	38.94
OTMS_3hr	159.3	114.6	41.27
OTMS_24hr	159.3	114.1	42.62



(a)



(b)

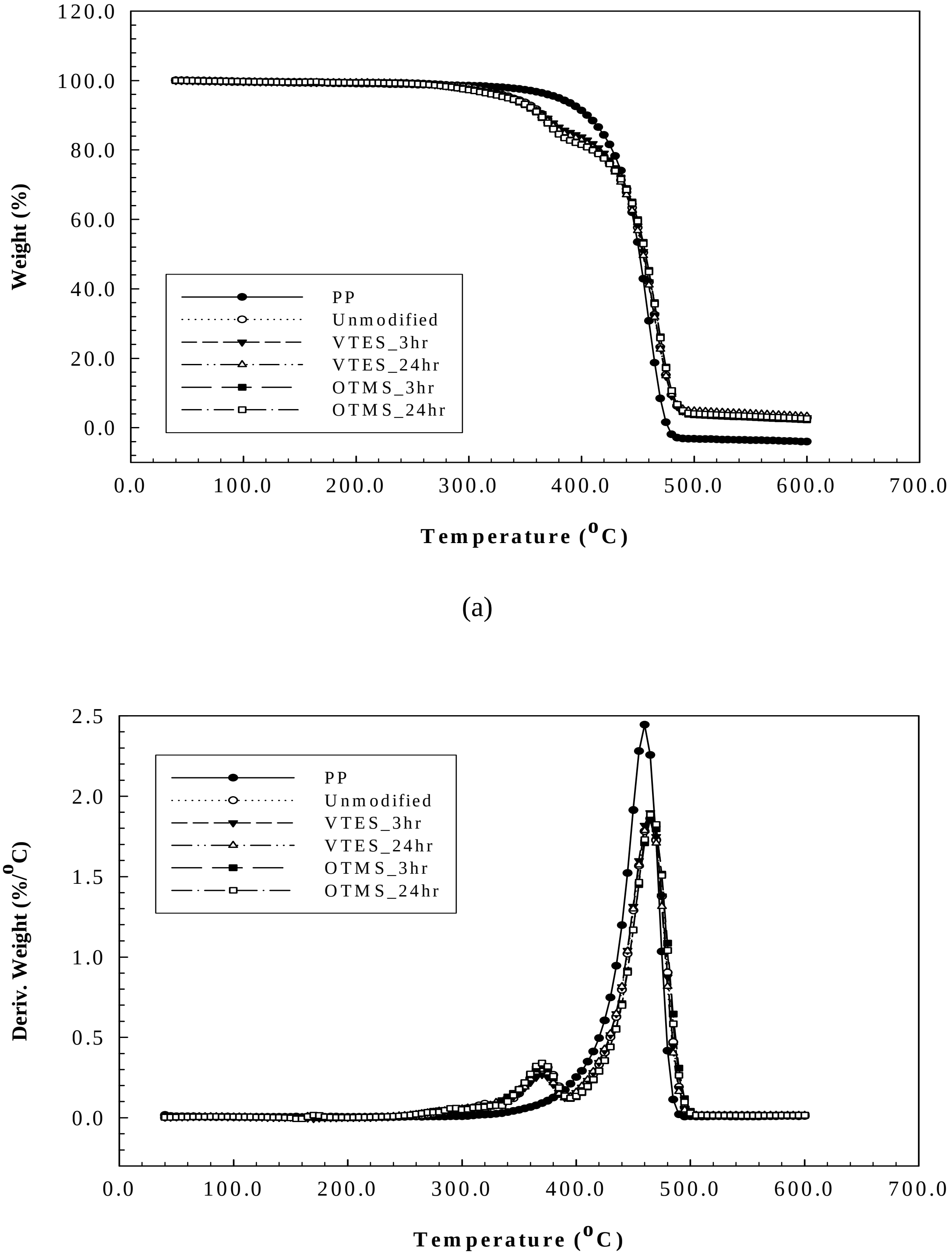
Figure 4.32 DSC thermograms of PP, unmodified, and silane treated sisal-PP composites; (a) heating scan, (b) cooling scan.

TGA and DTGA thermograms of PP, unmodified and silane treated sisal-PP composites are shown in Figure 4.33. The decomposition temperature of fibers about 370ºC did not change with the addition of silane treated fibers but the decomposition temperature of PP about 460ºC was increased. However, the effect of treatment times on degradation temperature of fibers and PP did not observe both VTES and OTMS treated sisal-PP composites.

Heat distortion temperature of PP was enhanced with adding the fibers while the HDT of VTES and OTMS treated sisal-PP composites showed no remarkable difference compared to the unmodified sisal-PP composite. The results are shown in Table 4.24. This indicated that silane treatment did not affect on heat distortion temperature of sisal-PP composites.

Table 4.23 Decomposition temperature of fibers and PP of unmodified, and silane treated sisal-PP composites.

Materials	**Cellulose decomposition temperature (ºC)**	**PP decomposition temperature (ºC)**
Unmodified	370.7	464.9
VTES_3hr	370.8	464.8
VTES_24hr	369.4	464.3
OTMS_3hr	369.3	466.3
OTMS_24hr	370.0	466.3



(a)

(b)

Figure 4.33 TGA (a) and DTGA (b) thermograms of PP, unmodified, and silane treated sisal-PP composites.

Table 4.24 Heat distortion temperature of PP, unmodified, and silane treated sisal-PP composites.

Materials	**HDT (ºC)**
PP	79.4±2.52
Unmodified	133.0±1.32
VTES_3hr	132.7±2.93
VTES_24hr	132.8±2.75
OTMS_3hr	134.0±1.26
OTMS_24hr	135.5±1.50

4.6.2 Rheological properties

MFI of PP, unmodified and silane treated sisal-PP composites was listed in Table 4.25. MFI of PP was decreased with the addition of the fibers whereas MFI of VTES and OTMS treated sisal-PP composites did not change compared with the unmodified sisal-PP composite. Flow curves as shown in Figure 4.34 were also showed insignificant change in viscosity of unmodified and silane treated sisal-PP composites.

Table 4.25 Melt flow index of PP, unmodified, and silane treated sisal-PP composites.

Materials	MFI (g/10min)
PP	4.16±0.06
Unmodified	2.22±0.02
VTES_3hr	2.18±0.06
VTES_24hr	2.28±0.04
OTMS_3hr	2.27±0.02
OTMS_24hr	2.16±0.13

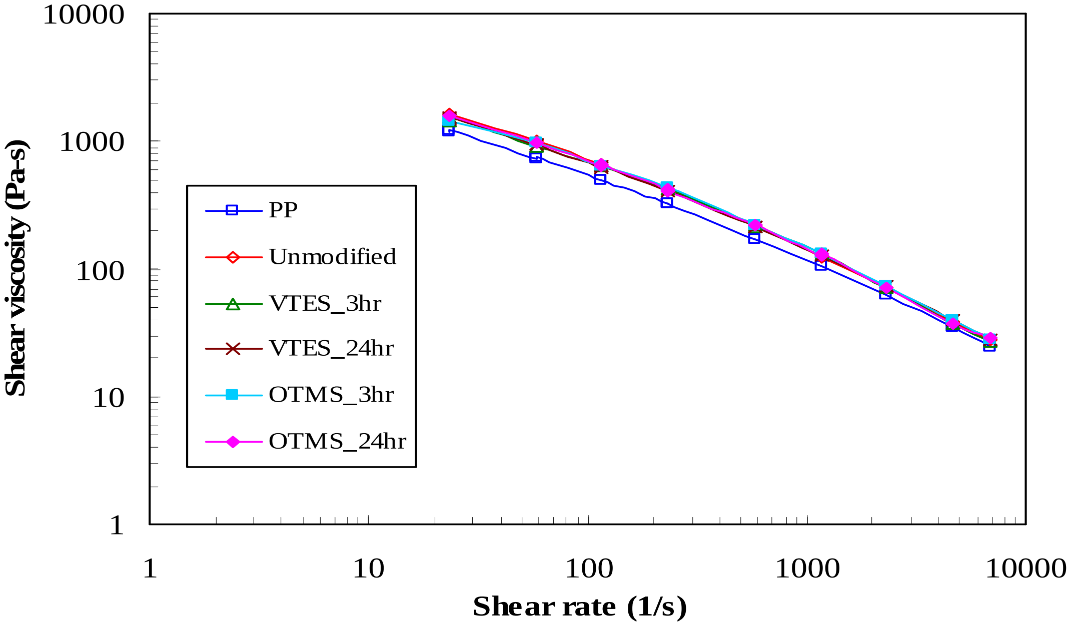


Figure 4.34 Flow curves of PP, unmodified, and silane treated sisal-PP composites.

4.6.3 Mechanical properties

Tensile strength, Young's modulus, tensile strain at break and impact strength of PP were increased with the addition of sisal fibers as shown in Table 4.26 and Figure 4.35 and 4.36. On comparing between the unmodified sisal-PP composite and the silane treated sisal-PP composites, these mechanical properties were not different. Herrera-Franco and Aguilar-Vega (1997) reported the use of the silane-coupling agent resulted in a small increment in the mechanical properties of henequen fiber-HDPE composites. They explained that the enhancement of mechanical properties was attributed to an improvement in the interface between the fibers and the matrix. In addition, silane coupling agent could improve a fiber dispersion of the composite. Treatment time showed no significant effect on these properties.

Flexural properties of PP, unmodified and silane treated sisal-PP composites are shown in Table 4.26 and Figure 4.37. Flexural strength and modulus of PP were improved with the incorporating the fibers. No remarkable difference of flexural strength and modulus of silane treated and unmodified sisal-PP composites were found.

Table 4.26 Mechanical properties of PP, unmodified, and silane treated sisal-PP composites.

Materials	**Tensile Strength (MPa)**	**Impact strength (kJ/m^2)**	**Young's Modulus (GPa)**	**Tensile strain at break (%)**	**Flexural strength (MPa)**	**Flexural modulus (GPa)**
PP	13.9±2.0	85.8±1.1	1.08±0.03	248.8±56.4	46.4±1.5	1.43±0.04
Unmodified	24.8±0.7	17.6±1.2	1.86±0.06	7.2±0.6	58.7±0.5	3.21±0.06
VTES_3hr	24.4±0.9	18.4±2.3	1.89±0.03	7.8±1.0	57.0±0.8	3.30±0.02
VTES_24hr	24.5±0.6	17.3±3.0	1.90±0.06	7.7±1.1	57.4±0.8	3.31±0.05
OTMS_3hr	24.6±0.8	17.9±2.3	1.89±0.02	8.0±0.8	57.0±0.5	3.35±0.03
OTMS_24hr	24.7±0.7	17.2±2.0	1.91±0.03	7.9±1.3	57.2±0.8	3.30±0.06

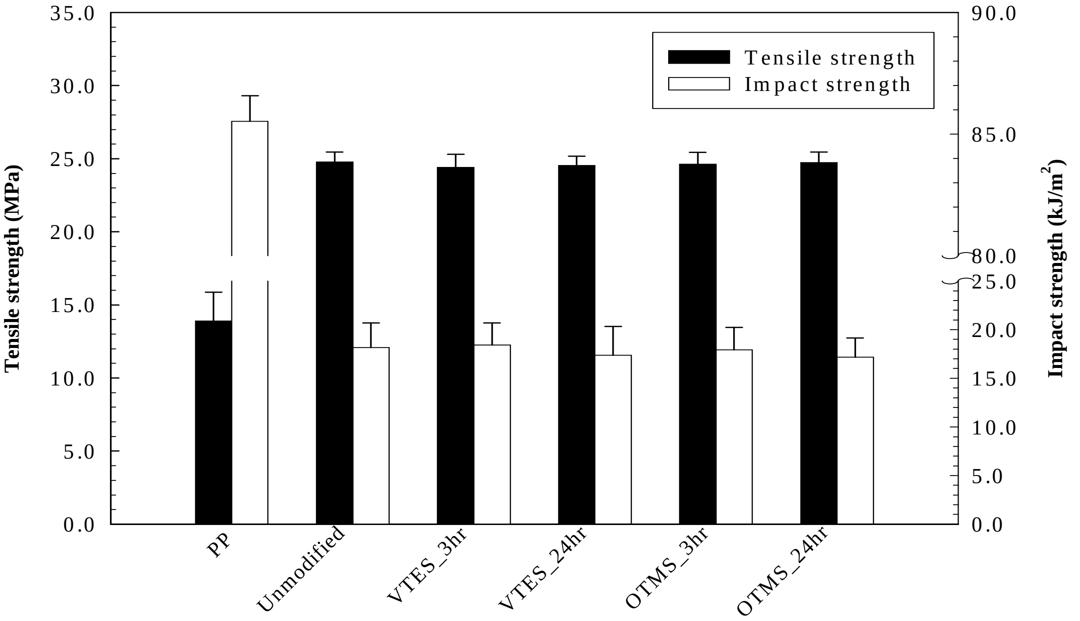


Figure 4.35 Tensile and impact strength of PP, unmodified, and silane treated sisal-PP composites.

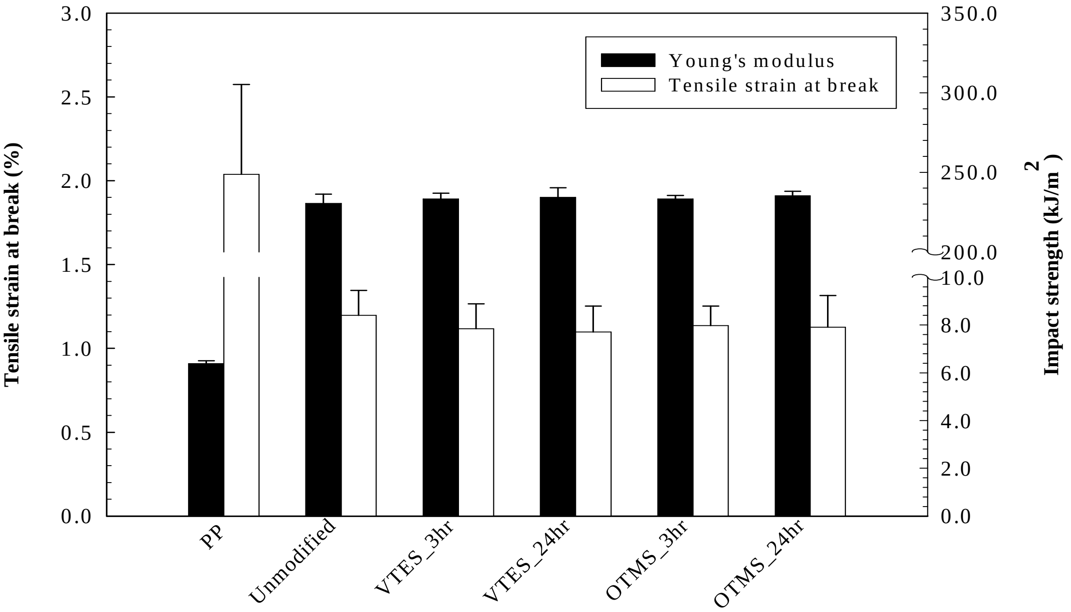


Figure 4.36 Young's modulus and tensile strain at break of PP, unmodified, and silane treated sisal-PP composites.

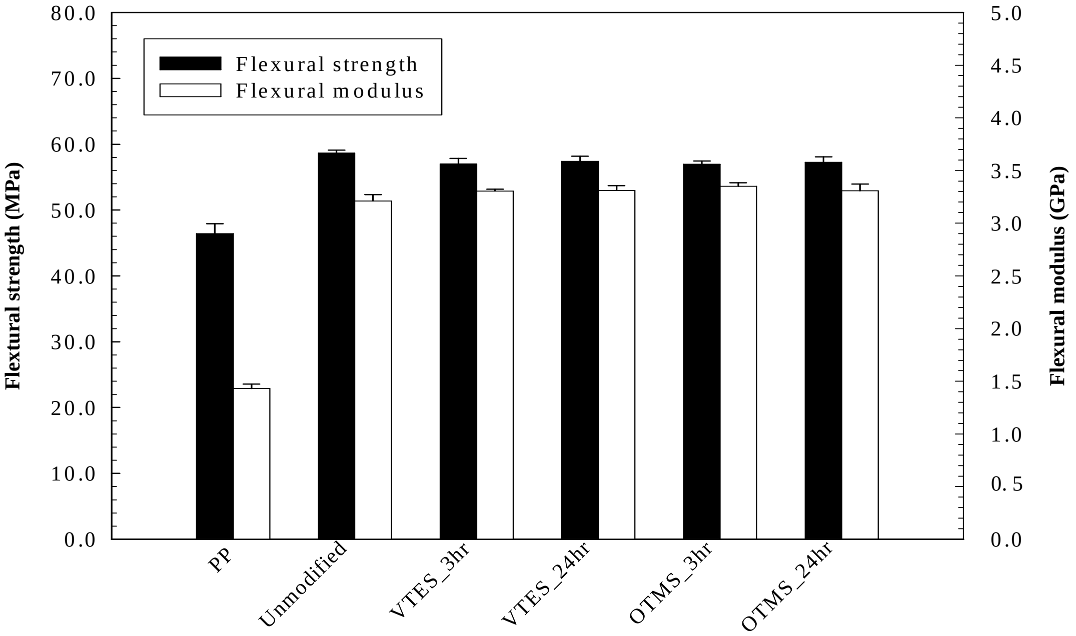
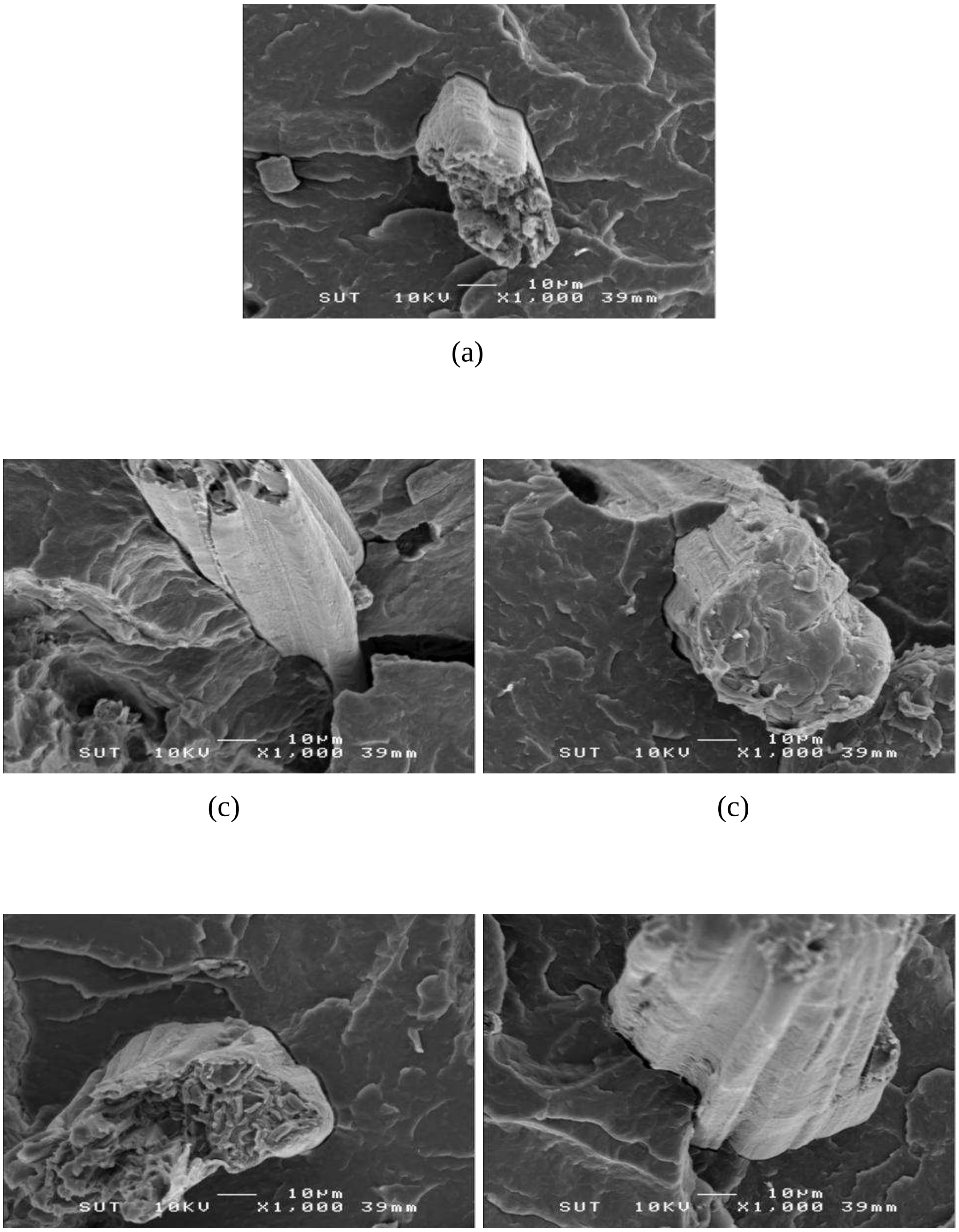


Figure 4.37 Flexural strength and flexural modulus of PP, unmodified, and silane treated sisal-PP composites.

4.6.4 Morphological properties

The fracture surface of unmodified, VTES and OTMS treated sisal-PP composite are shown in Figure 4.38 (a)-(e). Small gap between fiber surface and matrix was observed in VTES and OTMS treated sisal-PP composites. This indicated that surface adhesion between fibers and matrix was no sufficient improvement by VTES and OTMS treatment as agree with no different in mechanical properties. .



(a)

(c) (c)

(d) (e)

Figure 4.38 SEM micrographs at 1,000x magnification of sisal-PP composites; (a) Unmodified, (b) VTES_3hr, (c) VTES_24hr, (d) OTMS_3hr, (e) OTMS_24hr.

4.6.5 Water absorption

Water absorption of VTES and OTMS treated sisal-PP composites was not different compared with the unmodified sisal-PP composite as shown in Figure 4.39. This was not similar to the study of Singh, Gupta, Verma, and Tyagi (2000); they explained that an irregular physisorption/chemisorption of coupling agents decreased the hydrophilicity of sisal fibers. When treated sisal fiber was used as reinforcement in an unsaturated polyester resin matrix, the composites absorbed less moisture than those prepared from untreated fibers.

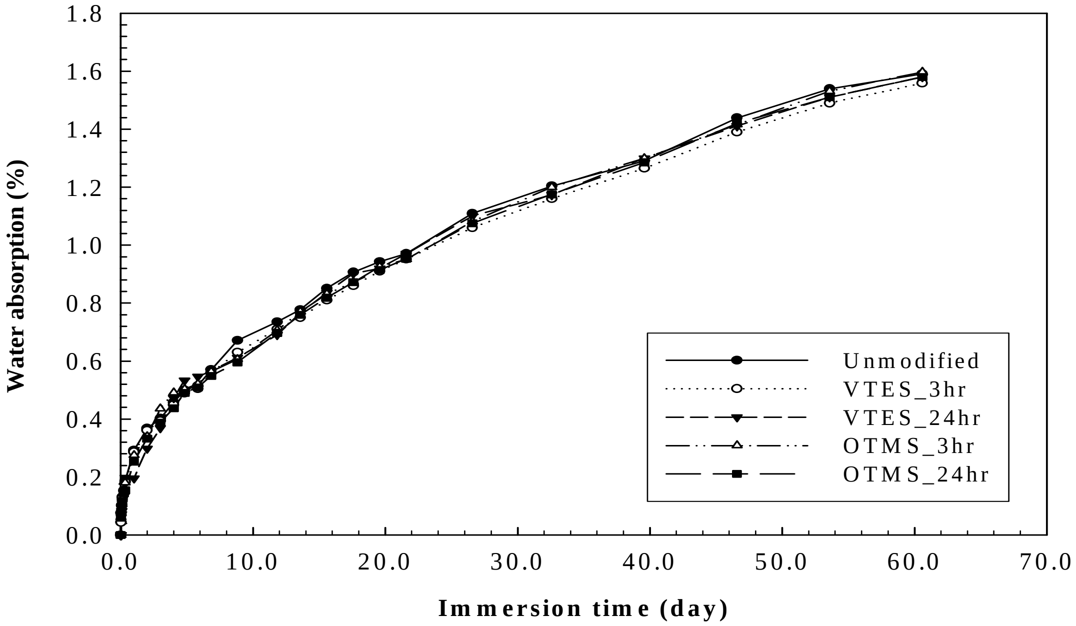


Figure 4.39 Water absorption of unmodified and silane treated sisal-PP composites.

4.7 Mechanical properties comparison for rossells-PP composites versus sisal-PP composites

In this section, the effect of compatibilizer (MAPP) and silane coupling agents (VTES and OTMS) on the mechanical properties of rossells-PP and sisal-PP composites was compared. From the mechanical properties investigated, MAPP content at 2 phr was found to be sufficient for the improvement in surface adhesion of the rossells-PP and sisal-PP composites. Higher contents of the compatibilizer did not give rise to further significant improvement. Tensile properties and impact strength of PP, unmodified, MAPP modified and silane treated rossells-PP and sisal-PP composites are shown in Table 4.27. In case of silane treatment, treatment time of the fibers for 3 hrs was sufficient to improve the properties of fibers-PP composites. Figure 4.40 shows that the addition of MAPP had produced the composites with superior tensile strength compared to VTES and OTMS treatments. Tensile strength of VTES treated rossells-PP and sisal-PP composites are higher than that of OTMS treated rossells-PP and sisal-PP composites. Young’s moduli of the composites are presented in Figure 4.41. It can be seen that both surface modifications showed no remarkable change in Young’s modulus of the composites.

Table 4.27 Tensile strength, impact strength, Young’s modulus, and tensile strain at break of PP, unmodified, and modified PP composites from rossells and sisal fibers.

Materials	**Tensile strength (MPa)**		**Impact strength (kJ/m^2)**		**Young’s modulus (GPa)**		**Tensile strain at break (%)**	
	Rossells	**Sisal**	**Rossells**	**Sisal**	**Rossells**	**Sisal**	**Rossells**	**Sisal**
PP	13.9±1.98		85.8±1.05		1.08±0.027		248.8±56.41	
Unmodified	22.9±0.82	25.7±0.55	19.0±0.80	17.6±1.19	1.71±0.066	1.90±0.033	8.8±1.45	7.2±0.63
MAPP_2phr	30.3±0.34	28.6±0.30	19.6±1.44	14.8±1.54	2.01±0.045	2.00±0.037	5.2±0.25	4.9±0.24
VTES_3hr	24.4±0.76	24.4±0.91	18.2±1.92	18.4±2.25	1.80±0.089	1.89±0.034	7.0±0.44	7.8±1.03
OTMS_3hr	20.7±0.52	24.6±0.81	23.8±0.58	17.9±2.32	1.66±0.045	1.89±0.021	11.9±1.16	8.0±0.81

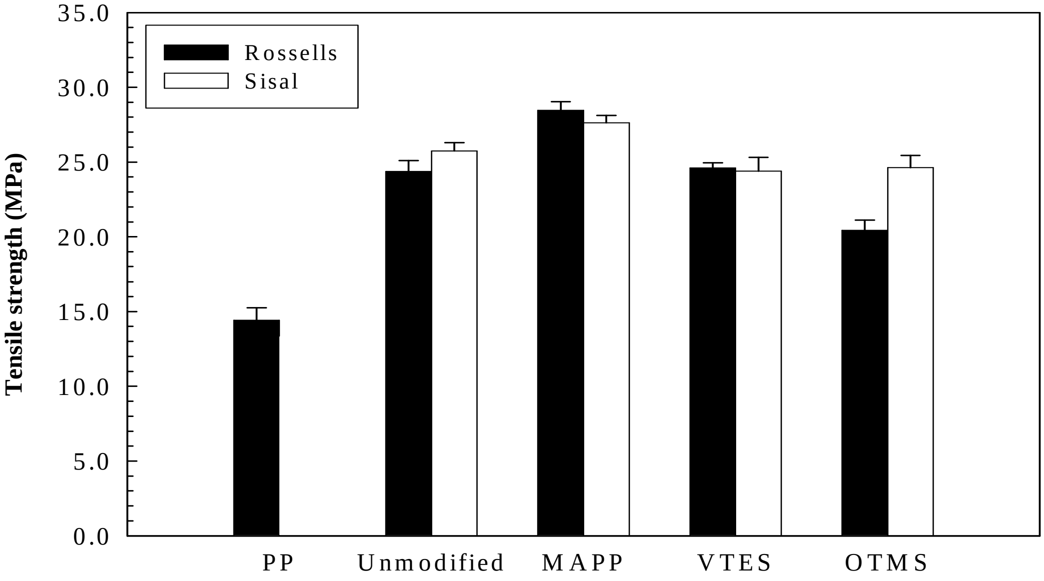


Figure 4.40 Tensile strength of PP, unmodified, and modified PP composites from rossells and sisal fibers.

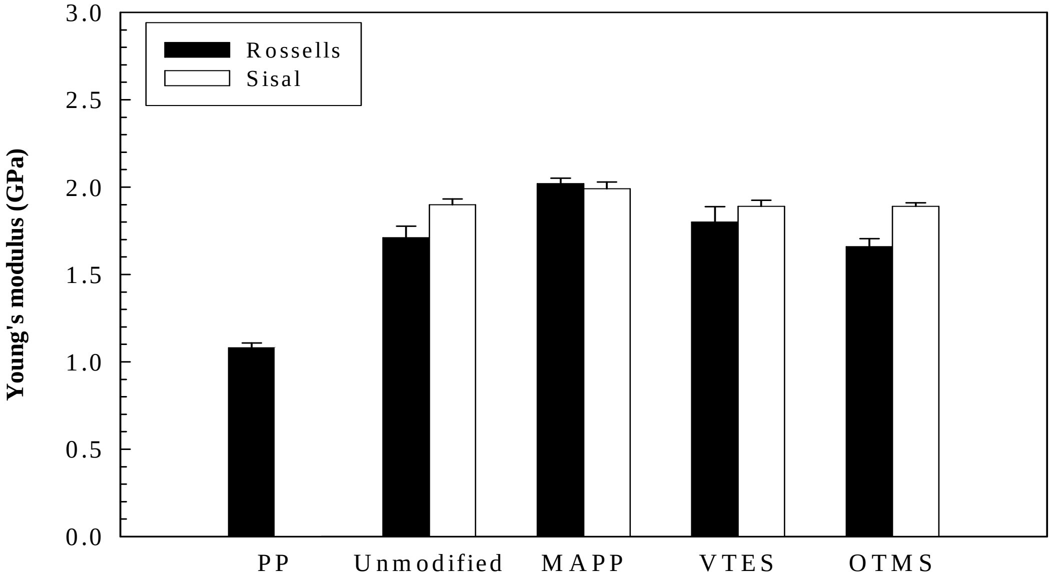


Figure 4.41 Young’s modulus of PP, unmodified, and modified PP composites from rossells and sisal fibers.

The small reduction in tensile strain at break of the composites with incorporation of MAPP, as shown in Figure 4.42, indicated that tensile strain at break could not be enhanced by the improvement of the fiber-matrix interaction. OTMS treated rossells-PP composites showed the highest tensile strain at break. Impact strength of the composites is shown in Figure 4.43. MAPP and VTES treated composites showed no significant effect on impact strength of the composites while OTMS treated composites produced the highest impact strength. This might be because the long and flexible octadecyl group of OTMS silane improved flexibly at interfacial layer between the fiber and matrix.

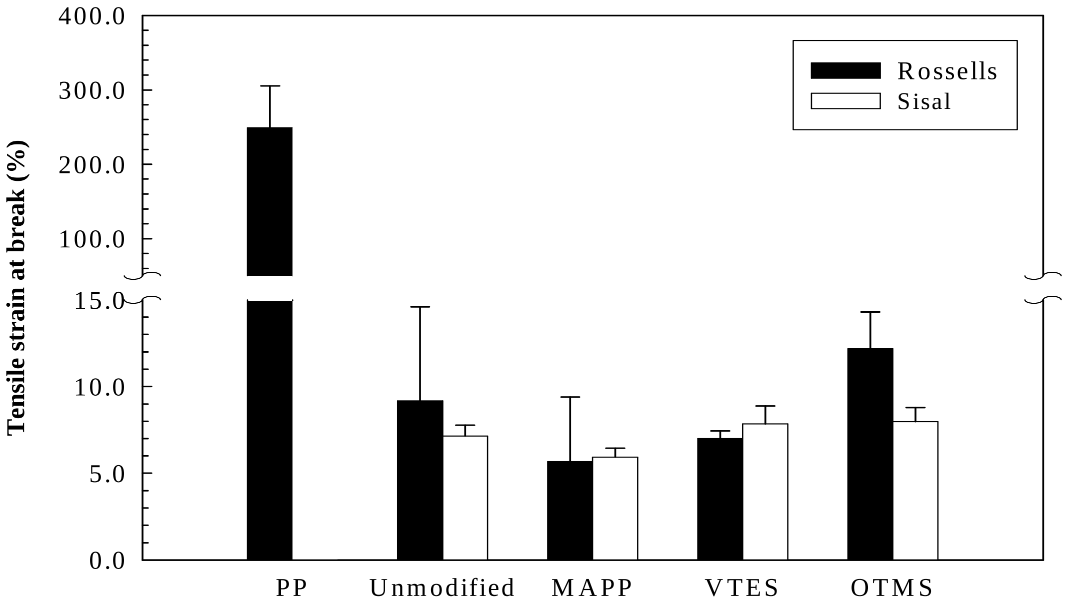


Figure 4.42 Tensile strain at break of PP, unmodified, and modified PP composites from rossells and sisal fibers.

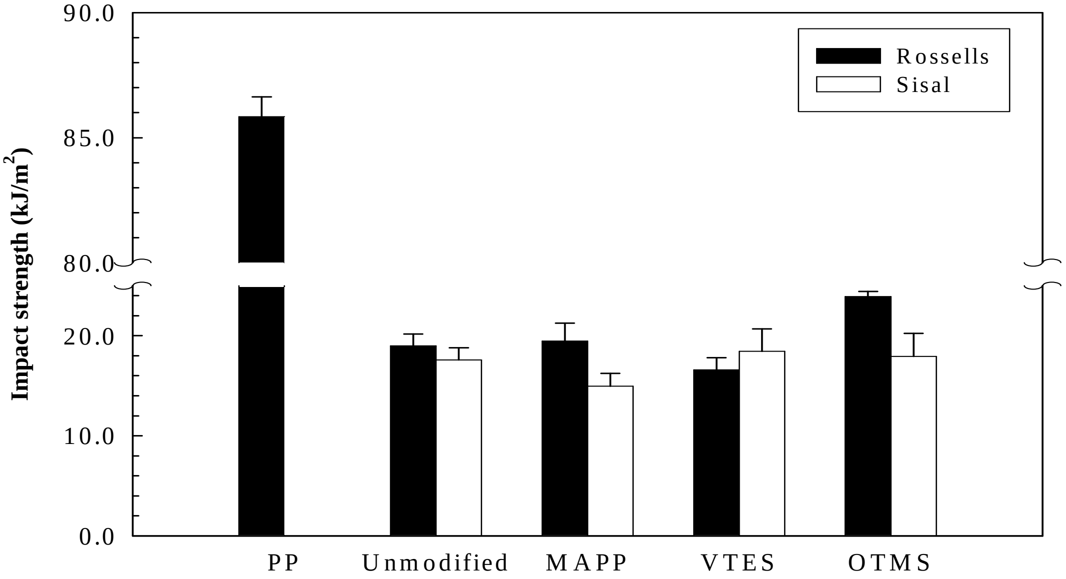


Figure 4.43 Impact strength of PP, unmodified, and modified PP composites from rossells and sisal fibers.

Table 4.28 Flexural strength and flexural modulus of PP, unmodified, and modified PP composites from rossells and sisal fibers.

Materials	Flexural strength (MPa)		Flexural modulus (GPa)	
	Rossells	Sisal	Rossells	Sisal
PP	46.4±1.5		1.43±0.04	
Unmodified	50.9±0.2	60.5±0.3	2.67±0.01	3.32±0.11
MAPP_2phr	59.5±0.3	64.1±0.6	3.24±0.08	3.54±0.07
VTES_3hr	50.8±0.4	57.0±0.8	2.81±0.04	3.30±0.02
OTMS_3hr	57.0±0.8	57.0±0.5	3.19±0.15	3.35±0.03

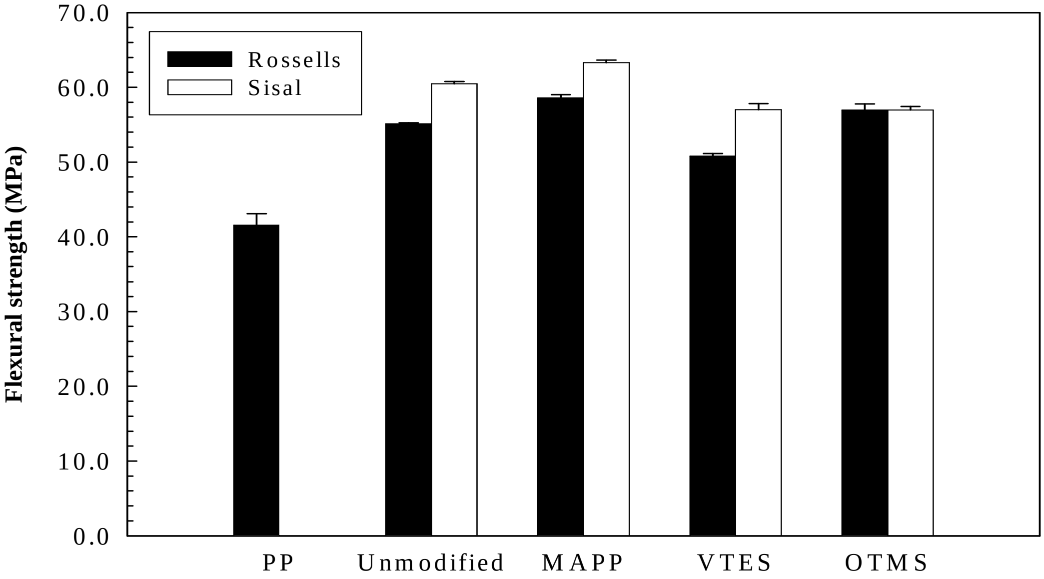


Figure 4.44 Flexural strength of PP, unmodified, and modified PP composites from rossells and sisal fibers.

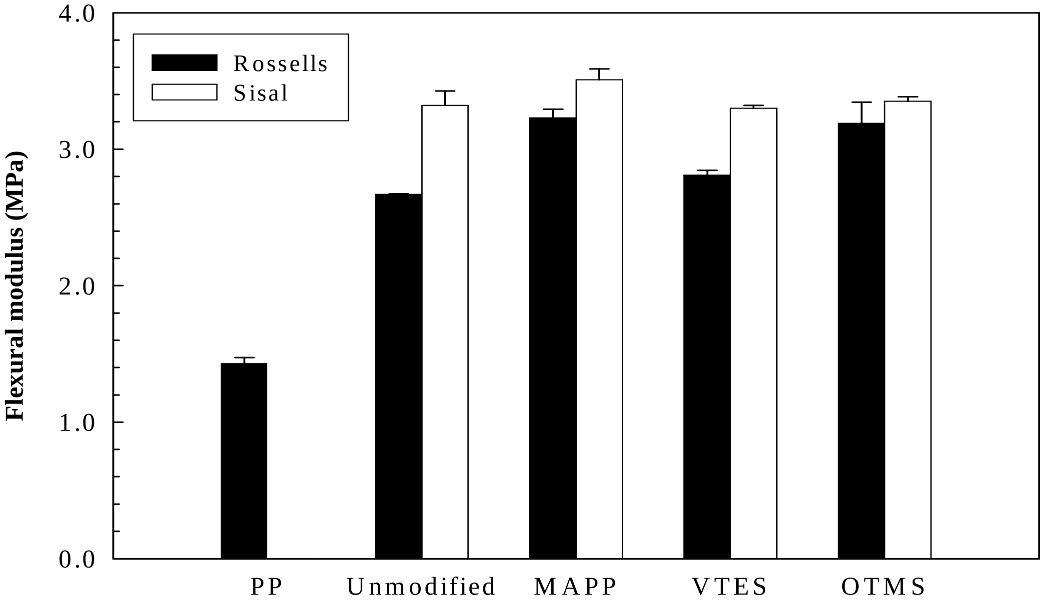


Figure 4.45 Flexural modulus of PP, unmodified, and modified PP composites from rossells and sisal fibers.

Flexural properties of the composites are shown in Table 4.28 and Figure 4.44 and 4.45. The improvement in the properties of the MAPP modified composites indicated that the compatibility between PP and the fibers was enhanced. Flexural strength and modulus of unmodified, MAPP modified, and VTES treated sisal-PP composites were slightly higher than rossells-PP except OTMS treated fiber-PP composites that showed no difference between rossells-PP and sisal-PP composites.

The mechanical properties of fiber reinforced composites depends on several factors e.g. properties of fibers and matrix, and fibers volume fraction. The fibers properties are related to chemical compositions and internal structure of fibers due to the overall environmental conditions during growth. The mechanical properties difference between rossells-PP composites and sisal-PP composites can be described by the differences in fiber properties. In the case of unmodified composite, rossells-PP composite gave lower tensile strength and Young's modulus than sisal-PP composite. For the MAPP modified fibers-PP composites, rossells-PP composite gave higher tensile strength and Young's modulus than sisal-PP composite.

In addition, cost analysis summary for preparing rossells-PP and sisal-PP composites is shown in Appendix A. MAPP modification is a cost effective method for preparing both rossells-PP and sisal-PP composites compared to the silane treatment.

CHAPTER V

CONCLUSIONS

The effect of compatibilizer and silane coupling agents on the properties of natural fibers-PP composites were studied. Cleaning with mixed solvent and alkalization were able to remove low molecular weight species, hemicelluloses, and lignin from the surface of rossells and sisal fibers. This was confirmed by the reduction of fiber diameter, and the absence of these components from thermal analysis. The removal of these components from the fiber surface resulted in a decrease of tensile strength of the fibers. Alkalization made a fine structure and rough surface topography. The degradation temperature of cellulose of silane treated fibers was higher than CL fibers. Silane treatment showed no effect on the tensile strength and Young's modulus of the fibers. SEM micrographs revealed that the surface of silane treated fibers was rougher than the CL fibers.

Crystallization temperature, decomposition temperature, and HDT of PP increased with the addition of fibers whereas crystallinity decreased. The incorporation of the fibers into PP enhanced tensile strength, Young's modulus, and flexural properties. On the other hand, impact strength and tensile strain at break were decreased. Viscosity and water absorption were increased by adding the fibers.

MAPP improved surface adhesion between the fibers and PP matrix; thus, the mechanical properties of both rossells-PP and sisal-PP composites were enhanced. MAPP increased tensile and flexural strength of the composites without any significant effect on Young’s modulus, and impact strength. Adding MAPP to the composites improved crystallization temperature, crystallinity, decomposition temperature of PP and HDT. MAPP also reduced the water absorption of the composites. The only 2 phr of MAPP was found to be sufficient for improvement in surface adhesion between fibers and matrix.

Effect of silane coupling agents on the properties of rossells-PP composites was evaluated. Tensile strength and Young’s modulus of VETS treated rossells-PP composites increased whereas impact strength, tensile strain at break, flexural strength and flexural modulus were not different from the unmodified composite. Tensile strength and Young’s modulus of OTMS treated rossells-PP composites showed no remarkable difference while impact strength, tensile stain at break, flexural strength and flexural modulus were greater than the unmodified composites. Viscosity and water absorption of both VTES and OTMS treated rossells-PP composites slightly decreased while melting temperature, crystallization temperature, crystallinity, and decomposition temperature of fiber and PP did not change. In the case of silane treated sisal-PP composites, both VTES and OTMS treatments showed no effect on thermal, mechanical, and rheological properties. However, the water absorption of VTES and OTMS treated sisal-PP composites slightly lower than the unmodified sisal-PP composite. The treatment times insignificantly affected the mechanical properties of both VTES and OTMS treated rossells-PP and sisal-PP composites.

Rossells-PP composite gave lower tensile strength and Young’s modulus than sisal-PP composite in the case of unmodified composites. However, rossells-PP composite gave higher tensile strength and Young’s modulus than sisal-PP composite for the MAPP modified composites.

Recommendation for Future Work

The main interesting topics for the further studied related to this research study should be followed:

(i) To investigate the effect of other types of compatibilizer and silane coupling agent on the properties of rossells-PP and sisal-PP composites

(ii) To apply the rossells-PP and sisal-PP composites in the automotive parts and other products

(iii) To study the degradation behaviour of rossells-PP and sisal-PP composites

Research Publication

Parts of this work were presented and published in the following conferences and journal;

Sutapun, W., Ruksakulpiwat, Y., Jarukumjorn, K., Supakarn, N., Chumsamrong, P., and Kluengsamrong, J. (2004). Studies of thermal properties and surface characteristics of pretreated jute fibers by boiling and soxhlet extraction. **In the 30th Congress on Science and Technology of Thailand** (pp. 175). Bangkok, Thailand

Sutapun, W., Ruksakulpiwat, Y., Jarukumjorn, K., Supakarn, N., Chumsamrong, P., and Kluengsamron, J. (2005). Studies of thermal properties and surface characteristics of pretreated and silane treated rossell fibers. **In the 31th Congress on Science and Technology of Thailand** (pp. 241). Nakhon Ratchasima, Thailand.

Ruksakulpiwat, Y., Kluengsamrong, J., Sutapun, W., and Supakarn, N. (2005). Injection molding of rossells-polypropylene composites: Effect of processing parameters on mechanical properties. **In the 31th Congress on Science and Technology of Thailand** (pp. 227). Nakhon Ratchasima, Thailand.

Ruksakulpiwat, Y., Kluengsamrong, J., Somnuk, U., Sutapun, W., and Supakarn, N. (2005). Comparison of rheological properties and mechanical properties of polypropylene composites from various types of natural fibers. **In the 31th Congress on Science and Technology of Thailand** (pp. 221). Nakhon Ratchasima, Thailand.

Jarukumjorn, K., Sutapun, W., Ruksakulpiwat, Y., and Kluengsamrong, J. (2005). Short rossells fiber/polypropylene composites: effect of compatibilizer on mechanical and rheological properties, and heat distortion temperature. **In the 31th Congress on Science and Technology of Thailand** (pp. 227). Nakhon Ratchasima, Thailand.

Jarukumjorn, K., Ruksakulpiwat, Y., Sutapun, W., and Kluengsamrong, J. (2006). Compatibilization of natural fibers/PP composites. **In the 64th Annual Technical Conference of the Society of Plastics Engineering** (pp. 330). Charlotte, North Carolina, USA.

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APPENDIX A

Cost calculation for fiber cleaning, silane treatment, and MAPP modification

Cost analysis of fiber cleaning, silane treatment, and MAPP modification

1. Cost of fiber cleaning

Fibers were first cleaned with mixed solvent (methanol: benzene, 50:50 by volume), and then cleaned with NaOH solution (2 wt%) at a liquor ratio of 15:1 (liter: kg). The cost of chemicals used for preparation 1 kg of fiber is shown in the Table A.1.

Table A.1 Cost of chemicals for cleaning 1 kg of fiber.

Chemicals	Contents	Price/Unit	Price
Methanol	7.50 liters	24.00 baht/liters	180.00 baht
Benzene	7.50 liters	55.00 baht/liters	412.50 baht
NaOH	0.30 kg	250.00 baht/kg	75.00 baht
Total			667.50 baht

2. Cost of silane treatment

In case of VTES treated fibers, cleaned fibers were then treated with 2 wt% VTES solution at a liquor ratio of 15:1 (liter: kg). The VTES solution was prepared by dissolving VTES in distilled water. The pH of the solution was adjusted to 3.5 with acetic acid. The content of acetic acid used to adjust the pH of VTES solution was about 5% of the VTES solution. The cost of chemicals used for treating 1 kg of fiber with VTES is shown in Table A.2

Table A.2 Cost of chemicals for the preparation 1 kg of VTES treated fiber.

Chemicals	Contents	Price/Unit	Price
VTES	0.30 kg	850.00 baht/kg	255.00 baht
Acetic acid	0.075 liters	180.00 baht/liters	13.50 baht
Total			268.50 baht

For the OTMS treated fibers, cleaned fibers were then treated with 2 wt% OTMS solution at a liquor ratio of 15:1 (liter: kg). The OTMS solution was dissolved in ethanol and distilled water mixture (90:10 wt/wt). The pH of the solution was adjusted to 3.5 with acetic acid. The content of acetic acid used to adjust the pH of OTMS solution was about 5% of the OTMS solution. The cost of chemicals used for treating 1 kg of fiber with OTMS is shown in Table A.3

Table A.3 Cost of chemicals for the preparation 1 kg of OTMS treated fiber.

Chemicals	Contents	Price/Unit	Price
Ethanol	13.50 liters	60.00 baht/liters	810.00 baht
OTMS	0.30 liters	194.80 baht/ml	58,440.00 baht
Acetic acid	0.075 liters	180 baht/liters	13.50 baht
Total			59,263.50 baht

3. Cost of MAPP modification

Table A.4 is shown the cost of MAPP used to preparation fibers-PP composites. MAPP 2 phr was sufficient to improve surface adhesion between fibers and PP matrix. The 20 wt% cleaned fibers were used to prepare the fibers-PP composites.

Table A.4 Cost of MAPP for modification 1 kg of fiber.

Chemicals	Contents	Price/Unit	Price
MAPP	2 phr	250.00 baht/kg	25.00 baht
Total			25.00 baht

4. Cost analysis summary

Cost analysis summary is shown in Table A.5. It was clear that MAPP modification is a cost effective method for preparing natural-PP composites.

Table A.5 Cost comparison for silane treated fiber versus MAPP modified fiber for preparation of 1 kg fiber.

Cost	VTES treated fibers (baht)	OTMS treated fibers (baht)	MAPP modified fibers (baht)
1. Fibers (rossells, sisal)	12.00, 120.00	12.00, 120.00	12.00, 120.00
2. Fiber cutting	800.00	800.00	800.00
3. Fiber cleaning	667.50	667.50	667.50
4. Silane treatment	268.50	59,263.50	-
5. MAPP	-	-	25.00
Total costs (rossells, sisal)	1,748.00, 1,856.00	60,743.00, 60,851.00	1,504.50, 1,612.50

BIOGRAPHY

Mr. Thanatiwat Naraprateep was born on May 12, 1981 in Nakhon Ratchasima, Thailand. He earned his Bachelor's Degree in Polymer Engineering from Suranaree University of Technology (SUT) in 2004. After graduation, he has been employed under the position of research assistant at the School of Polymer Engineering, Suranaree University of Technology. He then continued his Master's degree in Polymer Engineering at School of Polymer Engineering, Institute of Engineering at Suranaree University of Technology. During his master's degree study, he presented three papers. One entitled "*Effect of silane coupling agent and compatibilizer on properties of short rossells fiber/polypropylene composites*" at the 2nd International Conference on Advances in Petrochemicals and Polymers, Bangkok, Thailand. Two entitled "*Short rossells fiber/polypropylene composites: effect of compatibilizer on mechanical and rheological properties, and heat distortion temperature*" at the 31th Congress on Science and Technology of Thailand, Nakhon Ratchasima, Thailand. The last entitled "*Mechanical and Morphological Properties of Rossells Fiber Reinforced Polypropylene Composites: Effect of Fiber Content and Compatibilizer*" at the 1st SUT Graduation Conferences**,** Nakhon Ratchasima, Thailand.