EFFECT OF FLAME RETARDANTS ON PHYSICAL PROPERTIES OF SISAL FIBER/POLYPROPYLENE COMPOSITES

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อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.กษมา จารุกำจร, 92 หน้า

วิทยานิพนธ์นี้มีจุดมุ่งหมายเพื่อศึกษาผลของสารหน่วงไฟต่อสมบัติการติดไฟ สมบัติทางความร้อน สมบัติทางกล สมบัติทางสัณฐานวิทยา และสมบัติทางวิทยากระแสของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีน เส้นใยป่านศรนารายณ์ถูกเตรียมเป็นเส้นใยที่ไม่ผ่านการปรับเปลี่ยน และเส้นใยที่ผ่านการปรับเปลี่ยนด้วยสารละลายด่าง ปริมาณป่านศรนารายณ์คือ 30 ส่วนใน 100 ส่วนของพอลิโพรพิลีน พอลิเมอร์เชิงประกอบถูกเตรียมโดยใช้เครื่องบดผสมภายใน และชิ้นงานทดสอบถูกขึ้นรูปโดยใช้เครื่องฉีดขึ้นรูป

แอมโมเนียมโพลีฟอสเฟตถูกใช้เป็นสารหน่วงไฟ ปริมาณแอมโมเนียมโพลีฟอสเฟตถูกเปลี่ยนเป็น 10 20 30 และ 40 ส่วนใน 100 ส่วนของพอลิโพรพิลีน แอมโมเนียมโพลีฟอสเฟตปรับปรุงสมบัติการหน่วงไฟและความเสถียรทางความร้อนของพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีนโดยไม่ทำให้สมบัติทางกลของพอลิเมอร์เชิงประกอบลดลงอย่างมาก เมื่อเพิ่มปริมาณของแอมโมเนียมโพลีฟอสเฟต สมบัติการหน่วงไฟและความเสถียรทางความร้อนของพอลิเมอร์เชิงประกอบถูกปรับปรุง พอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์กับพอลิโพรพิลีนทุกระบบแสดงความไม่แตกต่างอย่างมีนัยสำคัญของความหนืดเฉือน ภาพถ่ายจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงการยึดติดและการกระจายตัวที่ไม่ดีของเส้นใยป่านศรนารายณ์หรือแอมโมเนียมโพลีฟอสเฟตในพอลิโพรพิลีนเมทริกซ์ นอกจากนี้การทำอัลคาไลน์เซชันไม่ส่งผลอย่างมีนัยสำคัญต่อสมบัติของพอลิเมอร์เชิงประกอบ

ในบรรดาพอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์ที่ไม่ผ่านการปรับเปลี่ยนกับพอลิโพรพิลีนที่มีการใส่แอมโมเนียมโพลีฟอสเฟต พอลิเมอร์เชิงประกอบระหว่างเส้นใยป่านศรนารายณ์ที่ไม่ผ่านการปรับเปลี่ยนกับพอลิโพรพิลีนที่มีการใส่แอมโมเนียมโพลีฟอสเฟตปริมาณ 40 ส่วนใน 100 ส่วนของพอลิโพรพิลีน แสดงสมบัติการหน่วงไฟและความเสถียรทางความร้อนที่สูงสุด ดังนั้น พอลิเมอร์เชิงประกอบนี้ถูกเลือกไปตรวจสอบผลของพอลิโพรพิลีนกราฟท์ด้วยมาเลอิกแอนไฮไดรด์ ซึ่งเป็นสารช่วยให้เข้ากันต่อสมบัติของพอลิเมอร์เชิงประกอบ ปริมาณพอลิโพรพิลีนกราฟท์ด้วยมาเลอิกแอนไฮไดรด์ คือ 1 3 และ 5 ส่วนใน 100 ส่วนของพอลิโพรพิลีน การยึดติดและการกระจายตัวของเส้นใยป่านศรนารายณ์และแอมโมเนียมโพลีฟอสเฟตในพอลิโพรพิลีนเมทริกซ์เพิ่มขึ้นเมื่อมีการใส่พอลิโพรพิลีนกราฟท์ด้วย

มาเลอิกแอนไฮไดรด์ ส่งผลต่อการปรับปรุงค่าการทนแรงดึงและค่าการทนต่อการดัดโค้งของพอลิเมอร์เชิงประกอบ สมบัติการติดไฟ สมบัติทางความร้อน และสมบัติทางวิทยากระแสของพอลิเมอร์เชิงประกอบไม่ถูกกระทบเมื่อมีการเติมพอลิโพรพิลีนกราฟท์ด้วยมาเลอิกแอนไฮไดรด์ ปริมาณพอลิโพรพิลีนกราฟท์ด้วยมาเลอิกแอนไฮไดรด์ที่เหมาะสมคือ 3 ส่วนใน 100 ส่วนของพอลิโพรพิลีน

นอกจากนี้แมกนีเซียมไฮดรอกไซด์หรือซิงค์บอเรท ถูกนำไปใช้ร่วมกันกับแอมโมเนียมโพลีฟอสเฟต อัตราส่วนระหว่างแอมโมเนียมโพลีฟอสเฟตต่อซิงค์บอเรทหรืออัตราส่วนระหว่างแอมโมเนียมโพลีฟอสเฟตต่อแมกนีเซียมไฮดรอกไซด์คือ 10 ต่อ 30 20 ต่อ 20 และ 30 ต่อ 10 พอลิเมอร์เชิงประกอบที่ใส่แอมโมเนียมโพลีฟอสเฟตและซิงค์บอเรทที่อัตราส่วน 30 ต่อ 10 แสดงสมบัติหน่วงไฟสูงสุด ผลที่เสริมกันต่อสมบัติการหน่วงไฟของพอลิเมอร์เชิงประกอบถูกพบเมื่อซิงค์บอเรท 10 ส่วนใน 100 ส่วนของพอลิโพรพิลีนถูกใช้ร่วมกันกับแอมโมเนียมโพลีฟอสเฟต 30 ส่วนใน 100 ส่วนของพอลิโพรพิลีน อย่างไรก็ตามการใส่แอมโมเนียมโพลีฟอสเฟตและแมกนีเซียมไฮดรอกไซด์ในพอลิเมอร์เชิงประกอบให้ผลทางลบต่อสมบัติการหน่วงไฟ พอลิเมอร์เชิงประกอบที่มีการใส่แมกนีเซียมไฮดรอกไซด์แสดงความเสถียรทางความร้อนที่สูงสุด เมื่อเปรียบเทียบกับพอลิเมอร์เชิงประกอบที่มีการใส่แอมโมเนียมโพลีฟอสเฟตและพอลิเมอร์เชิงประกอบที่มีการใส่แอมโมเนียมโพลีฟอสเฟตและแมกนีเซียมไฮดรอกไซด์ร่วมกัน ในกรณีของการเติมซิงค์บอเรท 40 ส่วนใน 100 ส่วนของพอลิโพรพิลีนเข้าไปในพอลิเมอร์เชิงประกอบ พอลิเมอร์เชิงประกอบนี้แสดงความเสถียรทางความร้อนที่ต่ำสุด การเติมของการรวมกันของสารหน่วงไฟคือแอมโมเนียมโพลีฟอสเฟตกับแมกนีเซียมไฮดรอกไซด์หรือแอมโมเนียมโพลีฟอสเฟตกับซิงค์บอเรทเข้าไปในพอลิโพรพิลีนเชิงประกอบ เปลี่ยนแปลงสมบัติทางความร้อนของพอลิเมอร์เชิงประกอบเล็กน้อย ไม่พบการเปลี่ยนแปลงอย่างมีนัยสำคัญของสมบัติทางกลและความหนืดของพอลิเมอร์เชิงประกอบเมื่อมีการใส่สารหน่วงไฟร่วมกัน ภาพถ่ายจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงการกระจายตัวที่ดีของสารหน่วงไฟและเส้นใยป่านศรนารายณ์ในพอลิโพรพิลีนเมทริกซ์

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ปีการศึกษา 2553 ลายมือชื่ออาจารย์ที่ปรึกษา____________________
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RACHASIT JEENCHAM : EFFECT OF FLAME RETARDANTS ON PHYSICAL PROPERTIES OF SISAL FIBER/POLYPROPYLENE COMPOSITES. THESIS ADVISOR : ASST. PROF. KASAMA JARUKUMJORN, Ph.D., 92 PP.

POLYPROPYLENE/NATURAL FIBERS/COMPOSITE/AMMONIUM POLYPHOSPHATE/MAGNESIUM HYDROXIDE/ZINC BORATE/ MALEIC ANHYDRIDE GRAFTED POLYPROPYLENE

This thesis aimed to study effect of flame retardants on flammability, thermal properties, mechanical properties, morphological properties and rheological properties of sisal fiber/polypropylene composites. Sisal fiber was prepared as an untreated fiber (UT) and an alkali treated fiber (AT). Sisal fiber content was 30 phr. The composites were prepared using an internal mixer, and the test specimens were molded by an injection molding machine.

Ammonium polyphosphate (APP) was used as a flame retardant. APP content were varied as 10, 20, 30, and 40 phr. APP improved flame retardancy and thermal stability of sisal fiber/PP composites without extreme deterioration of the mechanical properties of the composites. With increasing APP content, flame retardancy and thermal stability of the composites were improved. All sisal/PP composites exhibited insignificant difference in shear viscosity. SEM micrographs revealed poor adhesion and distribution of sisal fiber or APP in PP matrix. In addition, alkalization showed no remarkable effect on the properties of the composites.

Among PP/UT composites containing APP, the PP/UT composite containing 40 phr of APP showed the highest flame retardancy and thermal properties. Therefore this composite was selected to investigate effect of maleic anhydride grafted polypropylene (MAPP) as a compatibilizer on the properties of the composites. MAPP contents were 1, 3, and 5 phr. Adhesion and distribution of sisal fiber and APP in PP matrix were enhanced with addition of MAPP leading to the improvement of tensile strength and flexural strength of the composites. Flammability, thermal properties, and rheological properties of the composites were not much affected by the incorporation of MAPP. The optimum content of MAPP was 3 phr.

In addition, magnesium hydroxide ($Mg(OH)_2$) or zinc borate (Zb) was used in combination with APP. APP/Zb or APP/$Mg(OH)_2$ ratios were 10/30, 20/20, and 30/10. The composite filled with APP/Zb at the ratio of 30/10 exhibited the highest flame retardancy. A synergistic effect in flame retardancy was observed when 10 phr of Zb was used in combination with 30 phr of APP. However, adding combination of APP and $Mg(OH)_2$ into the composites gave a negative effect on flame retardancy. Composite containing $Mg(OH)_2$ showed the highest thermal stability when compared to composites with APP and those with combination of APP and $Mg(OH)_2$. In case of adding 40 phr of Zb into composite, this composite exhibited the lowest thermal stability. Addition of combination of flame retardants, APP/$Mg(OH)_2$ or APP/Zb, into PP composites slightly changed thermal properties of the composites. No significant change in the mechanical properties and viscosity of the composites were observed with the addition of combination of flame retardants. SEM micrographs of the composites showed good distribution of flame retardants and sisal fiber in PP matrix.

School of Polymer Engineering
Student's Signature______________________

Academic Year 2010
Advisor's Signature______________________

Co-Advisor's Signature___________________

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SYMBOLS AND ABBREVIATIONS

°C = Degree Celsius
GPa = Gigapascal
T_g = Glass transition temperature
hrs = Hours
kJ = Kilojoule
kV = Kilovolt
MPa = Megapascal
min = Minute
% = Percent
wt% = Percent by Weight
s = Second
m^2 = Square meter
$T_{5\%}$ = Thermal decomposition at which 5% weight loss
$T_{50\%}$ = Thermal decomposition at which 50% weight loss
rpm = Revolutions per minute
phr = Parts per hundred of resin
AT = Alkali treated fiber
$Al(OH_3)$ = Aluminum trihydrate
APP = Ammonium polyphosphate
CO = Carbon monoxide
LOI = Limiting oxygen index
MAPP = Maleic anhydride grafted polypropylene

SYMBOLS AND ABBREVIATIONS (Continued)

MFI = Melt flow index

$Mg(CO)_3$ = Magnesium carbonate

$Mg(OH)_2$ = Magnesium hydroxide

NaOH = Sodium hydroxide

PP = Polypropylene

SEM = Scanning electron microscope

TPP = Triphenylphosphate

TGA = Thermogravimetric analyzer

UT = Untreated fiber

WF = Wood flour

Zb = Zinc borate

CHAPTER I

INTRODUCTION

1.1 General introduction

Nowadays, natural fiber/polypropylene composites are used worldwide for many applications, e.g. automotive components, building materials, electronic devices, and aerospace industry (Andreas and Hartmut, 2001). Various types of natural fibers such as cotton, kapok, flax, hemp, jute, ramie, and sisal are used as fillers for thermoplastic composites since they are high tensile strength and stiffness, low cost, biodegradability, renewability, and absence of toxic by products. Among those types of natural fibers, sisal fiber is one of the interesting plants for reinforcing thermoplastics due to its high tensile strength and stiffness (Bledzki and Gassan, 1999). Moreover, sisal fiber has grown in a wide range of areas in Thailand.

Polypropylene (PP) is one of the most popular matrices to produce natural fiber reinforced composites. The advantages of PP are low density, low cost, high water and chemical resistance. However, main factors limiting the use of natural fiber to reinforce PP include its low compatibility with the hydrophobic PP, and high flammability.

The compatibility between natural fibers and PP matrix can be improved by fiber modification, matrix modification or adding compatibilizer. Maleic anhydride grafted polypropylene (MAPP) is known to be an effective compatibilizer for natural fiber/PP composites (Arbelaiz et al., 2005). The chemical (ester bond) and physical interaction can be formed between hydroxyl groups of the fiber and anhydride groups of MAPP while PP chains of MAPP diffuse into the PP matrix. Therefore, the surface adhesion between fibers and matrix can be improved by use of MAPP compatibilizer (Doan, Gao, and Madar, 2006).

Since PP and natural fiber are highly flammable this limits the applications of their composites. Addition of flame retardant is a possible way to reduce flammability and enhance thermal stability of natural fiber/PP composites. The most widely used flame retardants for PP composites are halogen compounds, phosphorus compounds, metal hydroxides, antimony, aluminium and boron-containing compounds (Montezin, Lopez-Cuesta, Crespy, and Georlette, 1997). Among various types of the flame retardants, phosphorus compounds such as ammonium polyphosphate (APP) is a very efficient halogen-free flame retardant mainly used in polyolefin composites. APP is a non toxic and environmental friendly flame retardant and it does not generate additional quantities of smoke (Ashton, 2005). The decomposition mechanism of APP can be explained as follows. At about 250°C, APP decomposes to yield polyphosphoric acid and evolving ammonia.

$$[NH_4PO_3] \xrightarrow{250°C} [HPO_3]_n + nNH_3 \qquad (1.1)$$

Between 360 and 420°C, the polyphosphoric acid reacts with the carbonaceous compound to form the char as an insulating protective layer which prevents further flame spread.

$$[HPO_3]_n + \text{Carbon source} \xrightarrow{360°C\text{-}420°C} -\!\boxed{C}\!- + H_3PO_4 \qquad (1.2)$$

Moreover, many researchers have reported that a combination of two types of flame retardants exhibited the synergistic effect on flame retardancy and mechanical properties of polymer. Zinc borate (Zb) is one of the flame retardant to use in combination with halogen free flame retardants in polymers resulting in the polymers with enhanced flame retardancy and mechanical properties (Carpentier, Bourbigot, Bras, and Delobel, 2007). The decomposition of Zb is shown as follows (Samyn, Bourbigot, Duquesne, and Delobel, 2007). At about 320°C, it decomposes endothermically and releases water.

$$2ZnO.3B_2O_3.3H_2O \xrightarrow{320°C} 2ZnO.3B_2O_3 + 3H_2O \qquad (1.3)$$

In addition, combination of magnesium hydroxide ($Mg(OH)_2$) and halogen free flame retardants give high thermal stability of the polymers (Shehata, 2004). The decomposition mechanism of $Mg(OH)_2$ is shown as follows (Sain, Park, Suhara, and Law, 2004). $Mg(OH)_2$ provides effective flame retarding effects by producing char insulating layer and releasing water at about 360°C.

$$Mg(OH)_2 \xrightarrow{360°C} MgO + H_2O \qquad (1.4)$$

1.2 Research objectives

The main objectives of this study are as follows:

(i) To investigate the effect of flame retardant on flammability, thermal properties, mechanical properties, morphological properties and rheological properties of sisal fiber/PP composites.

(ii) To study the effect of a compatibilizer and its contents on the properties of sisal fiber/PP composites containing a flame retardant.

(iii) To study the effect of combination of flame retardants on the properties of sisal fiber/PP composites.

1.3 Scope and limitation of the study

In this study, sisal fiber was used to reinforce PP. The effect of flame retardant on flammability, thermal properties, mechanical properties, morphological properties and rheological properties of sisal fiber/PP composites was studied. APP was used as a flame retardant. The composites with 30 phr of sisal fiber (untreated or alkali treated) were prepared using an internal mixer, and the test specimens were molded by injection molding machine. APP contents were varied from 10-40 phr. In addition, MAPP was used to improve the surface adhesion between the fiber and matrix. MAPP content was varied as 1, 3, and 5 phr. Furthermore, effect of combination of APP with $Mg(OH)_2$ or Zb on the properties of sisal fiber/PP composites was also investigated.

CHAPTER II

LITERATURE REVIEW

2.1 Flammability and thermal properties of polypropylene, natural fiber, and natural fiber/polypropylene composites

2.1.1 Flammability and thermal properties of polypropylene

The crystalline melting point of isotactic PP with a crystallinity of around 45% and containing 90-95% isotactic material is quoted as 165°C. The glass transition temperature (T_g) value of isotactic PP ranges from -30 to 25°C depending on method of measurement and heat-annealing treatments (Allen, 1983). Because of its wholly aliphatic hydrocarbon structure, PP by itself burns very rapidly with a relatively smoke-free flame and without leaving a char residue. The heat of combustion for PP was reported by Einsele, Koch, and Herlinger (1984) to be 40 kJ/g and this is higher than many other polymers. PP pyrolysis is dominated by initial chain scissions, consequently considerable research has been undertaken in the conversion of waste PP into clean hydrocarbon fuels (Ballice and Reimerta, 2002). The thermal decomposition of both isotactic PP and atactic PP has been investigated under non-isothermal conditions. The maximum volatile product evolution temperature is 420°C for atactic PP and 425°C for the isotactic PP. The recovery of carbon as organic volatile products comprises dienes, alkanes, and alkenes. The hydrogen content of pyrolysis products obtained by flash pyrolysis at 520°C indicates the magnitude of the flammability problem in term of its fuel-forming potential (Jha, Misra, and Bajai, 1984). Cool flame combustion of PP at 350°C leads to the formation of toxic compounds which can cause death in mice, probably because of incomplete combustion and CO formation (Chaigneau and Le Moan, 1982).

2.1.2 Flammability and thermal properties of natural fiber

Natural fibers compose of cellulose, hemicellulose, lignin and other compounds. Their chemical compositions depend on the plant nature such as tree, annual, biannual and perennial plant rich in cellulose (Kozlowski and Wladka- Przybylak, 2001). The basic chemical compositions of the natural fibers are given in Table 2.1. The ignition temperature of natural fiber occurs at 300-400°C. Ignition temperature of various natural fibers depends on lignin content. The higher lignin content of natural fiber results in high ignition temperature (Janssens, 1991). The combustion of natural fiber is complete at temperature above 500ºC. Thermal decomposition of natural fiber was a three-step process. The first, decomposition temperature ranges of 50-125°C corresponded of moisture and other volatiles. The second, decomposition temperature of natural fiber occurs at 220-300°C was associated with decomposition of hemi cellulose and some part of the lignin (Saheb and Jog, 1999). The third decomposition temperature was decomposition of almost all cellulose and lignin as observed in the range of 300-400°C (Obi, Uma, Jeevan, and Varada, 2009).

Table 2.1 Basic chemical compositions of natural fibers (Kozlowski and Wladka- Przybylak, 2001)

Natural fibers	**Approximate contents of main chemical compounds (%)**		
	Cellulose	**Lignin**	**Hemicellulose**
Coniferous wood	40-45	26-34	7-14
Deciduous wood	38-49	23-30	19-26
Cotton	90-95	-	-
Kapok	65-70	5-15	2-10
Flax fiber	64-71	2-15	2-5
Flax shive	36-47	24-30	21-30
Hemp fiber	60-67	3-14	5-10
Hemp shive	40-52	22-30	17-25
Kenaf	31-39	15-19	22-23
Rosselle fiber	70-72	12-13	1-3
Jute	55-65	10-15	15-20
Ramie	60-70	1-10	5-12
Abaca (Manila)	55-65	7-10	16-19
Sisal	63	7.5	22
Date-plam	58	15.3	20
Pineapplae	69.5	7.5	21.8
Bagasse	32-44	19-24	27-32
Esparto	33-38	17-19	27-32
Elephant grass (Miscantus)	35-40	10-15	10-20
Bamboo	33-45	20-25	30
Reed	44.75	22.8	20
Grian straw	27-37	12-21	20-34

2.1.3 Flammability and thermal properties of natural fiber/ polypropylene composites

The flammability and thermal properties of natural fiber/PP composites have been studies by many researchers. Sain et al. (2004) studies flammability of PP and sawdust or rice husk filed PP composites. Flammability of PP and sawdust or rice husk filled PP composites was investigated by horizontal burning rate and limiting oxygen index (LOI). Sawdust or rice husk/PP composites showed a higher burning rate than pure PP. This indicated the high sensitivity of the composites to flame. In addition, sawdust or rice husk/PP composites required a relative low concentration of oxygen to burn.

Le Bras, Duquesne, Fois, Grisel, and Poutch (2004) investigated the flammability of flax fiber/PP composites. Flammability of PP and flax fiber/PP composites were measured by UL 94 test. UL 94 testing showed a dripping of material during complete combustion of pure PP and flax fiber/PP composites.

Suppakarn, N., Jarukumjorn, K., and Tananimit, S. (2008) observed flammability and thermal properties of sisal fiber/PP composites. The PP composites showed a higher burning rate than that of the pure PP. Under nitrogen and oxygen atmosphere, thermal decomposition temperature at a 5% weight loss of sisal fiber/PP composites was lower than that of pure PP.

Abu Bakar, Mohd Ishak, Mat Taib, Rozman, and Mohamad Jani (2010) studied the flammability of wood flour (WF)/PP composite. They reported that the pure PP and the 60 wt% WF filled PP composite burned easily with accompanying melt dripping in UL testing. This observation indicated the high sensitivity of the pure PP and WF to flame. In addition, the pure PP and the PP/WF composite showed LOI values of

19% and 20% respectively. Because normal atmosphere air is approximately 21% oxygen, both PP and PP/WF composite were flammable materials.

2.2 Flame retardants for polypropylene

Flame retardancy of PP may be achieved in one of the following ways (Jha et al., 1984).

(1) By changing the pyrolysis reactions to form a carbonaceous char, which will block heat transformation and hence reduce the volatile formation and protect the polymer from further oxidation. This method poses real challenges for PP because the polymer has no reactive side chains thereby preventing char formation following elimination of these groups.

(2) By inhibiting the initiating radicals in the pre-flame and flame zones; typically, antimony–halogen based additives are effective here.

(3) By adding some hydrated inorganic additives which decompose endothermically and release water, and hence withdraw heat from the substrate and dilute the combustible volatiles.

(4) By modifying the chemical structure of the polymer to change its decomposition procedure and/or to improve the compatibility with other flame retardants.

(5) By addition of char-forming additives preferably having an intumescent property.

2.2.1 Halogen compounds flame retardants

Various formulations for the flame retardancy of PP composites consisting of halogen compounds have been developed over the years. The nature of the group to which the halogen atom is attached is very important because it determines the carbon–halogen ratio and carbon–halogen bond energy and hence the amount of halogen releases during burning. In general, aliphatic or alicyclic halogen compounds are more effective than aromatic halogen compounds due to the lower carbon–halogen bond energies, and hence relatively easier halogen-release.

The hydrogen halides released by decomposition of halogenated flame retardants are believed to react with these radicals to produce radicals which are much less active and thus inhibit the propagation of fire. The activity of halogenated flame retardants occurs mainly in the gas phase but they are thought to inhibit further burning in the solid or liquid phase where the heavy halogenated molecular fragments help to exclude oxygen from burning material and possibly encourage char formation (Horrocks and Price, 2001).

Halogen compounds are an effective flame retardant. However the halogen compounds have a high smoke density and emit corrosive gases on burning and thus limit their use in some application (Sen, Mukherjee, and Bhowmick, 1991).

2.2.2 Phosphorus compounds flame retardants

Phosphorus compounds flame retardants used in PP composites may be both inorganic and organic. It is also common for them to be used in the presence of especially those that generate intumescent char-forming characteristics (Lu and Hamerton, 2002). The reactive type organophosphorus flame retardants, which have attracted more attention in flame retardant chemistry, can be broadly divided into three categories: (a) simple reactive phosphate monomers; (b) linear polyphosphazenes; and (c) aromatic cyclic phosphazenes (Lu and Hamerton, 2002). Phosphorus compounds such as APP, pentaerythritol phosphate and melamine phosphate (MP) are very commonly used flame retardants in PP (Zhou, Song, Wang, Hu, and Xing, 2008). For intumescent flame retardant, APP, pentaerythritol phosphate, and MP are used as an acid source, a carbonization agent, and blowing agent, respectively (Hendrickson and Connole, 1995).

Phosphorus compounds flame retardants produce a char during burning that result in further flame retardant protective and less smoke generation. Phosphorus compounds products do not emit corrosive gases in a fire.

2.2.3 Silicon compounds flame retardants

Silicon compounds flame retardants such as silanes, siloxanes and silsesquioxanes are considered to be ‘environmentally friendly’ additives because their use is claimed to lead to a reduction in the harmful impact on environment. Although silicon has been used previously as flame retardants, few have been reported to be effective enough to achieve a V-0 rating on the UL94 test for PP (Frye and Zembayashi, 1985). The silicon in conjunction with a metal soap can provide a degree of flame retardancy for certain thermoplastics (Maelaury and Holub, 1981). Lower viscosity silicon in combination with a metal stearate showed some flame retardancy, but tend to give flaming drips. Other advantages of the silicon-based additives are that they can improve the impact resistance dramatically of PP (Zhang and Horrocks, 2003).

2.2.4 Metal hydroxides and oxides flame retardants

The main interest for metal hydroxide flame retardants for PP composites lies in their low toxicity, corrosion properties and emission of smoke during processing and burning. Typical metal hydroxide flame retardants are aluminum trihydrate ($Al(OH)_3$), magnesium carbonate ($MgCO_3$), and $Mg(OH)_2$. $Al(OH)_3$ and $MgCO_3$ are known to have a decomposition temperature in the range of 180-340°C, with a peak at about 320°C. $Mg(OH)_2$ has a peak decomposition temperature at about 410°C. Of these three components, magnesium hydroxide is the most endothermic upon burning. $MgCO_3$ is the least and $Al(OH)_3$ is between the other two. Among the aluminium compounds, hydrated alumina is the most widely used one (Wang, Z., Liu, and Wang, Q., 2010). Apart from the dilution of the potential fuels in the flame zone, its retardant activity is a consequence of the endothermicity of this dehydration. These metal hydroxides decompose endothermically and release water during burning and thus reduce the heat and temperature from the substrate. More over, metal hydroxides provide effective flame retarding effects by generating a metal oxide coating that can act as an insulating protective layer during combustion. However, very high metal hydroxide concentrations are usually required to achieve an acceptable degree of flame retardancy (Rothon, 1990).

2.2.5 Nanoparticles flame retardants

Fire retardancy is one of the fields where the nanomaterials could be used successfully. Nanoparticles, e.g. nanoscale (fumed) silica, nanoclay, and carbon nanotubes are increasingly used to improve flame retardancy of polymers (Zanetti, Camino, and Wilkie, 2002). Nanoparticles embedded various polymer matrices are reported to reduce considerably the thermal decomposition of these materials (Lee, Kang, and Wu, 2008).

The flame retardant mechanism of nanoparticles is a consequence of high performance carbonaceous-silicate char on the surface during burning, which insulates the underlying material and slows down the mass loss rate of decomposition products. Moreover, nanoparticles such as carbon nanotube and nanoclay significantly increased mechanical properties and electric conductivity of polymers (Lee, Kang, and Wu, 2008).

2.3 Effect of flame retardants on physical properties of natural fiber/polypropylene composites

2.3.1 Flammability and thermal properties

Several researchers studied the effect of flame retardants on flammability and thermal properties of natural fiber/polypropylene composites. Schartel, Braun, Schwarz, and Reinemann (2003) investigated the flammability and the thermal properties of flax fiber/PP composites containing APP and expandable graphite as flame retardants. Flame ratardancy of flax fibers/PP composites was improved with adding APP and expandable graphite. The concentration of CO and smoke production of the composites containing APP increased whereas the composites filled with expandable graphite showed the lowest value. In addition, the combination of expandable graphite, APP and polyol synergist was found to be efficient flame retardants for flax fiber/PP composites. Polyols are essential char forming components in intumescent flame retardant for polyolefin composites (Schwarz, Pflug, and Reinemann, 2002).

Sain et al. (2004) studied the effect of $Mg(OH)_2$, boric acid and zinc borate as flame retardants on flammability of sawdust/PP composites and rice husk/PP composites. $Mg(OH)_2$ remarkably enhanced flame retardant properties of sawdust or rice husk filled polypropylene composites. No synergistic effect on flammability was observed when $Mg(OH)_2$ was used in combination with boric acid and zinc borate.

Jang and Lee (2004) investigated the effect of various flame retardants: triphenyphosphate (TPP), ethylenebispentabromodiphenylethane (Saytex8010), ($Mg(OH)_2$), and antimony trioxide on the flame retardant properties of paper sludge/PP (50:50 by weight) composites. The flame retardancy of the composites was measured by the UL94 test. The paper sludge/PP composites without flame retardants continued burning for a long time. The composites with Saytex8010 showed very short burning time. Composites containing TPP exhibited burning time to 180 s. On the other hand, paper sludge/PP composites containing $Mg(OH)_2$ gave burning times more than 300 s. The result of the UL94 test exhibited that Saytex8010 highly enhanced the flame retardancy of paper sludge/PP composites. In order to investigate the effect of hybrid flame retardant on flame retardancy of paper sludge/PP composites, Saytex8010 and antimony trioxide were introduced. The burning time of the composites containing Saytex8010/antimony trioxide (30:10 phr) showed the shortest burning time. The composition containing Saytex8010 and antimony trioxide rapidly decomposed at lower temperature than the composition containing only Saytex8010. Hybrid flame retardant composed of Saytex8010 30 phr and antimony trioxide 10 phr gave the most powerful flame retardancy to the composites via a synergistic effect.

Matko et al. (2005) examined flammability of wood flakes/PP/APP composites. APP (10 and 20 wt%) was an effective flame retardant for 50 wt% wood flakes/PP composites. These compositions achieved the V-0 rate of flame retardancy.

The effects of nanoclay on the thermal properties of PP/WF composites were studied by Lee et al. (2008). The addition of clay (1 to 5 phr) increased the decomposition temperature, crystalline peak temperature, and melting temperature of the PP/WF composites.

Suppakarn, N., et al. (2008) studied the effect of magnesium hydroxide ($Mg(OH)_2$) as a flame retardant on flammability and thermal properties of sisal fiber/PP composites. The addition of $Mg(OH)_2$ reduced the flammability while improved thermal decomposition temperatures of the composites. In addition, Suppakarn, N., and Jarukumjorn, K. (2009) studied the effect of combination of $Mg(OH)_2$ and zinc borate on flammability and thermal properties of sisal fiber/PP composites. They reported that no synergistic effect on flammability and thermal properties was found when both $Mg(OH)_2$ and zinc borate were incorporated in the sisal fiber/PP composites.

Abu Bakar et al. (2010) found that the thermal gravimetric analysis (TGA) data showed APP could enhance the thermal stability of the PP/WF/APP composites at high temperatures and effectively increased the char residue formation. The APP could effectively reduce the flammability of the PP/WF composites by achieving V-0 UL94-V classification. The increased LOI also showed that the flammability of the PP/WF composites was reduced with the addition of APP.

2.3.2 Mechanical properties

The effect of flame retardants on mechanical properties of natural fiber/PP composites have been reported by many researchers. Sain et al. (2004) studied the mechanical properties of PP, sawdust or rice husk composites containing $Mg(OH)_2$ as a flame retardant, and maleated PP based coupling agent (E-43). The addition of $Mg(OH)_2$ showed a negative impact on the tensile and flexural strength of the composites. However, these composites exhibited better performance compared to pure PP. Rice husk/PP composites exhibited inferior tensile and flexural strength compared to sawdust/PP composites. Impact strength of PP was better than those of sawdust/PP composites and the sawdust/PP composites containing flame retardants.

Jang and Lee (2004) observed the effect of various flame retardants, e.g. $Mg(OH)_2$, TPP, Saytex8010, and antimony trioxide on mechanical properties of paper sludge/PP composites. The paper sludge/PP composite with $Mg(OH)_2$ showed the highest flexural strength, which was higher than the composite without flame retardants. In the case of paper sludge/PP/Saytex8010 composite, flexural strength was lower than paper sludge/PP without flame retardants. TPP exhibited the largest depression of flexural strength. The composites containing hybrid flame retardants (Saytex8010 and antimony trioxide) gave higher flexural strength than composites containing Saytex8010. Moreover, the flexural strength of the composites increased with increasing the contents of antimony trioxide.

Suppakarn, N., and Jarukumjorn, K. (2009) studied the effect of $Mg(OH)_2$ and zinc borate on mechanical properties of sisal fiber/PP composites. They reported that sisal fiber/PP composites and sisal fiber/PP composites with the addition of $Mg(OH)_2$ and zinc borate had lower impact strength than the neat PP. However, sisal fiber/PP composites containing flame retardants exhibited comparable tensile and flexural properties to the sisal fiber/PP composites without adding those flame retardants.

CHAPTER III

EXPERIMENTAL

3.1 Materials

A commercial grade of isotactic PP (700J) was supplied by Thai Polypropylene Co., Ltd. Maleic anhydride grafted polypropylene (MAPP, Fusabond® P MZ 109D, DuPont) was supplied by Chemical Innovation Co., Ltd.. Sisal fiber (Agave sisalana) was purchased from Sisal-Handicraft OTOP Group, Tambon Ban Kao, Amphur Dan Khun Thod, Nakhon Ratchasima, Thailand. Ammonium polyphosphate (APP, Exolit AP 765, Clariant, average diameter of 8 μm) was supplied from Clariant Chemical (Thailand), Co., Ltd. Zinc borate (Zb, Firebrake® ZB, Rio Tinto Mineral, average diameter of 9 μm) was pherchased from Global Connections Public Co., Ltd. Magnesium hydroxide ($Mg(OH)_2$, APYMAG® 40, Nabaltec AG, average diameter of 5 μm) was provided from Behn Meyer Chemical Co., Ltd.

3.2 Experimental

3.2.1 Fiber preparation

Sisal fiber was cut into an approximate length of 2 mm. It was dried in an oven at 60ºC overnight. This fiber was called “untreated fiber (UT)”. Some of the UT fiber was further cleaned with 2 wt% sodium hydroxide (NaOH) solution for 2 hrs to eliminate waxes and low molecular weight compounds. Then, the fiber was washed with water several times and dried in an oven at 60ºC overnight. This fiber was called "alkali treated fiber (AT)".

3.2.2 Composite preparation

Composites were prepared using an internal mixer (Hakke Rheomix, 3000p). The rotor speed was 50 rpm and the mixing temperature was 170°C. PP was, firstly, added into the mixing chamber for 3 min, after that the UT or AT was added. To prepare PP composite containing a flame retardant, the flame retardant was incorporated after 6 min of mixing time. The total mixing time was 13 min. The test specimens were molded by an injection molding machine (Chuan Lih Fa, CLF 80T).

Designation and composition of PP and PP composites at various APP contents are shown in Table 3.1. According to flammability and mechanical properties of the PP composites, the PP composite having optimum properties, i.e. PP/UT/40APP was chosen to study effect of MAPP as a compatibilizer on properties of the PP composites. MAPP content was varied as 1, 3, and 5 phr. Composition of PP composites at various MAPP contents and their designation are shown in Table 3.2. Furthermore, the PP composite containing optimum MAPP content, i.e. PP/UT/40APP/3MAPP was selected to investigate the effect of combination of APP with $Mg(OH)_2$ or Zb on the properties of sisal fiber/PP composites. The ratios of APP to $Mg(OH)_2$ or Zb were varied. Composition of PP composites with combination of flame retardants and their designation are shown in Table 3.3.

Table 3.1 Designation and composition of PP and PP composites at various APP contents.

Designation	**PP (phr)**	**Untreated sisal fiber (phr)**	**Alkali treated sisal fiber (phr)**	**APP (phr)**
PP	100	-	-	-
PP/UT	100	30	-	-
PP/UT/10APP	100	30	-	10
PP/UT/20APP	100	30	-	20
PP/UT/30APP	100	30	-	30
PP/UT/40APP	100	30	-	40
PP/AT	100	-	30	-
PP/AT/10APP	100	-	30	10
PP/AT/20APP	100	-	30	20
PP/AT/30APP	100	-	30	30
PP/AT/40APP	100	-	30	40

Table 3.2 Designation and composition of PP composites at various MAPP contents.

Designation	**PP (phr)**	**Untreated sisal fiber (phr)**	**APP (phr)**	**MAPP (phr)**
PP/UT/40APP	100	30	40	-
PP/UT/40APP/1MAPP	100	30	40	1
PP/UT/40APP/3MAPP	100	30	40	3
PP/UT/40APP/5MAPP	100	30	40	5

Table 3.3 Designation and composition of PP composites with combination of flame retardants.

Designation	**PP (phr)**	**Untreated sisal fiber (phr)**	**APP (phr)**	**$Mg(OH)_2$ (phr)**	**Zb (phr)**	**MAPP (phr)**
PP/UT/40APP/3MAPP	100	30	40	-	-	3
PP/UT/30APP/10Mg/3MAPP	100	30	30	10	-	3
PP/UT/20APP/20Mg/3MAPP	100	30	20	20	-	3
PP/UT/10APP/30Mg/3MAPP	100	30	10	30	-	3
PP/UT/40Mg/3MAPP	100	30	-	40	-	3
PP/UT/30APP /10Zb/3MAPP	100	30	30	-	10	3
PP/UT/20APP /20Zb/3MAPP	100	30	20	-	20	3
PP/UT/10APP /30Zb/3MAPP	100	30	10	-	30	3
PP/UT/40Zb/3MAPP	100	30	-	-	40	3

3.2.3 Composites characterization

3.2.3.1 Flammability

Flammability of PP and PP composites were studied by a horizontal burning test, vertical burning test, and limiting oxygen index test according to ASTM D635, ASTM D3801, and ASTM D2863 respectively. In a case of the horizontal burning test, the specimen was held horizontally and a flame was applied to one end of the specimen. The time for the flame to reach from the first reference mark to the second reference mark was measured. The first reference mark was at 25 mm from the end and the second was at 100 mm from the end. Five specimens from each composite were tested. Then, burning rates of the composites were calculated as follows:

$$V = 60L/t \qquad (3.1)$$

where V is the burning rates (millimeters per minute). L is the burned length (millimeters). t is the time (seconds) of burning.

Flammability of PP and PP composites were classified by the vertical burning test as well. The specimen was held vertically at 300 $\pm$ 10 mm above a horizontal layer of cotton. Distance between the lower end of the specimen and the burner tube was 10 $\pm$ 1 mm. The flame was applied for 10 s and then removed until flaming stops at which time the flame is reapplied for another 10 s and then remove. The time was recorded. Five specimens from each composite were tested. The V-0, V-1, and V-2 classification according to ASTM D3801 marks self extinguishing behaviour of the materials in the vertical burning test. The lowest flame retardancy rating is V-2 (flaming time $\leq$ 30 s and cotton indicator ignited by flaming particles or drops) and V-0 (no dripping, flaming time reduced (≤ 10 s) represent a strongly flame retarded material, while V-1 (flaming time ≤ 30 s) is intermediate term between V-0 and V-2. The flammable materials which cannot be classified according to this method, are marked with code NC (no classification, complete combustion of the specimen)

Limiting oxygen index (LOI) of PP and PP composites were measured by an in house LOI tester according to ASTM D2863. The specimen was held vertically in the glass chamber, where there was a controlled flow of oxygen and nitrogen. The top end of specimen was ignited and time to burn 50 mm of the specimen was measured. Five specimens from each composite were tested. The test was repeated under various concentrations of oxygen and nitrogen to determine the minimum concentration of oxygen needed for burning the specimen. The LOI was determined from the following relationship:

$$LOI = \frac{100\,V_O}{V_O + V_N} \qquad (3.2)$$

where LOI is the limiting oxygen index (percent by volume). V_O is volume of oxygen per volume of mixture. V_N is volume of nitrogen per volume of mixture.

3.2.3.2 Thermal properties

Thermal behaviors of PP and PP composites were examined using a thermogravimetric analyzer (TGA, Mettler Toledo model TGA/DSC 1). Thermal decomposition temperature of each sample was examined under nitrogen atmosphere. The sample with a weight between 10 to 15 mg was used for each run.

Each sample was heat from room temperature to 700°C at a heating rate of 20°C/min. The weight change was recorded as a function of temperature.

3.2.3.3 Mechanical properties

Tensile properties of PP and PP composites were tested by following ASTM D638 using a universal testing machine (UTM, Instron model 5565) with a load cell of 5 kN, a crosshead speed of 50 mm/min, and a gauge length of 80 mm.

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

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

3.2.3.4 Morphological properties

A scanning electron microscope (SEM, Jeol model JSM6400) was employed to examine morphology of tensile fracture surfaces of PP composites. The specimen was coated with gold before analysis. Acceleration voltage of 20 kV was used to collect SEM images of the sample.

3.2.3.5 Rheological properties

Melt flow index (MFI) of PP and PP composites were obtained using a melt flow indexer (Kayeness 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 a capillary rheometer (Kayeness model D5052m) at 180ºC.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The effect of flame retardant on physical properties of sisal fiber/PP composites

4.1.1 Flammability

Burning rates of PP and PP composites measured by horizontal burning test are shown in Table 4.1. The addition of sisal fiber, both UT and AT, into PP accelerated the burning rate of the PP composites. However, the burning rate of PP/UT and PP/AT composites decreased with increasing APP content. In addition, the PP/UT or PP/AT composites containing 40 phr of APP did not burn under the testing condition. This indicated that APP enhanced flame retardancy of sisal fiber/PP composites.

The results from the vertical burning test of the PP and PP composites are presented in Table 4.1. The neat PP and PP composites containing 10, 20, or 30 phr of APP showed complete combustion (NC). On the other hand, PP/UT or PP/AT composites containing 40 phr of APP gave very short burning times (≤ 10 s) and classified as V-0 rating. This indicated that adding 40 phr of APP resulted in an effective improvement in flame retardancy of sisal fiber/PP composites.

Limiting oxygen index (LOI) measures the minimum oxygen concentration required to support continuous combustion of a sample. Therefore, according to the LOI test, a high flame retardancy material needs high oxygen to burn and presents high LOI. LOI of PP and PP composites with various APP contents are shown in Table 4.1. The PP/UT and PP/AT composites showed lower LOI than that of the PP and other PP composites. This indicated that the incorporation of sisal fiber made the PP composites were flammable. On the other hand, LOI of sisal fiber/PP composites increased with increasing APP content. The sisal fiber/PP composites containing 40 phr of APP, i.e. PP/UT/40APP and PP/AT/40APP gave higher LOI compared to those of the PP and other PP composites. This suggested that APP could effectively improve the flame retardancy of sisal fiber/PP composites. This was similar to that observed by Matko et al. (2005). They found that APP improved flame retardancy of wood flakes/PP composites. Moreover, Abu Bakar et al. (2010) reported that APP could effectively reduce the flammability of the wood flour/PP composites.

Table 4.1 Horizontal burning rate, vertical burning rating**,** and limiting oxygen index of PP and PP composites at various APP contents.

Designation	**Horizontal burning rate (mm/min)**	**Vertical burning rating**	**Limiting oxygen index (%)**
PP	24.60 ± 1.02	NC	20
PP/UT	29.29 ± 0.83	NC	≤19*
PP/UT/10APP	22.17 ± 1.27	NC	21
PP/UT/20APP	13.38 ± 0.68	NC	23
PP/UT/30APP	10.07 ± 1.06	NC	25
PP/UT/40APP	No burning	V-0	31
PP/AT	29.66 ± 0.54	NC	≤19*
PP/AT/10APP	22.70 ± 0.38	NC	21
PP/AT/20APP	13.98 ± 0.61	NC	23
PP/AT/30APP	10.35 ± 0.62	NC	25
PP/AT/40APP	No burning	V-0	31

Remark : * Due to the limitation of the LOI instrument, LOI of PP/UT and PP/AT composites are less than 19%.

From horizontal burning test, vertical burning test, and limiting oxygen index test, alkalization showed no effect on the flammability of the sisal fiber/PP composites.

4.1.2 Thermal properties

Flame retardancy of the composites can be observed from their thermal decomposition temperature at 5% and 50% weight loss ($T_{5\%}$ and $T_{50\%}$ respectively) and amount of char residue formed during their thermal decomposition. Effective flame retardant action is indicated by the high thermal stability of the polymer, i.e. high $T_{5\%}$, $T_{50\%}$, and high char residue. TGA thermograms and thermal properties of PP and PP/UT composites at various APP contents are shown in Figure 4.1 and Table 4.2 respectively.

The decomposition temperature below 100ºC of the PP/UT composites corresponded to the evaporation of moisture. The moisture content about 2% was observed. PP/UT composites gave lower $T_{5\%}$ than PP. This was because hemicelluloses in sisal fiber started to decompose at lower temperature compared with the neat PP (Saheb and Jog, 1999). However, $T_{5\%}$ of the PP/UT composite was increased with addition of APP. This indicated that APP improved thermal stability of PP/UT composites. The thermal stability of PP/UT composites increased with increasing APP content. From Table 4.2, the presence of UT fiber increased $T_{50\%}$ of the PP. This may be because the sisal fiber has a component called lignin that acts as a char residue, which could increase the thermal decomposition temperature of the PP (Abu Bakar et al., 2010). Addition of APP into PP/UT composites resulted in an increase in $T_{50\%}$. This could be attributed to the polyphosphoric acid from the decomposition of APP reacted with the carbonaceous compound to form the char (phosphorcarbonaceous structure) at $T_{50\%}$. Char residue is a basic aspect of flame retardant additives because char residue delays thermal decomposition of polymeric materials by acting as an insulating protective layer. With increasing APP content, $T_{50\%}$ of the PP/UT composites were increased. In this TGA experiment, the amount of residue is the % weight of char residue observed at 600ºC. The neat PP was completely decomposed at 600ºC. The char residue of the PP/UT composites increased with increasing APP content. This was due to the formation of phosphorcarbonaceous structure during APP decomposition.

TGA thermograms and thermal properties of PP and PP/AT composites at various APP contents are shown in Figure 4.2 and Table 4.2 respectively. The PP/AT composite showed higher $T_{5\%}$ than PP/UT composite. This was because alkalization removed impurities and low molecular weight species which had low thermal stability from fiber surface (Obi et al., 2009). Thus PP/AT composite gave higher thermal stability than PP/UT composite. $T_{5\%}$ of the PP/AT composite was increased with addition of APP. This was similar to those observed in $T_{5\%}$ of the PP/UT composites containing APP. There was no significant change in $T_{50\%}$ and the amount of char residue of PP/UT and PP/AT composites containing APP. This may be because the impurities and low molecular weight species on the UT surface completely decomposed at $T_{50\%}$. Thus, at $T_{50\%}$ of these PP composites, chemical composition of UT fiber was similar to that observed in AT fiber.

From TGA results, sisal fiber/PP composites containing 40 phr of APP, i.e. PP/UT/40APP and PP/AT/40APP had higher thermal stability than the PP and other PP composites.

Table 4.2 Thermal properties of PP and PP composites at various APP contents.

Designation	**$T_{5\%}$ (°C)**	**$T_{50\%}$ (°C)**	**Char residue (%)**
PP	408	458	0
PP/UT	308	461	4.31
PP/UT/10APP	314	470	7.62
PP/UT/20APP	322	472	9.14
PP/UT/30APP	324	473	10.55
PP/UT/40APP	324	476	11.61
PP/AT	324	461	4.11
PP/AT/10APP	333	471	8.62
PP/AT/20APP	334	473	9.16
PP/AT/30APP	334	474	10.18
PP/AT/40APP	334	476	12.06

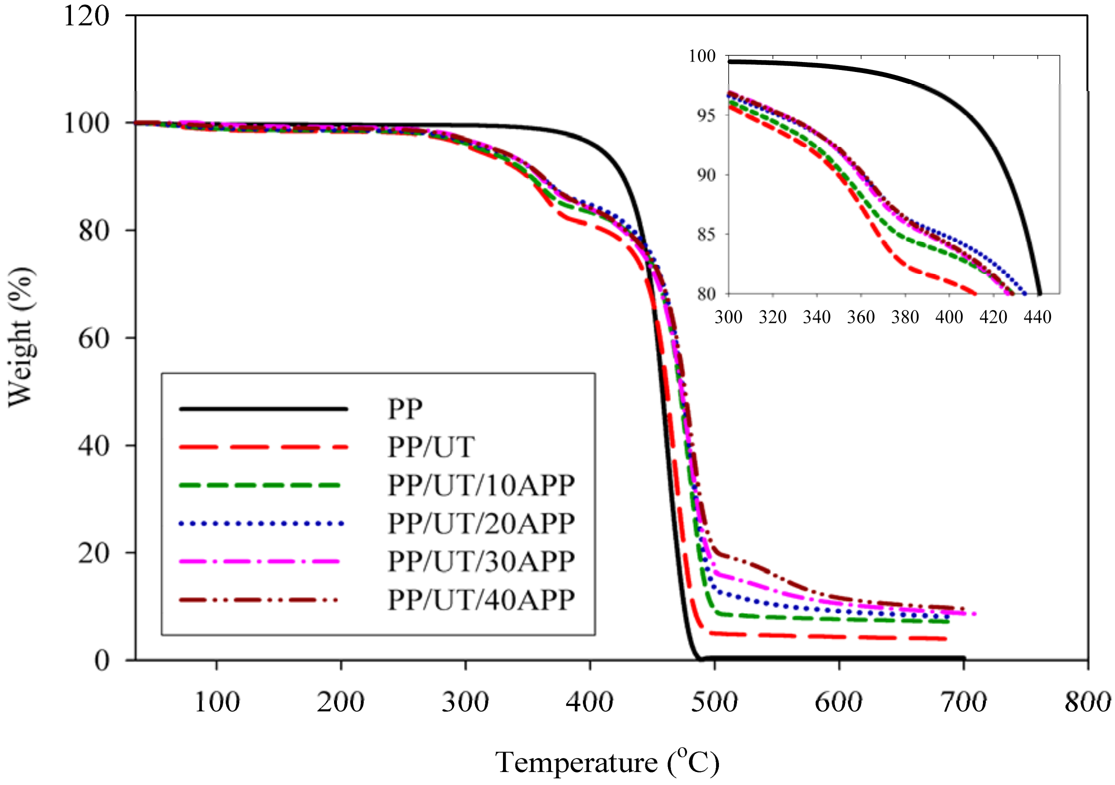


Figure 4.1 TGA thermograms of PP and PP/UT composites at various APP contents.

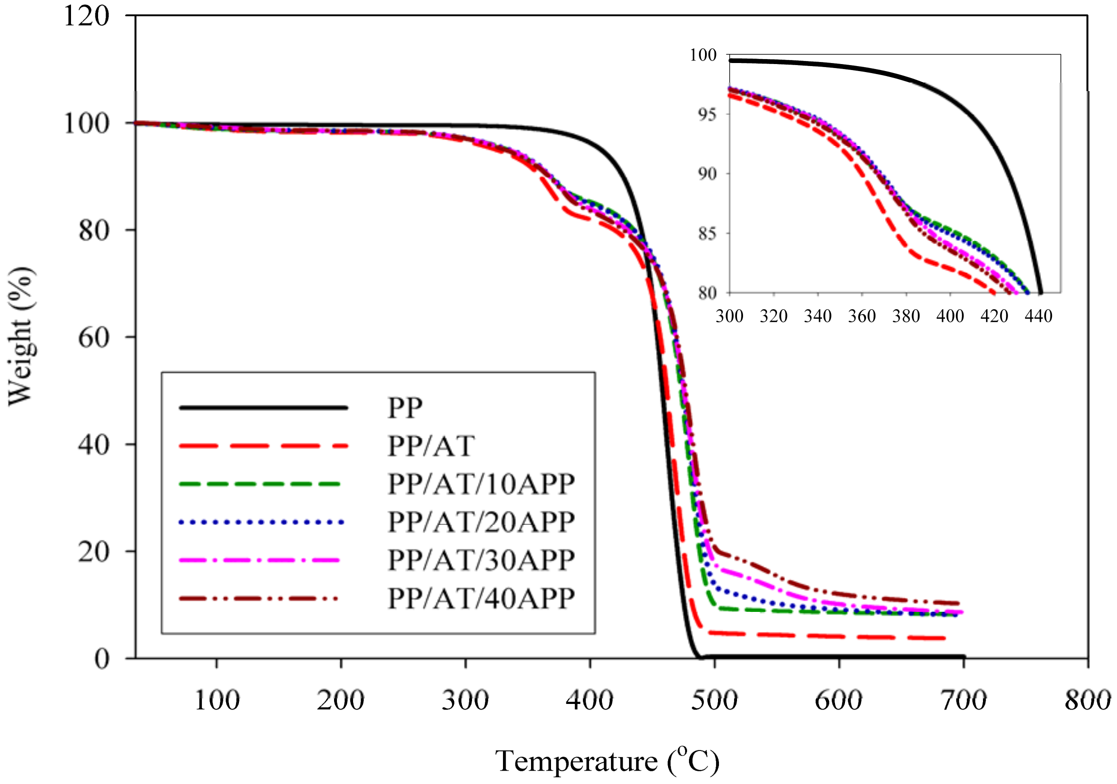


Figure 4.2 TGA thermograms of PP and PP/AT composites at various APP contents.

4.1.3 Mechanical properties

Mechanical properties of PP and PP composites are listed in Table 4.3. There was no significant change in tensile modulus of sisal fiber/PP composites and sisal fiber/PP composites containing APP as shown in Figure 4.3. PP/UT and PP/AT composites exhibited higher tensile strength and modulus than PP. This indicated that sisal fiber is a good reinforcing filler for PP. The incorporation of APP into sisal fiber/PP composites slightly decreased tensile strength of sisal fiber/PP composites as shown in Figure 4.4. Moreover, the tensile strength of sisal fiber/PP composites showed a marginal decrease with increasing APP content. This could be attributed to the incompatibility between APP and PP confirmed by SEM micrographs of the PP composites as shown in Figures 4.8 (c-j).

Flexural strength of PP and PP composites are illustrated in Figure 4.5. Among PP composites, the PP/UT and PP/AT composites showed higher flexural strength than those of the PP and other PP composites. Similar to those observed in tensile tests, the flexural strength of PP composites slightly decreased with increasing APP content. This can be explained by the poor compatibility between APP and PP matrix resulting from the relatively great polarity of APP. Flexural moduli of PP composites were higher than that of the neat PP as shown in Figure 4.6. With addition of APP, flexural moduli of sisal fiber/PP composites increased. The APP was a rigid small particle resulting in enhancing the flexural moduli of the composites. This was similar to that observed by Abu Bakar et al. (2010). They reported that the incorporation of rigid filler i.e. fiber and APP increased flexural moduli of the composites. With increasing APP content, the flexural moduli of the composites insignificantly changed. This might be caused by the non uniform distribution of APP in PP matrix, as shown in Figures 4.8 (c-j).

Impact strength of PP and PP composites are shown in Figure 4.7. Adding sisal fiber decreased impact strength of PP. This was because the fiber disturbed matrix continuity and each fiber was a site of stress concentration, which acted as a microcrack initiator (Mareri, Bastide, Binda, and Crespy, 1998). APP showed no remarkable effect on the impact strength of sisal fiber/PP composites.

Generally, flame retardants are added to polymers to reduce the flammability of the systems. However, they can adversely affect the mechanical properties of the polymers as found by Sain et al. (2004). They observed that the addition of $Mg(OH)_2$ showed a negative impact on tensile and flexural strength of sawdust/PP and rice husk/PP composites. Additionally, Jang and Lee (2004) reported that adding flame retardants, i.e. ethylenebispentabromodiphenylethane (Saytex8010) and triphenyphosphate (TPP) significantly decreased flexural strength of paper sludge/PP composites. However, we have found in this study that APP improved flame retardancy of sisal fiber/PP composites without extreme deterioration of the mechanical properties of sisal fiber/PP composites.

From Table 4.3, alkalization showed no remarkable effect on the tensile properties, flexural properties, and impact strength of the sisal fiber/PP composites. However, Gu (2009) studied the effect of alkalization on mechanical properties of coir fiber/polypropylene composites. Tensile strength of alkali treated coir fiber/polypropylene composites were greater than that of untreated fiber/PP composite due to improved the adhesion between the fiber and matrix resulting from the removal of pectin, and fats covering the fiber surface.

Table 4.3 Mechanical properties of PP and PP composites at various APP contents.

Designation	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m^2)
PP	18.67 ± 2.77	1.22 ± 0.04	47.47 ± 0.62	1.48 ± 0.04	74.70 ± 1.86
PP/UT	29.05 ± 0.96	2.08 ± 0.09	48.75 ± 0.48	2.94 ± 0.11	14.02 ± 0.52
PP/UT/10APP	27.93 ± 0.57	2.21 ± 0.06	48.22 ± 0.34	3.27 ± 0.09	13.19 ± 1.33
PP/UT/20APP	26.52 ± 1.43	2.22 ± 0.12	44.93 ± 0.72	3.24 ± 0.11	11.89 ± 0.34
PP/UT/30APP	25.65 ± 0.52	2.34 ± 0.04	42.71 ± 1.97	3.40 ± 0.23	11.22 ± 0.54
PP/UT/40APP	23.52 ± 0.19	2.35 ± 0.07	40.76 ± 0.61	3.17 ± 0.03	8.48 ± 0.61
PP/AT	28.89 ± 1.24	2.08 ± 0.08	49.27 ± 0.64	2.69 ± 0.06	14.13 ± 0.55
PP/AT/10APP	27.86 ± 0.17	2.13 ± 0.07	48.42 ± 0.17	3.11 ± 0.11	13.38 ± 0.43
PP/AT/20APP	26.38 ± 0.28	2.23 ± 0.11	45.32 ± 1.58	3.12 ± 0.07	12.78 ± 0.93
PP/AT/30APP	25.65 ± 0.65	2.23 ± 0.07	42.61 ± 1.49	3.28 ± 0.12	11.32 ± 1.08
PP/AT/40APP	23.46 ± 0.65	2.16 ± 0.02	41.71 ± 0.45	3.21 ± 0.06	9.67 ± 0.34

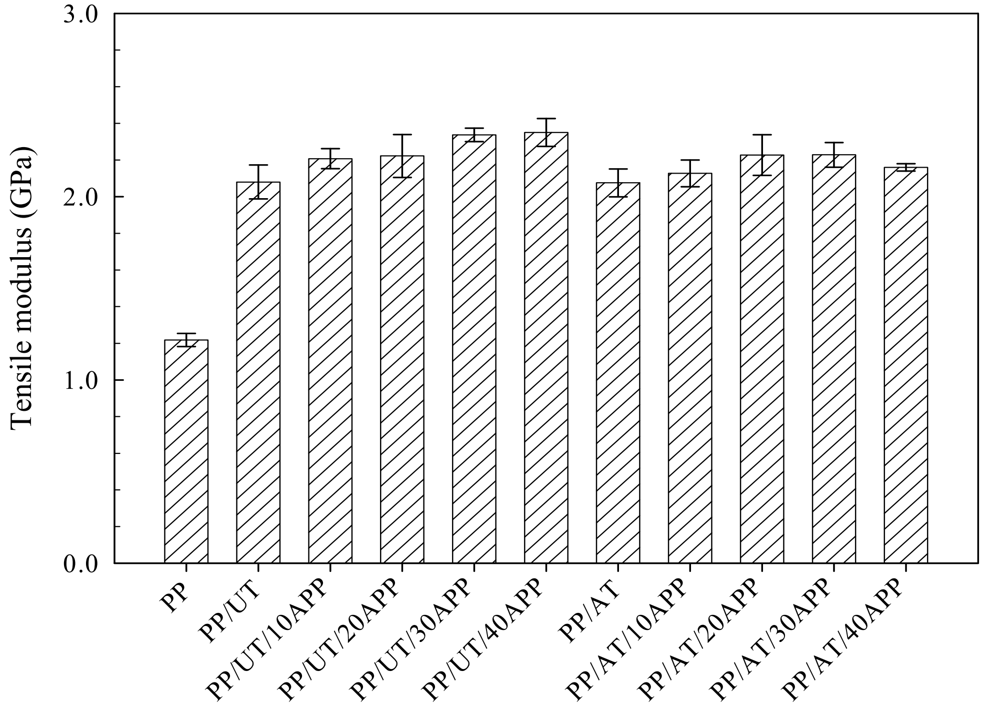


Figure 4.3 Tensile modulus of PP and PP composites at various APP contents.

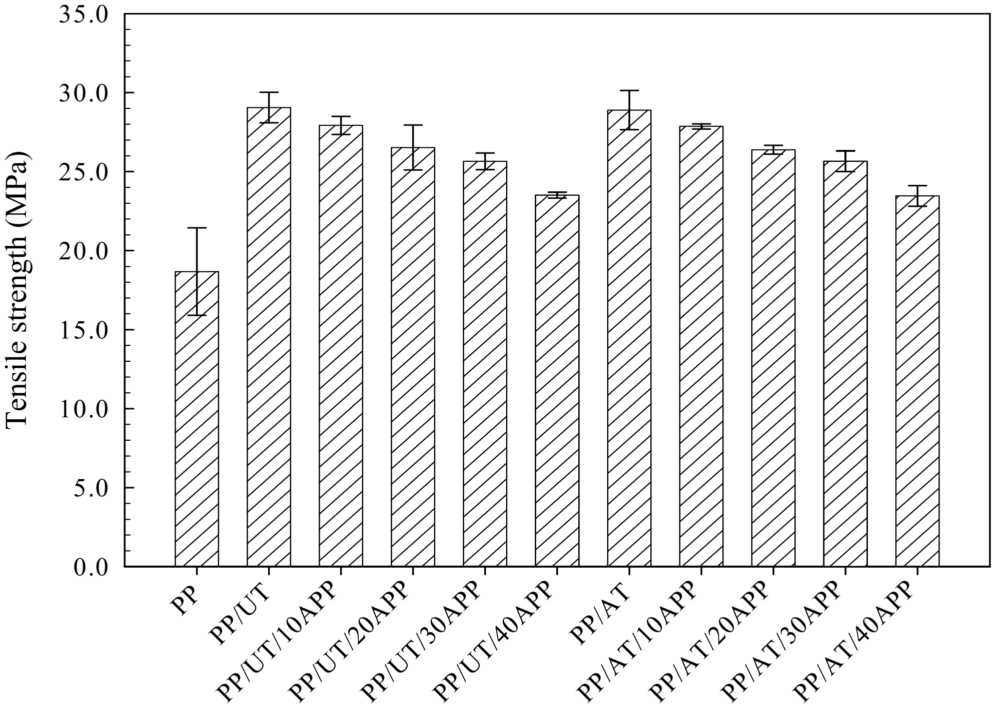


Figure 4.4 Tensile strength of PP and PP composites at various APP contents.

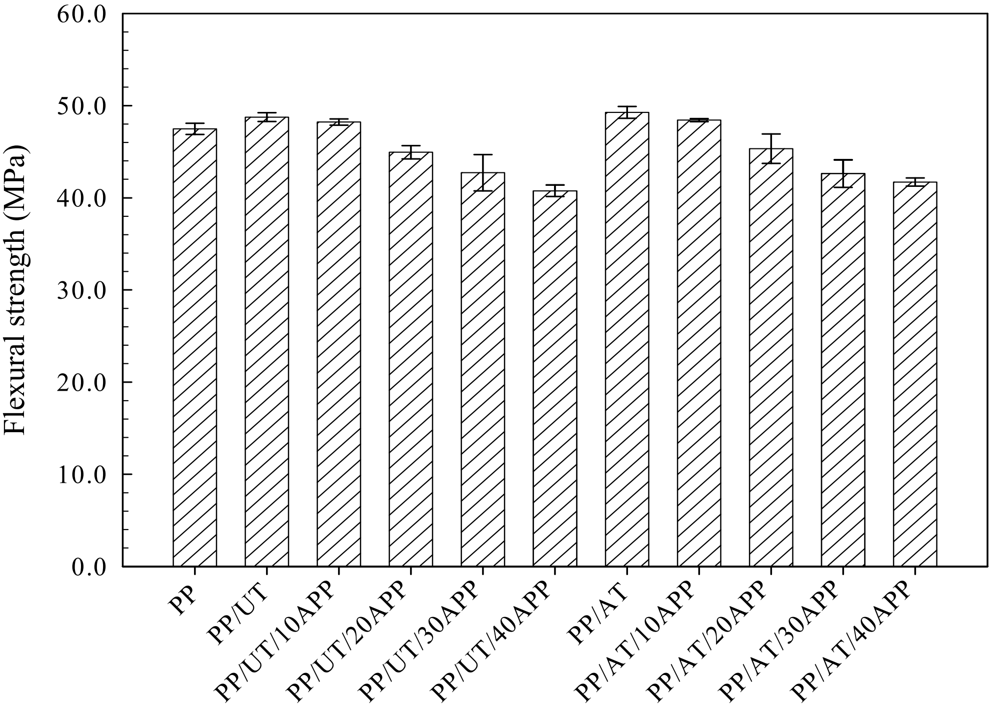


Figure 4.5 Flexural strength of PP and PP composites at various APP contents.

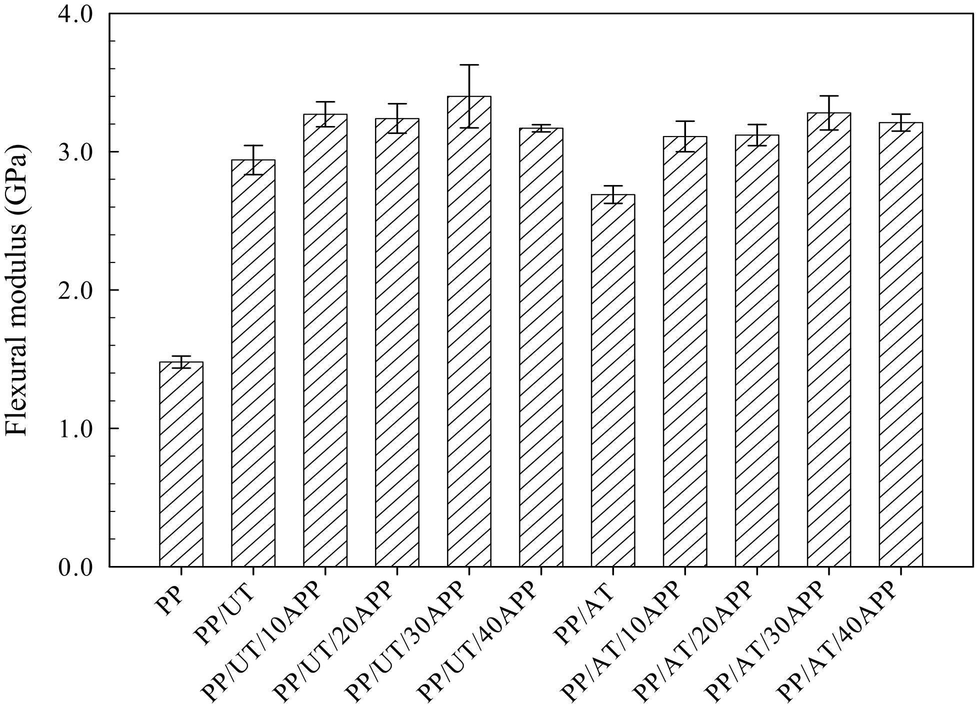


Figure 4.6 Flexural modulus of PP and PP composites at various APP contents.

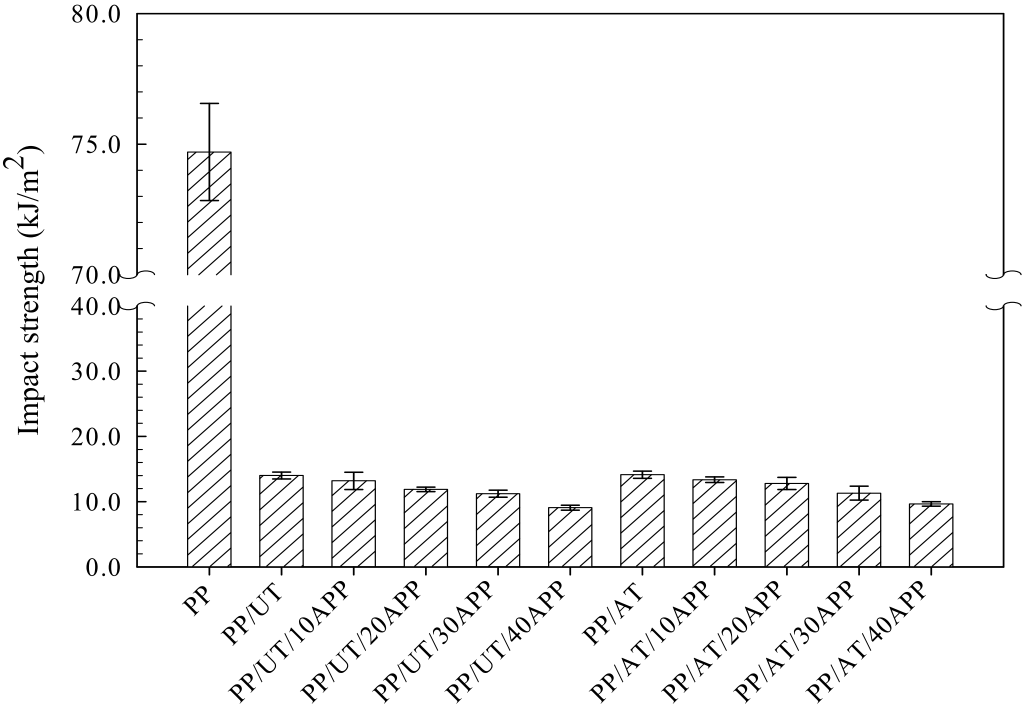
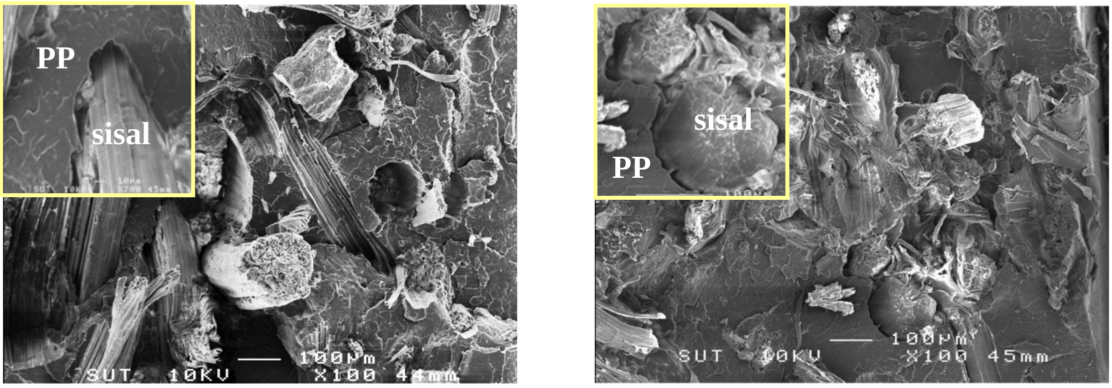


Figure 4.7 Impact strength of PP and PP composites at various APP contents.

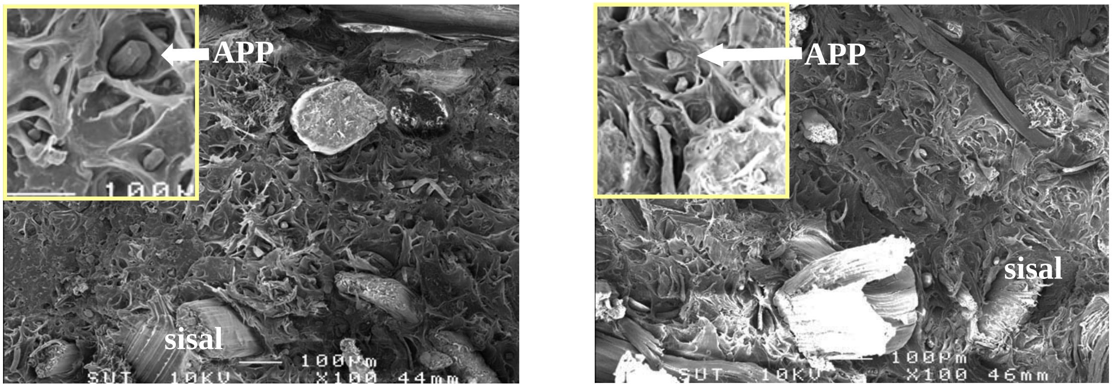
4.1.4 Morphological properties

SEM micrographs of tensile fracture surfaces of PP composites at various APP contents as shown in Figure 4.8 illustrates interfaces of sisal fiber, flame retardant, and PP. As shown in Figures 4.8 (a) and (b), the gaps between sisal fiber and PP were quite large. In addition, sisal fiber was also pulled out from the PP matrix without leaving any sign. This result demonstrated that the interfacial adhesion between sisal fiber and PP was poor. From Figures 4.8 (c-j), poor distribution of APP in the PP matrix was observed since PP and APP were not compatible. Moreover, the worse distribution of APP was observed with increasing APP content. This SEM result was well corresponding to the reported tensile and flexural properties of the composites. SEM micrographs of PP/UT and PP/AT composites were insignificant difference.

This suggested that alkalization of sisal fiber showed no effect on the morphology of the PP composites. On the other hand, some researcher reported the different evident. Paul et al. (2008) observed SEM micrographs of tensile fracture surfaces of banana fiber/PP composites. The untreated banana fiber partly adhered to the PP, demonstrating a week fiber-matrix adhesion. However, the alkali treated fiber was completely surrounded with the PP proving a better fiber-matrix adhesion.

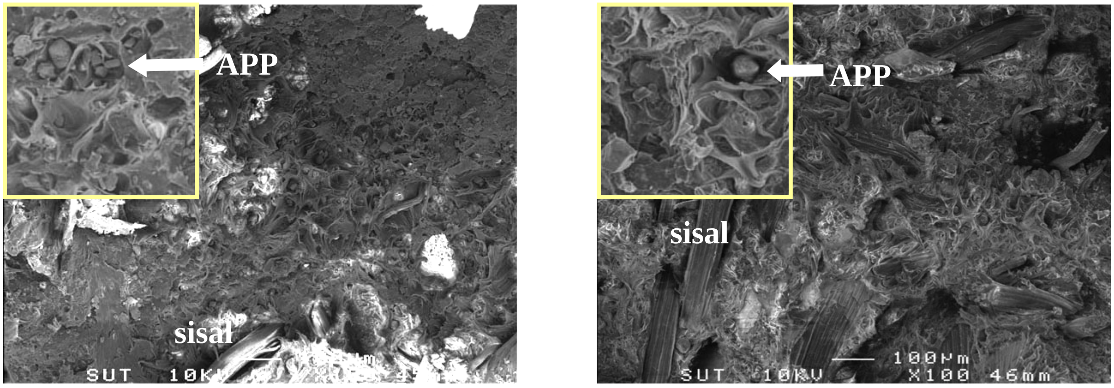


(a) PP/UT (b) PP/AT



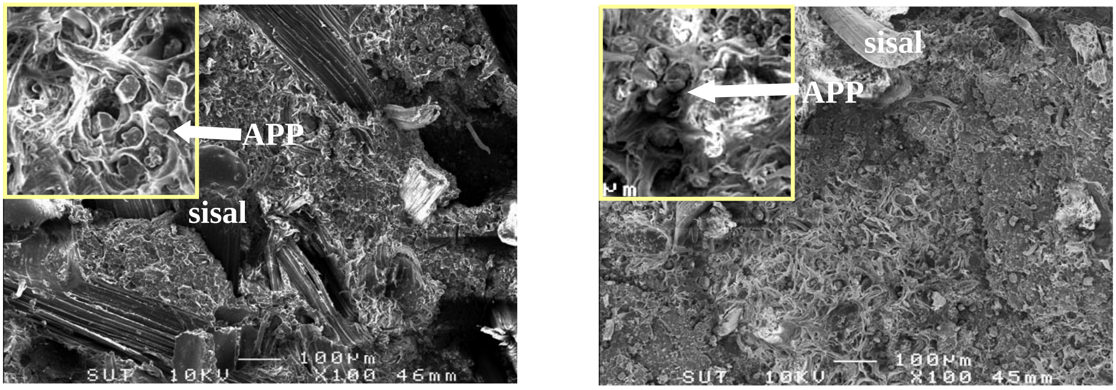
(c) PP/UT/10APP (d) PP/AT/10APP

Figure 4.8 SEM micrographs of PP composites at various APP contents: (a) PP/UT, (b) PP/AT, (c) PP/UT/10APP, (d) PP/AT/10APP.



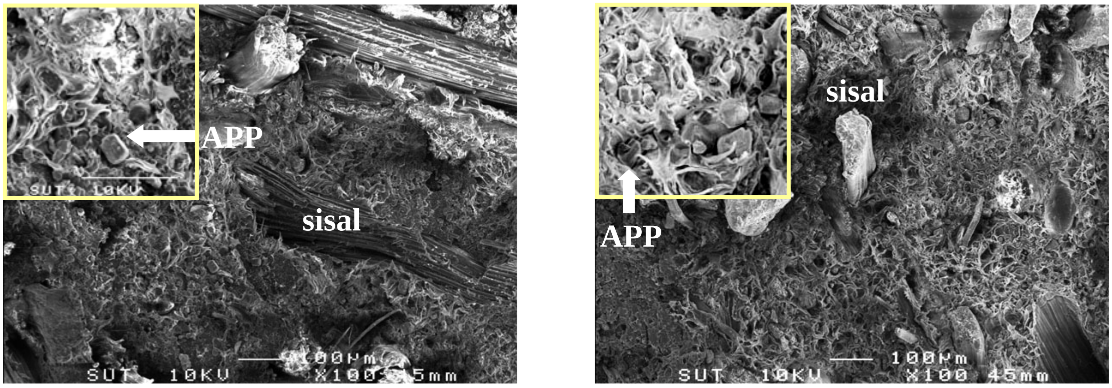
(e) PP/UT/20APP

(f) PP/AT/20APP



(g) PP/UT/30APP

(h) PP/AT/30APP



(i) PP/UT/40APP

(j) PP/AT/40APP

Figure 4.8 SEM micrographs of PP composites at various APP contents:

(e) PP/UT/ 20APP, (f) PP/AT/20APP, (g) PP/UT/30APP,

(h) PP/AT/30APP, (i) PP/ UT/40APP, (j) PP/AT/40APP. (Continued)

4.1.5 Rheological properties

Shear viscosity as a function of shear rate of PP/UT composites at various APP contents and PP/AT composites at various APP contents are shown in Figure 4.9 and 4.10 respectively. All the PP/UT composites had higher shear viscosity than the neat PP as shown in Figure 4.9. This was because the fibers perturbed the flow of polymer and hindered the mobility of chain segments in melt flow. Shear viscosity of the PP/UT composites was slightly increased with increasing content of APP. This suggested that APP had insignificant effect on the processability of the sisal fiber/PP composites. There was no remarkable difference in shear viscosity of PP/UT composites and PP/AT composites. This indicated that alkalization showed no effect on the shear viscosity of the PP composites.

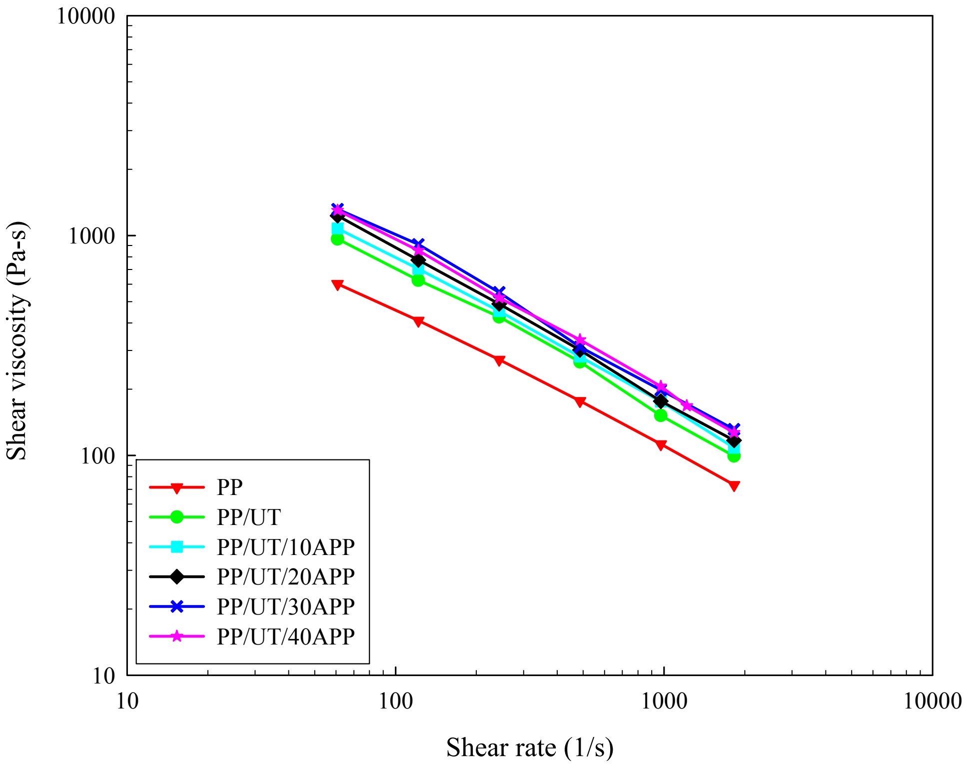


Figure 4.9 Shear viscosity of PP and PP/UT composites at various APP contents.

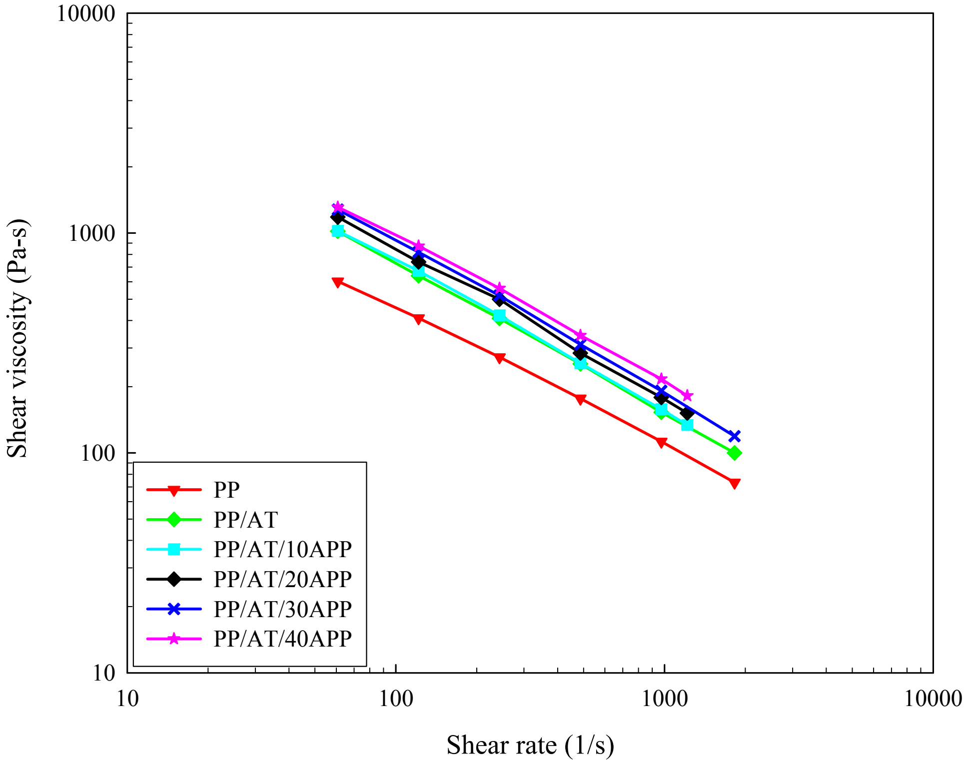


Figure 4.10 Shear viscosity of PP and PP/AT composites at various APP contents.

MFI of PP and PP composites were listed in Table 4.4. MFI of PP was decreased with the addition of the fibers. MFI of sisal fiber/PP composites did not significantly change with increasing APP content.

According to the flammability, thermal properties, and mechanical properties, PP/UT/40APP composite was selected to investigate effect of MAPP as a compatibilizer on the properties of the PP composites.

Table 4.4 Melt flow index of PP, PP/UT composites at various APP contents, and PP/AT composites at various APP contents.

Designation	MFI (g/10min)
PP	5.58 ± 0.02
PP/UT	1.76 ± 0.02
PP/UT/10APP	1.50 ± 0.05
PP/UT/20APP	1.31 ± 0.04
PP/UT/30APP	1.07 ± 0.05
PP/UT/40APP	1.04 ± 0.05
PP/AT	1.85 ± 0.05
PP/AT/10APP	1.59 ± 0.04
PP/AT/20APP	1.36 ± 0.01
PP/AT/30APP	1.13 ± 0.03
PP/AT/40APP	1.06 ± 0.07

4.2 The effect of compatibilizer content on physical properties of sisal fiber/PP and sisal fiber/PP composites containing a flame retardant

4.2.1 Flammability

Horizontal burning rates and vertical burning grade of PP composites are shown in Table 4.5. Both PP/UT/40APP composites with or without the addition of MAPP did not burn under the testing condition. In addition, from vertical burning test, all PP composites showed very short burning times and could be classified as V-0 rating. LOI of PP and PP composites at various APP contents are shown in Table 4.5. Adding MAPP did not change the LOI of PP/UT/40APP composites. These indicated that MAPP showed no impact on the flammability of PP/UT/40APP composites.

Table 4.5 Horizontal burning rate, vertical burning rating, and limiting oxygen index of PP composites at various MAPP contents.

Designation	**Horizontal burning rate (mm/min)**	**Vertical burning rating**	**Limiting oxygen index (%)**
PP/UT/40APP	No burning	V-0	31
PP/UT/40APP/1MAPP	No burning	V-0	31
PP/UT/40APP/3MAPP	No burning	V-0	31
PP/UT/40APP/5MAPP	No burning	V-0	31

4.2.2 Thermal properties

TGA thermograms of PP composites at various MAPP contents are shown in Figure 4.11 and thermal properties of PP composites at various MAPP contents are listed in Table 4.6. With addition of MAPP into PP/UT/40APP composites, $T_{5\%}$ and $T_{50\%}$ of the PP composites slightly reduced while char residue observed at 600 ºC of the PP composites insignificantly changed. Increasing MAPP content in PP composites slightly increased char residue of the PP composites however it had no effect on $T_{5\%}$ and $T_{50\%}$ of the PP composites.

Table 4.6 Thermal properties of PP composites at various MAPP contents.

Designation	**$T_{5\%}$ (°C)**	**$T_{50\%}$ (°C)**	**Char residue (%)**
PP/UT/40APP	324	476	11.61
PP/UT/40APP/1MAPP	321	474	11.15
PP/UT/40APP/3MAPP	322	474	12.25
PP/UT/40APP/5MAPP	321	474	12.83

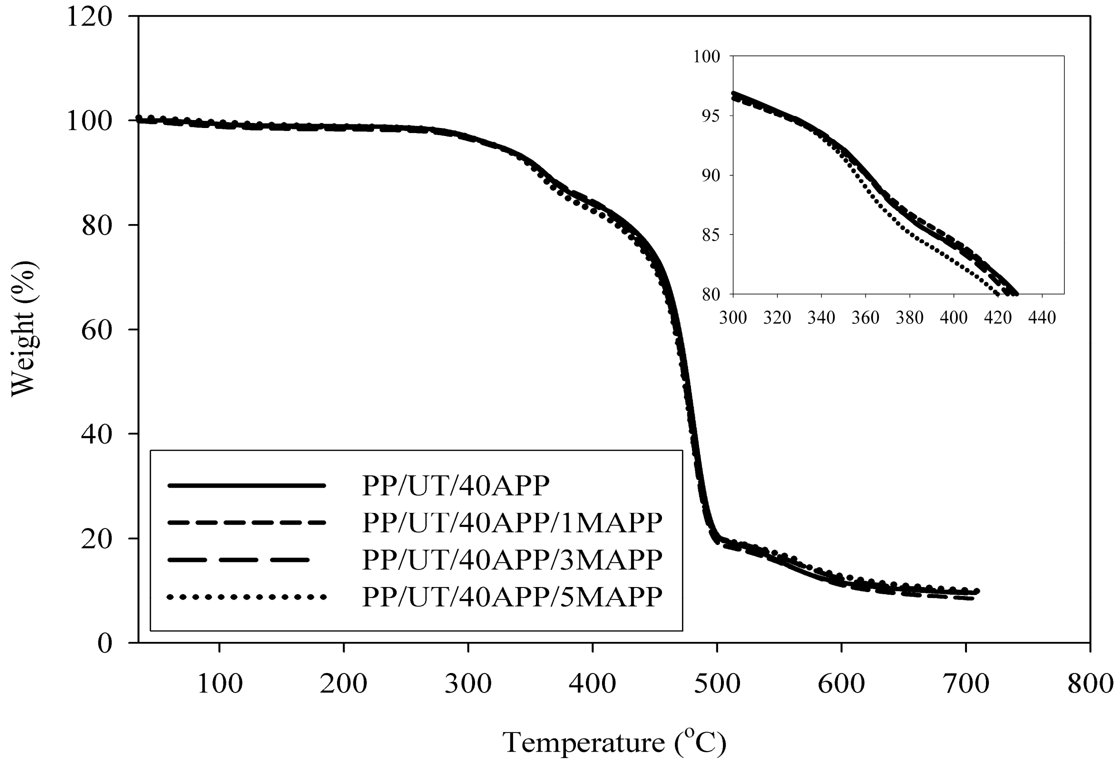


Figure 4.11 TGA thermograms of PP composites at various MAPP contents.

4.2.3 Mechanical properties

Mechanical properties of PP/UT/40APP composites at various MAPP contents are reported in Table 4.7. There was no significant change in tensile modulus and flexural modulus when MAPP was added into PP/UT/40APP composite. Adding 1 phr of MAPP into PP/UT/40APP composites insignificantly increased tensile strength and flexural strength of the PP/UT/40APP composite. However, the incorporation of 3 phr of MAPP into PP/UT/40APP composites remarkably increased tensile strength and flexural strength of the PP composite as shown in Figure 4.13 and 4.14 respectively. This was similarly to that observed by Abu Bakar et al (2010). They found that the interfacial adhesion between PP and wood flour or APP was enhanced with the addition of MAPP into the PP/WF/APP composites leading to improvement in tensile strength and flexural strength of the composites. The increase in tensile strength and flexural strength of PP/UT/40APP composites was attributed to improved interfacial adhesion between fiber and PP (Rana et al., 1998). A hypothetical model of hydroxyl groups of fibers and MAPP at the interface as shown in Figure 4.12 illustrated that the chemical (ester bond) and physical interaction can be formed between hydroxyl groups of the fiber and anhydride groups of MAPP while PP chains of MAPP diffuse into the PP matrix. Therefore, MAPP as a compatibilizer improved the interfacial adhesion between PP and fiber leading to enhanced mechanical properties of the composites (Doan et al., 2006).

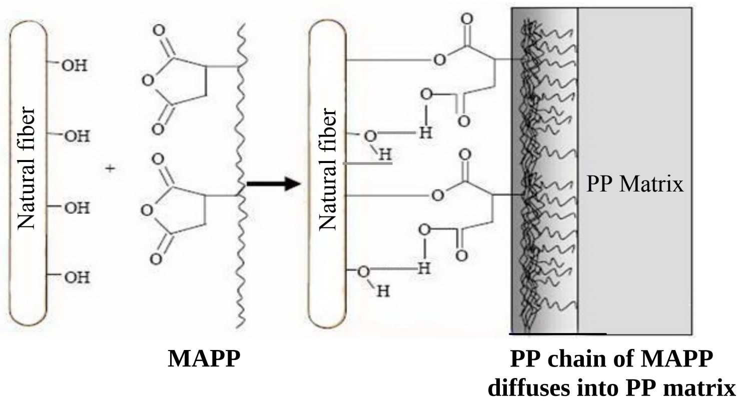


Figure 4.12 Hypothetical structure of maleic anhydride graft polypropylene (MAPP) and natural fiber at the interface (Doan et al., 2006).

However, there was no significant change of tensile properties and flexural properties of PP/UT/40APP composites with adding more than 3 phr of MAPP as shown in Figure 4.13 and 4.14, respectively. This indicated that the optimum loading of MAPP was 3 phr.

Impact strength of the PP composites are shown in Figure 4.15. As seen from the figure, MAPP showed no remarkable effect on the impact strength of PP/UT/40APP composites. This was similar to that observed by Yang, Kim, Park, Lee, and Hwang (2007). They reported that the rice husk/PP composites with or without the addition of MAPP also showed comparable impact strength. With the addition of the compatibilizer, the interfacial adhesion between the filler and the matrix polymer was improved. Thus the crack was not initiated at the interface but rather involved the filler itself.

Table 4.7 Mechanical properties of PP composites at various MAPP contents.

Designation	**Tensile strength (MPa)**	**Tensile modulus (GPa)**	**Flexural strength (MPa)**	**Flexural modulus (GPa)**	**Impact strength (kJ/m^2)**
PP/UT/40APP	23.52 ± 0.19	2.35 ± 0.07	40.76 ± 0.61	3.17 ± 0.03	9.08 ± 0.38
PP/UT/40APP/1MAPP	24.60 ± 0.29	2.32 ± 0.03	42.29 ± 0.64	3.25 ± 0.04	9.21 ± 0.98
PP/UT/40APP/3MAPP	28.43 ± 1.16	2.31 ± 0.05	48.65 ± 0.43	3.56 ± 0.11	9.21 ± 0.98
PP/UT/40APP/5MAPP	29.21 ± 1.14	2.29 ± 0.02	51.03 ± 0.64	3.47 ± 0.04	9.30 ± 0.12

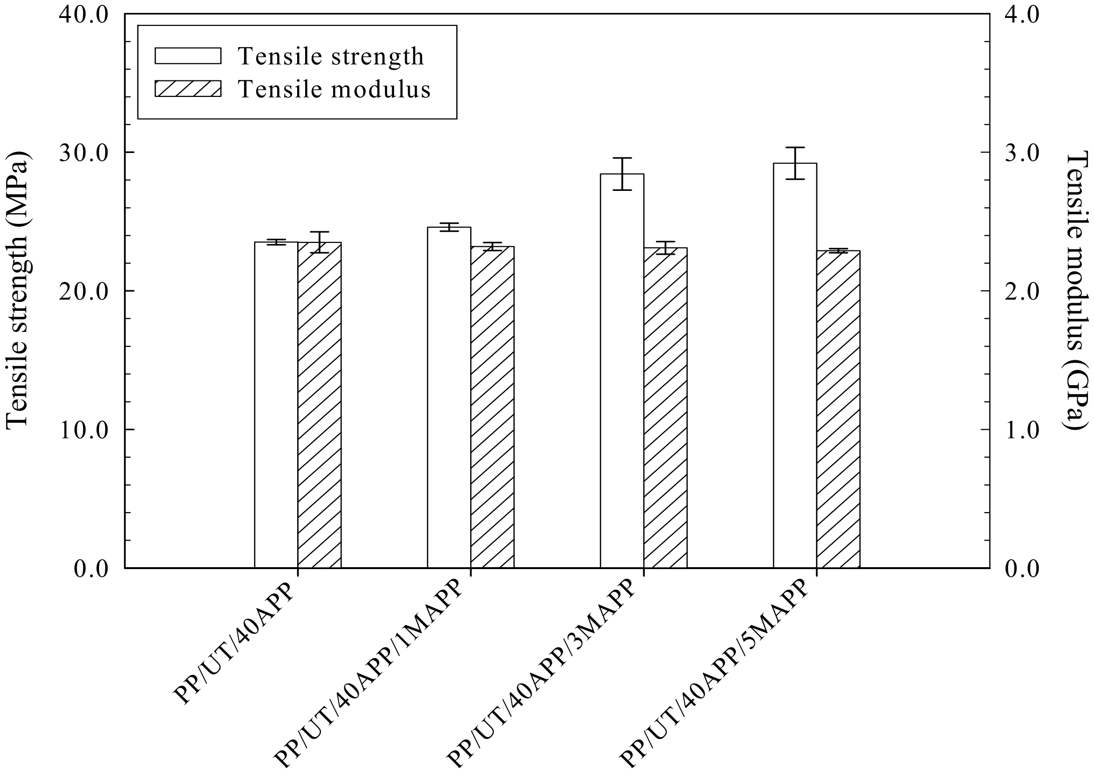


Fig 4.13 Tensile properties of PP composites at various MAPP contents.

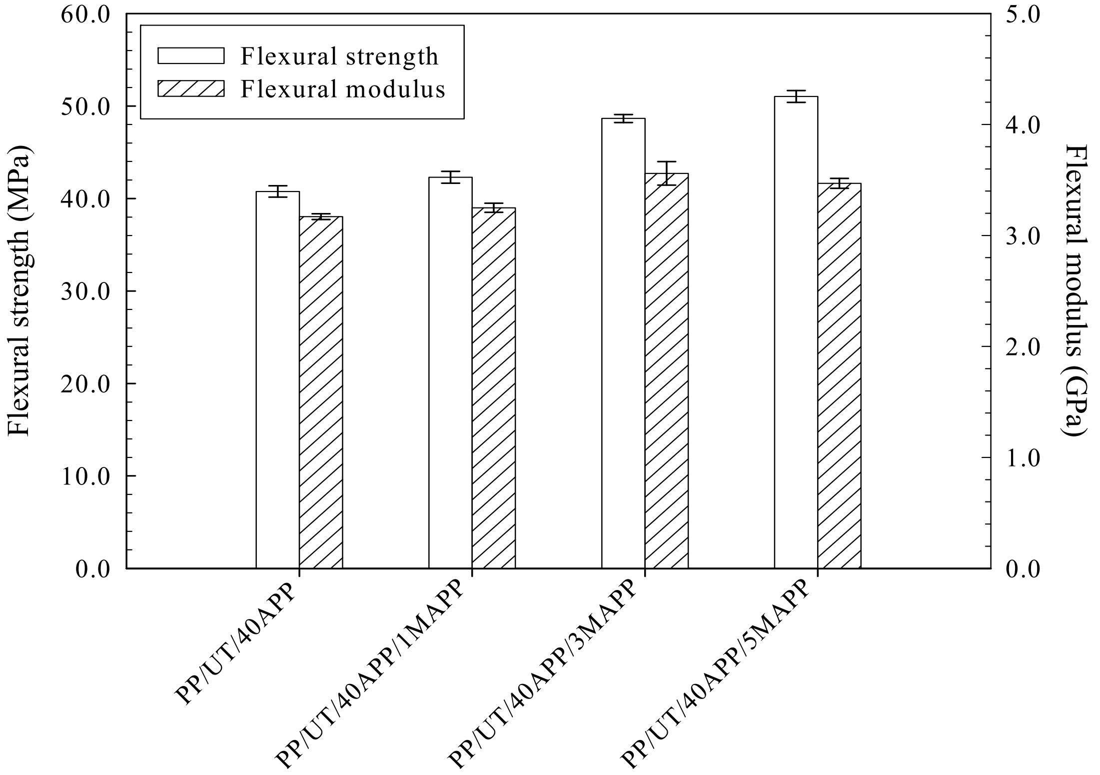


Fig 4.14 Flexural properties of PP composites at various MAPP contents.

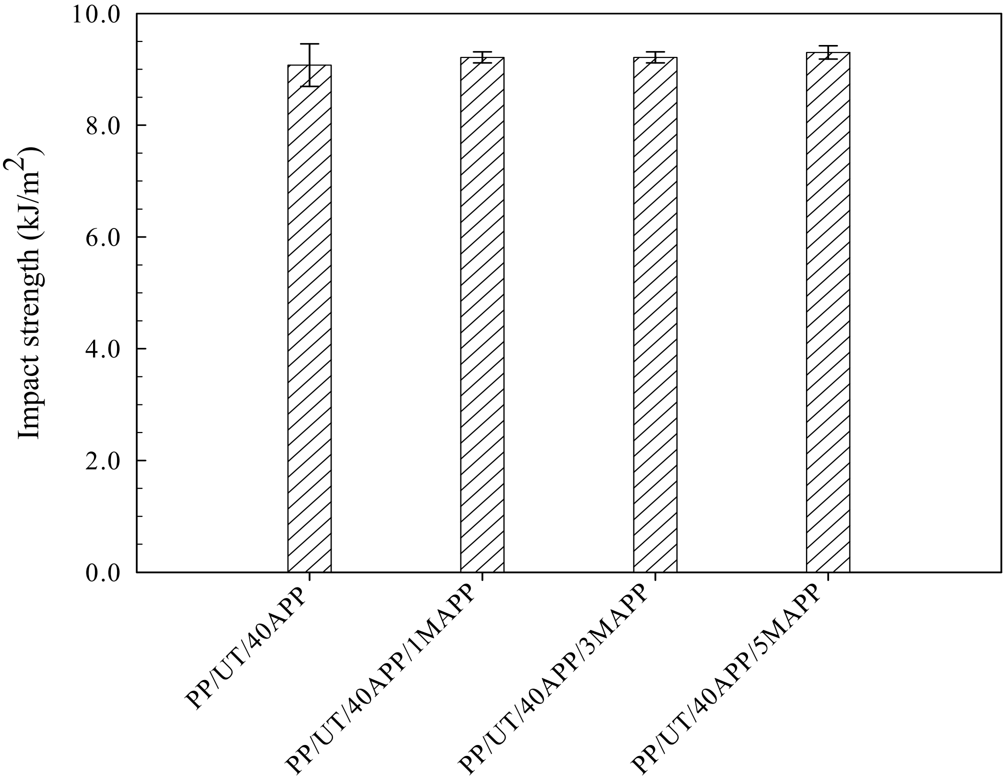
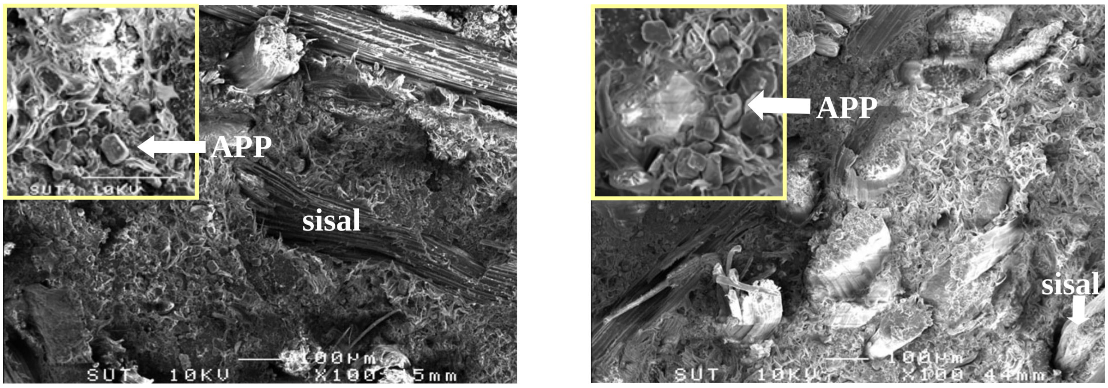


Figure 4.15 Impact strength of PP composites at various MAPP contents.

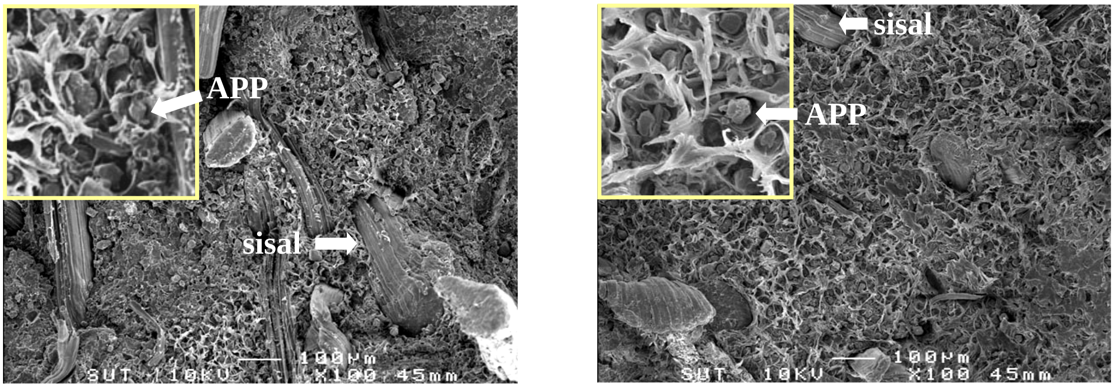
4.2.4 Morphological properties

SEM micrographs of tensile fracture surfaces of PP composites at various MAPP contents are shown in Figure 4.16. From Figure 4.16 (a), gap between sisal fiber and PP was quite large and APP was poorly distributed in the PP matrix. This was similar to that observed in PP/UT/40APP/1MAPP as shown in Figure 4.16 (b). This indicated that the improvement of interfacial adhesion between fillers and matrix was not sufficient by adding 1 phr of MAPP. On the other hand, in case of PP/UT/40APP/3MAPP (Figure 4.16 (c)), There was no gap between sisal fiber and PP. Moreover, good distribution of APP in PP matrix was observed. This suggested that the compatibility between fillers and PP was enhanced. There was no significant difference in morphology of PP/UT/40APP/3MAPP and PP/UT/40APP/5MAPP as shown in Figure 4.16 (c) and (d).



(a) PP/UT/40APP

(b) PP/UT/40APP/1MAPP



(c) PP/UT/40APP/3MAPP

(d) PP/UT/40APP/5MAPP

Figure 4.16 SEM micrographs of PP composites at various MAPP contents:

(a) PP/UT/40APP, (b) PP/UT/40APP/1MAP,

(c) PP/UT/ 40APP/3MAPP, (d) PP/UT/40APP/5MAPP.

4.2.5 Rheological properties

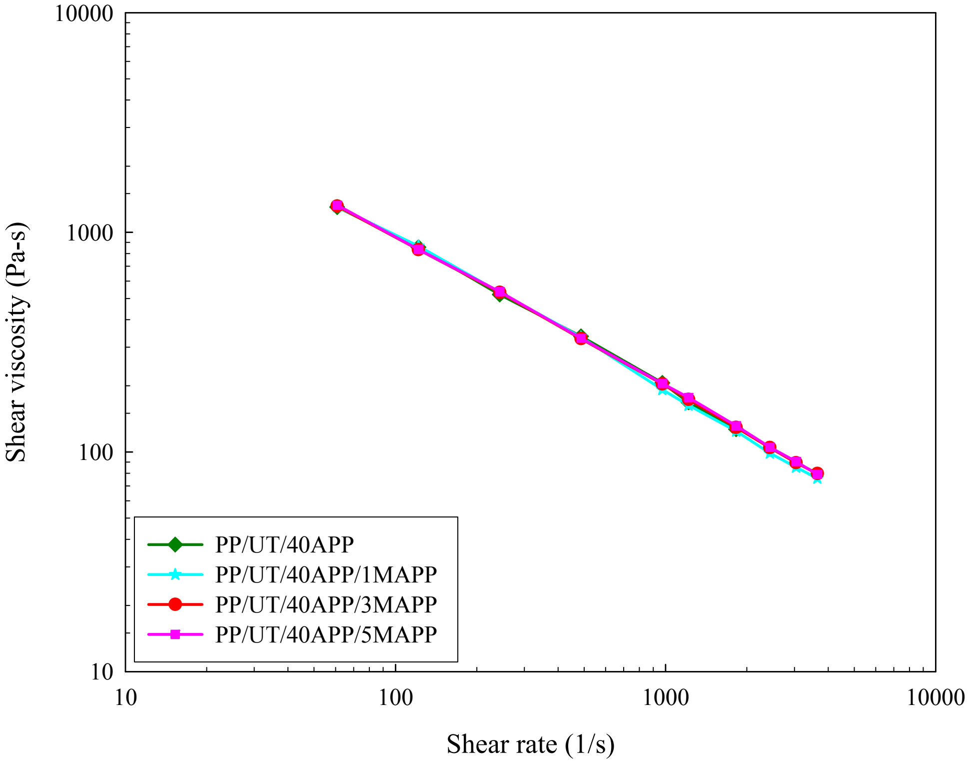


Figure 4.17 Shear viscosity of PP composites at various MAPP contents.

Viscosity of PP composites at various MAPP contents are shown in Figure 4.17. MAPP contents had no influence on shear viscosity of PP/UT/40APP composites. This indicated that MAPP had no effect on the processability of the PP/UT/40APP composites.

MFI of PP composites were listed in Table 4.8. MFI of sisal fiber/PP composites did not significantly change with adding various MAPP contents.

From the flammability, thermal properties, and mechanical properties, PP/UT/40APP/3MAPP composite was chosen to study the effect of combination of flame retardants on properties of PP composites.

Table 4.8 Melt flow index of PP composites at various MAPP contents.

Designation	MFI (g/10min)
PP/UT/40APP	1.04 ± 0.05
PP/UT/40APP/1MAPP	1.02 ± 0.02
PP/UT/40APP/3MAPP	0.97 ± 0.01
PP/UT/40APP/5MAPP	0.93 ± 0.03

4.3 The effect of combination of flame retardants on physical properties of sisal fiber/PP composites

4.3.1 Flammability

Horizontal burning rate of PP composites with combination of flame retardants are shown in Table 4.9. PP/UT/40APP/3MAPP composite did not burn under the testing condition. PP/UT/40Mg/3MAPP composite showed higher burning rate than PP/UT/40APP/3MAPP composite. In addition, adding combination of APP and $Mg(OH)_2$ at various ratio, i.e. 30APP/10$Mg(OH)_2$, 20APP/20$Mg(OH)_2$, and 10APP/30$Mg(OH)_2$, into PP/UT/3MAPP composites resulted in higher burning rates compared to that of PP/UT/40APP/3MAPP composite. This suggested that $Mg(OH)_2$ showed a negative impact on flame retardant properties of PP composites when it was used in combination with APP. The PP/UT/40Zb/3MAPP composite exhibited higher burning rate than PP/UT/40APP/3MAPP composite. This was similar to that observed by Suppakarn, N. and Jarukumjorn, K. (2009). They reported that sisal fiber/PP/15 % wt Zb gave higher burning rate than sisal fiber/PP/15% wt $Mg(OH)_2$. This indicated that Zb was poor flame retardancy for sisal fiber/PP composites. There was no significant change in horizontal burning rate of PP/UT/20APP/20Zb/3MAPP, PP/UT/10APP/30Zb/3MAPP, and PP/UT/40Zb/3MAPP composites. On the other hand, PP/UT/30APP/10Zb/3MAPP composite did not burn under the test condition. This implied that composite containing 30 phr of APP and 10 phr of Zb enhanced flame retardancy of sisal fiber/PP composites.

Vertical burning grade of PP composites with combination of flame retardants are represented in Table 4.9. PP/UT/40APP/3MAPP composite showed the shortest burning time (<10 s). This composite can be classified as V-0 rating. However, the composites containing 40 phr of $Mg(OH)_2$ or combination of APP and $Mg(OH)_2$ gave complete combustion (NC). This indicated that no synergistic effect was observed when APP and $Mg(OH)_2$ were incorporated in the sisal/PP composites. Adding 40 phr Zb into PP/UT/3MAPP composites showed complete combustion (NC). Similarly, addition of APP and Zb at 20:20 and 10:30 into PP/UT/3MAPP composites exhibited complete combustion (NC). On the contrary, the vertical burning grade of the PP/UT/30APP/10Zb/3MAPP composite gave burning time less than 10 s and was classified as V-0 rating.

LOI of PP composites with combination of flame retardants are shown in Table 4.9. PP/UT/40APP/3MAPP showed the highest LOI. Adding 40 phr of $Mg(OH)_2$ and combination of APP with $Mg(OH)_2$ at various ratios, i.e. $30APP/10Mg(OH)_2$, $20APP/20Mg(OH)_2$, and $10APP/30Mg(OH)_2$ into PP/UT/3MAPP composites gave lower limiting oxygen index compared with that of PP/UT/40APP/3MAPP composite. Similar to the horizontal burning tests, vertical burning tests also showed a reduction in the flame retardancy of the PP composites when $Mg(OH)_2$ was used in combination with APP. The PP/UT/40Zb/3MAPP composites showed lower limiting oxygen index than PP/UT/40APP/3MAPP composite. Addition of APP and Zb at 20:20 and 10:30 into PP/UT/3MAPP composites exhibited lower LOI compared to PP/UT/40APP/3MAPP composite. In contrast, LOI of PP/UT/30APP/10Zb/3MAPP was similar to PP/UT/40APP3MAPP. This implied that the combination of APP and Zb at this ratio provided.

It has been reported that addition of Zb in PP composites could give poor flame retardancy of PP (Jeencham, R., Suppakarn, N., and Jarukumjorn, K., 2009). However, adding combination of APP and Zb into PP resulted in a synergistic effect (Samyn, et al., 2007). This was believed to occur by a reaction to produce zinc pyrophosphate ($Zn_2P_2O_7$) under high temperature of the fire environment. The overall chemical reactions are depicted as follows:

$$[NH_4PO_3]_n \rightarrow [HPO_3]_n + nNH_3 \tag{4.1}$$

$$[HPO_3]_n + \text{Carbon source} \rightarrow \boxed{C} + H_3PO_4 \tag{4.2}$$

$$2ZnO.3B_2O_3.3H_2O \rightarrow 2ZnO.3B_2O_3 + 3H_2O \tag{4.3}$$

$$10H_3PO_4 + 2ZnO.3B_2O_3 \rightarrow 6BPO_4 + P_4O_{10} + 2ZnO + 15H_2O \tag{4.4}$$

$$3ZnO + 0.5P_4O_{10} \rightarrow Zn_3(PO_4)_2 \tag{4.5}$$

$$2Zn_3(PO_4)_2 + 2BPO_4 \rightarrow B2O_3 + 3Zn_2P_2O_7 \tag{4.6}$$

The obtained zinc pyrophosphate ($Zn_2P_2O_7$) is believed to serve as an efficient intumescent char, which could act as a physical barrier and a glassy cage for polymer chains. However, it was found in this study that adding more than 10 phr of

Zb into the composites gave a negative effect on flame retardancy. This was caused by the unbalance of stoichiometry between APP and Zb.

Table 4.9 Horizontal burning rate, vertical burning rating, and limiting oxygen index of PP composites with combination of flame retardants.

Designation	**Horizontal burning rate (mm/min)**	**Vertical burning rating**	**Limiting oxygen index (%)**
PP/UT/40APP/3MAPP	No burning	V-0	31
PP/UT/30APP/10Mg/3MAPP	15.02 $\pm$ 0.71	NC	24
PP/UT/20APP/20Mg/3MAPP	21.74 $\pm$ 0.11	NC	23
PP/UT/10APP/30Mg/3MAPP	25.16 $\pm$ 0.99	NC	22
PP/UT/40Mg/3MAPP	16.75 $\pm$ 0.07	NC	24
PP/UT/30APP/10Zb/3MAPP	No burning	V-0	30
PP/UT/20APP/20Zb/3MAPP	27.39 $\pm$ 0.35	NC	23
PP/UT/10APP/30Zb/3MAPP	27.53 $\pm$ 0.60	NC	22
PP/UT/40Zb/3MAPP	27.95 $\pm$ 0.25	NC	22

4.3.2 Thermal properties

TGA thermograms and thermal properties of PP composites with combination of APP and $Mg(OH)_2$ are shown in Figure 4.18 and Table 4.10 respectively. PP composite containing $Mg(OH)_2$ had the highest thermal stability since it showed the highest $T_{5\%}$, $T_{50\%}$, and char residue. In addition, when $Mg(OH)_2$ was added into PP composites filled with APP the char residue was increased. With the addition of both APP and $Mg(OH)_2$ into PP composites, thermal properties of the composites were slightly changed.

In case of adding 40 phr of Zb into PP composite, the composite exhibited the lowest thermal stability since it showed the lowest $T_{5\%}$ and $T_{50\%}$ as seen in Figure 4.19 and Table 4.10. Combination of APP and Zb showed slight effect on thermal properties of PP composites.

Table 4.10 Thermal properties of PP composites with combination of flame retardants.

Designation	**$T_{5\%}$ (°C)**	**$T_{50\%}$ (°C)**	**Char residue (%)**
PP/UT/40APP/3MAPP	322	474	12.25
PP/UT/30APP/10Mg/3MAPP	322	472	18.97
PP/UT/20APP/20Mg/3MAPP	322	472	18.88
PP/UT/10APP/30Mg/3MAPP	317	475	20.78
PP/UT/40Mg/3MAPP	329	477	21.27
PP/UT/30APP/10Zb/3MAPP	316	472	19.54
PP/UT/20APP/20Zb/3MAPP	323	472	21.13
PP/UT/10APP/30Zb/3MAPP	325	472	22.62
PP/UT/40Zb/3MAPP	320	466	23.60

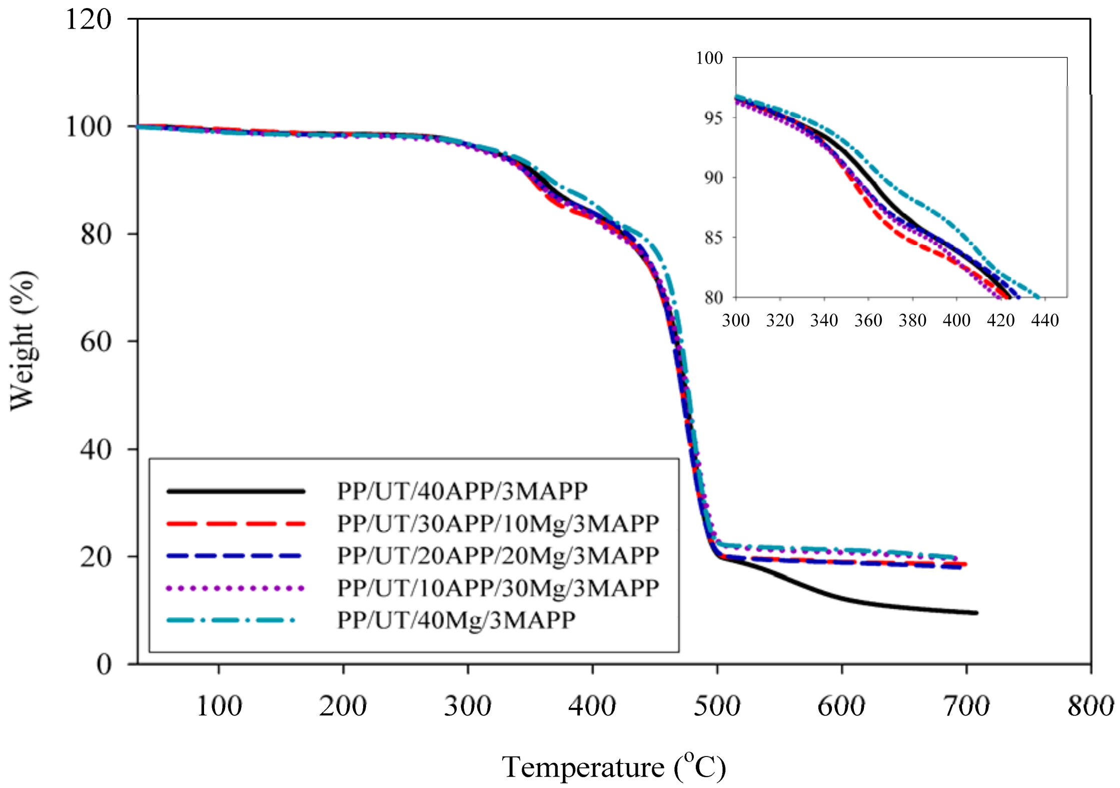


Figure 4.18 TGA thermograms of PP composites with combination of APP and $Mg(OH)_2$.

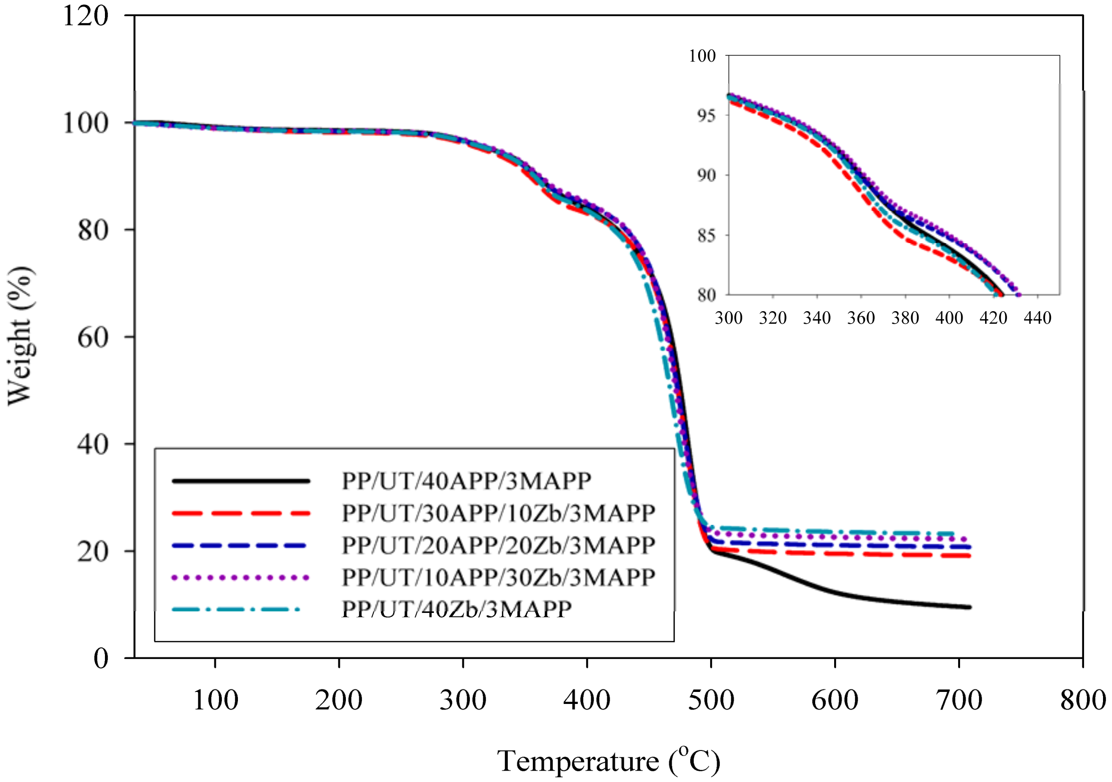


Figure 4.19 TGA thermograms of PP composites with combination of APP and Zb.

4.3.3 Mechanical properties

Mechanical properties of PP composites are represented in Table 4.11. Incorporation of various ratios of APP and $Mg(OH)_2$ into PP/UT/3MAPP composites resulted in insignificant change in tensile properties, flexural properties, and impact strength as shown in Figure 4.20-4.24. Moreover, the combination of APP and Zb insignificantly changed mechanical properties of the composites. PP/UT/3MAPP composite containing Zb exhibited higher tensile strength and flexural strength than the composites containing other flame retardants. This was because Zb had rougher surface than APP and $Mg(OH)_2$ as shown in Figure 4.25 (a), (e), and (i). Thus, it may promote mechanical interlocking between Zb and PP matrix.

Table 4.11 Mechanical properties of PP composites with combination of flame retardants.

Designation	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m^2)
PP/UT/40APP/3MAPP	28.43 ± 1.16	2.31 ± 0.05	48.65 ± 0.43	3.55 ± 0.10	9.21 ± 0.10
PP/UT/30APP/10Mg/3MAPP	28.88 ± 0.81	2.21 ± 0.06	47.13 ± 0.14	3.57 ± 0.05	10.49 ± 0.31
PP/UT/20APP/20Mg/3MAPP	29.18 ± 1.18	2.22 ± 0.06	47.75 ± 0.54	3.63 ± 0.15	10.77 ± 0.28
PP/UT/10APP/30Mg/3MAPP	29.54 ± 0.70	2.27 ± 0.11	47.60 ± 0.78	3.73 ± 0.05	10.95 ± 0.10
PP/UT/40Mg/3MAPP	29.92 ± 1.31	2.36 ± 0.11	47.72 ± 0.21	3.88 ± 0.02	11.22 ± 0.54
PP/UT/30APP/10Zb/3MAPP	28.66 ± 0.70	2.17 ± 0.06	48.05 ± 0.34	3.78 ± 0.05	10.72 ± 0.37
PP/UT/20APP/20Zb/3MAPP	29.88 ± 1.08	2.20 ± 0.02	48.12 ± 0.15	3.81 ± 0.05	11.41 ± 0.19
PP/UT/10APP/30Zb/3MAPP	29.74 ± 0.29	2.20 ± 0.08	47.76 ± 0.95	3.77 ± 0.03	11.86 ± 0.59
PP/UT/40Zb/3MAPP	32.62 ± 0.53	2.23 ± 0.10	51.54 ± 1.77	3.70 ± 0.12	12.96 ± 0.20

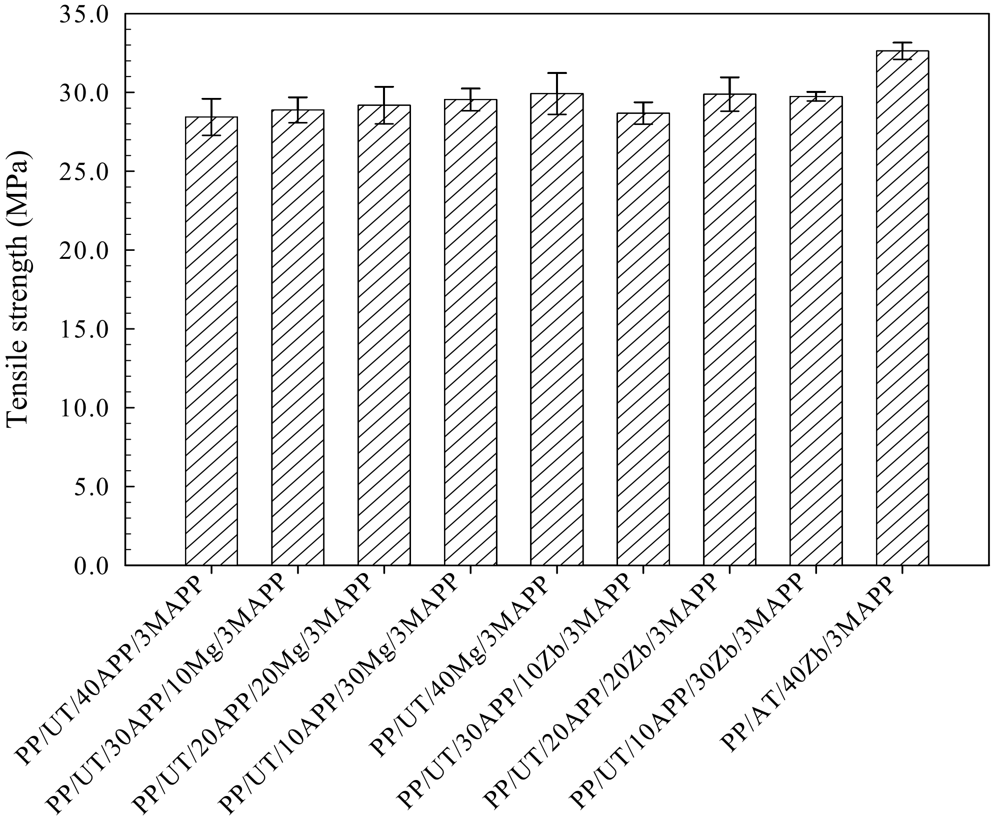


Figure 4.20 Tensile strength of PP composites with combination of flame retardants.

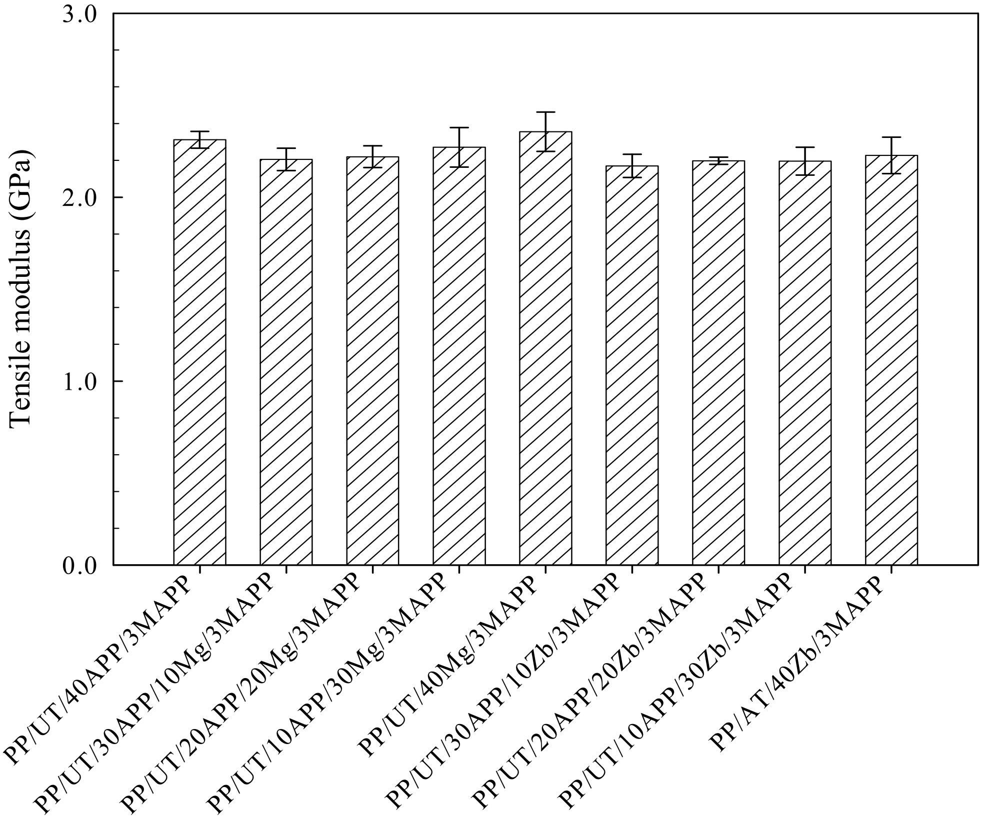


Figure 4.21 Tensile modulus of PP composites with combination of flame retardants.

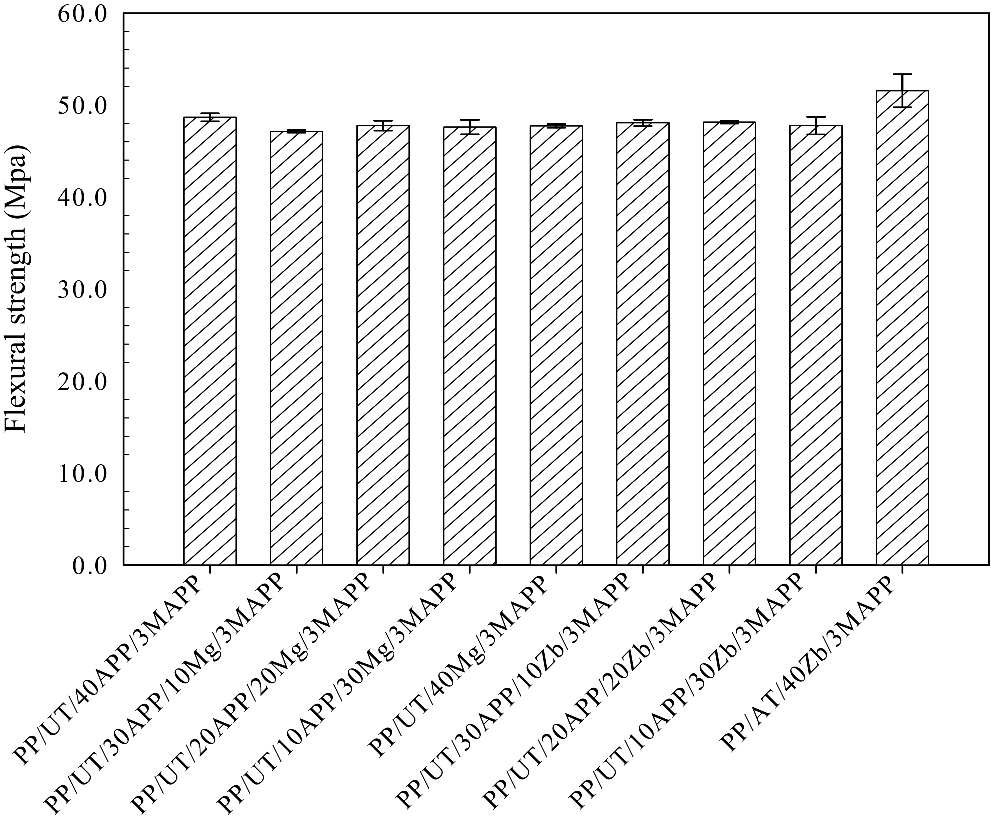


Figure 4.22 Flexural strength of PP composites with combination of flame retardants.

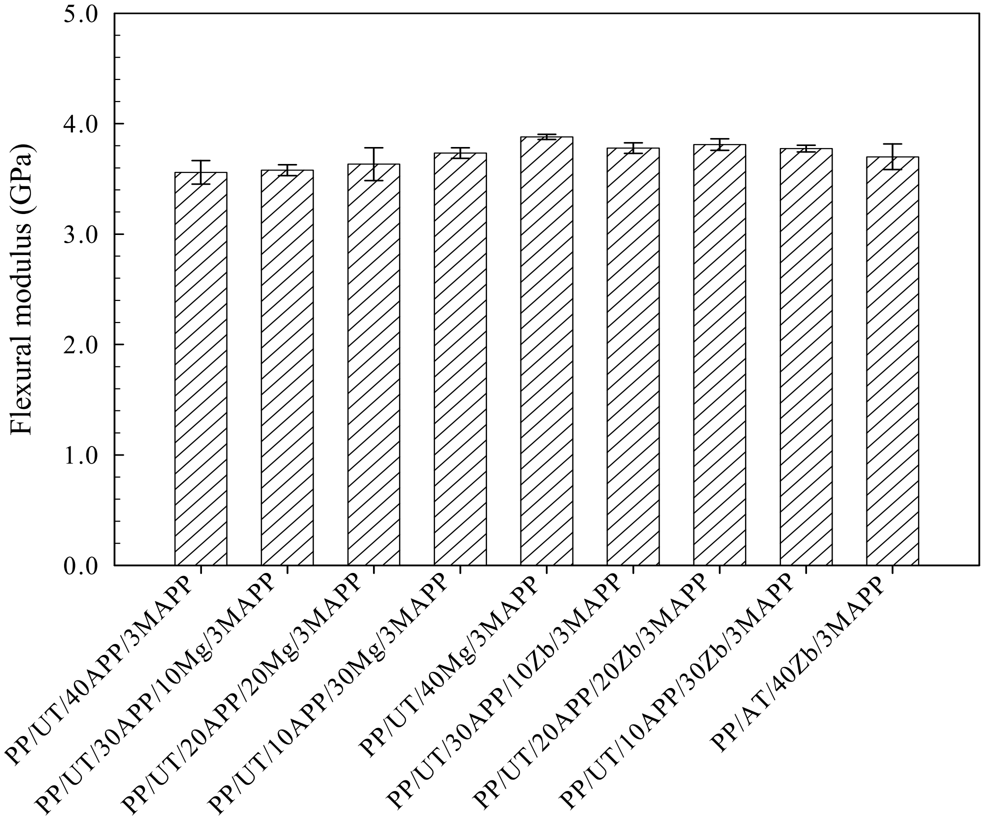


Figure 4.23 Flexural modulus of PP composites with combination of flame retardants.

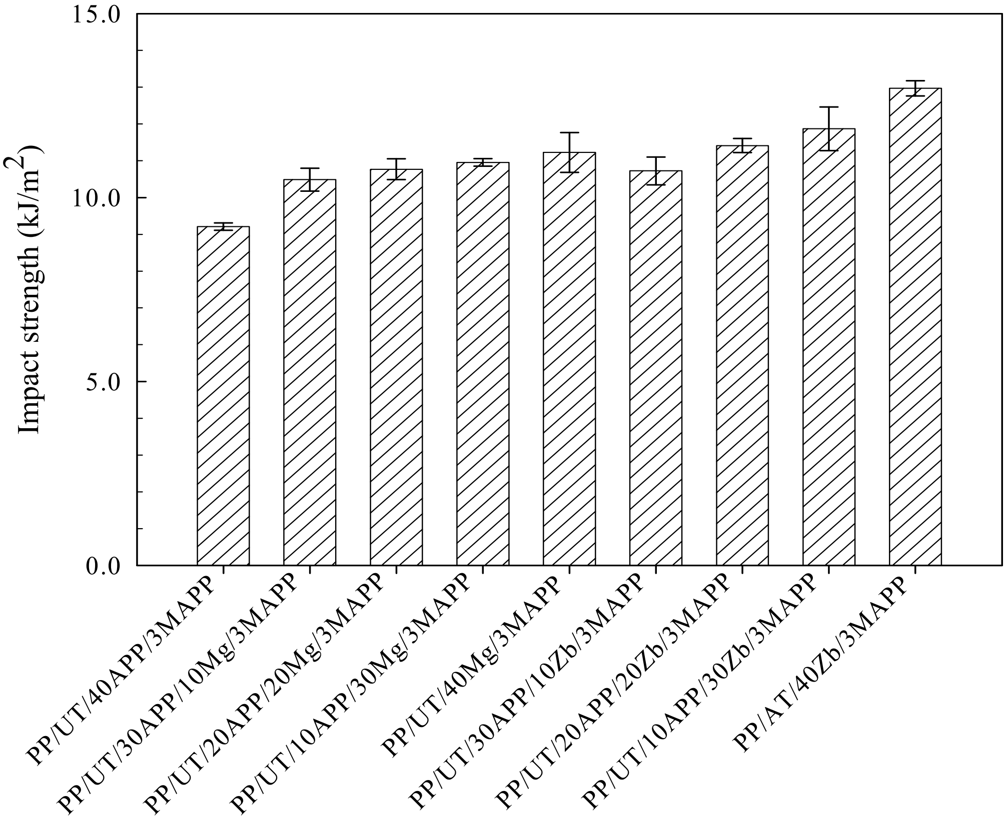
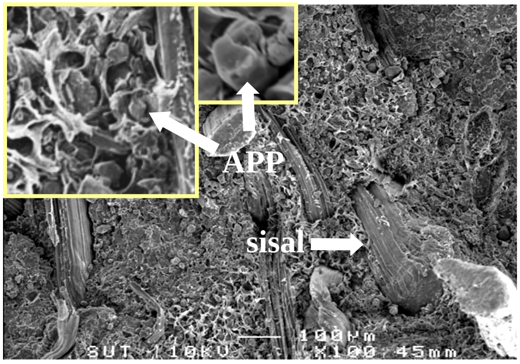


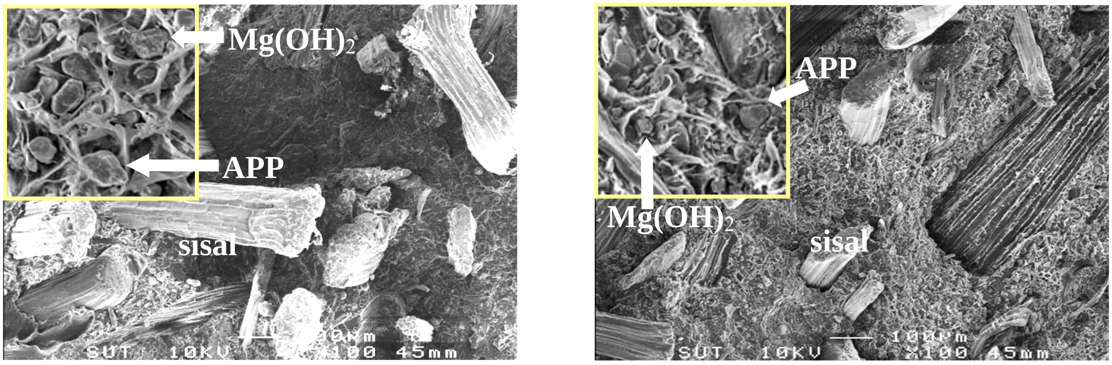
Figure 4.24 Impact strength of PP composites with combination of flame retardants.

4.3.4 Morphological properties

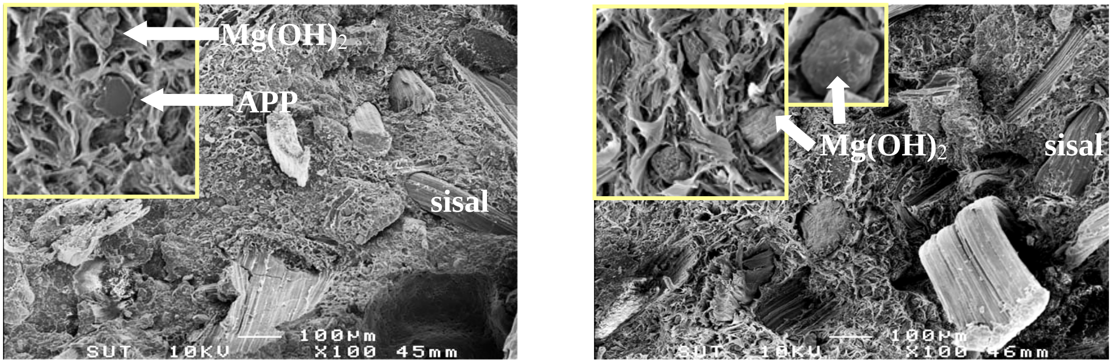
Figure 4.25 shows SEM micrographs of tensile fracture surfaces of PP composites with combination of flame retardants. For PP/UT/40APP/3MAPP as shown in Figure 4.25 (a), there was no gap between sisal fiber and PP. In addition, good distribution of APP in PP matrix was seen. From Figure 4.25 (b-i), the microstructure micrographs showed a good adhesion between sisal fiber and PP. In addition, APP, $Mg(OH)_2$, and Zb well distributed in the PP matrix. This indicated that MAPP improved the compatibility between PP and sisal fiber or flame retardants.



(a) PP/UT/40APP/3MAPP

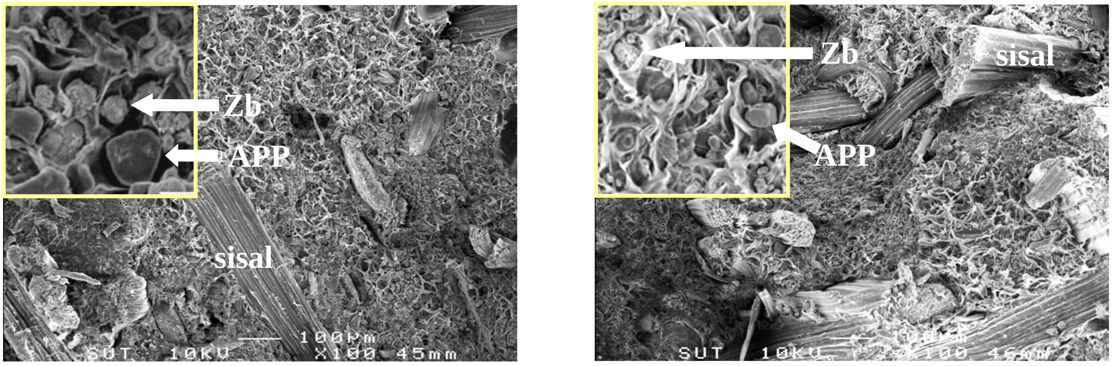


(b) PP/UT/30APP/10Mg(OH)$_2$/3MAPP (c) PP/UT/20APP/20Mg(OH)$_2$/3MAPP

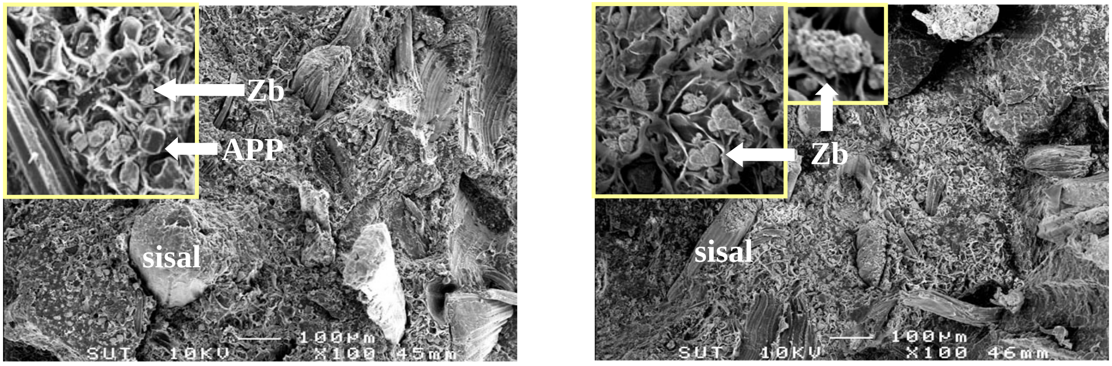


(d) PP/UT/10APP/30Mg/3MAPP (e) PP/UT/40Mg/3MAPP

Figure 4.25 SEM micrographs of PP composites with combination of flame retardants: (a) PP/UT/40APP/3MAPP, (b) PP/UT/30APP/10Mg/ 3MAPP, (c) PP/UT/20APP/20Mg/3MAPP, (d) PP/UT/10APP/30Mg/3MAPP, (e) PP/UT/40Mg/3MAPP.



(f) PP/UT/30APP/10Zb/3MAPP (g) PP/UT/20APP/20Zb/3MAPP



(h) PP/UT/10APP/30Zb/3MAPP (i) PP/UT/40Zb/3MAPP

Figure 4.25 SEM micrographs of PP composites with combination of flame retardants: (f) PP/UT/30APP/10Zb/3MAPP, (g) PP/UT/20APP/20Zb/3MAPP, (h) PP/UT/10APP/30Zb/3MAPP, (i) PP/UT/40Zb/3MAPP. (Continued)

4.3.5 Rheological properties

Viscosity curves of PP composites containing various combinations of flame retardants, APP/$Mg(OH)_2$ and APP/Zb, are shown in Figure 4.26 and 4.27 respectively. The combination of flame retardants had no effect on shear viscosity of PP composite. In addition, MFI of the PP composites with combination of APP and $Mg(OH)_2$ or Zb insignificantly changed with increasing content of $Mg(OH)_2$ or Zb as shown in Table 4.12. This indicated that combination of flame retardants did not affect the processability of the sisal fiber/PP composites.

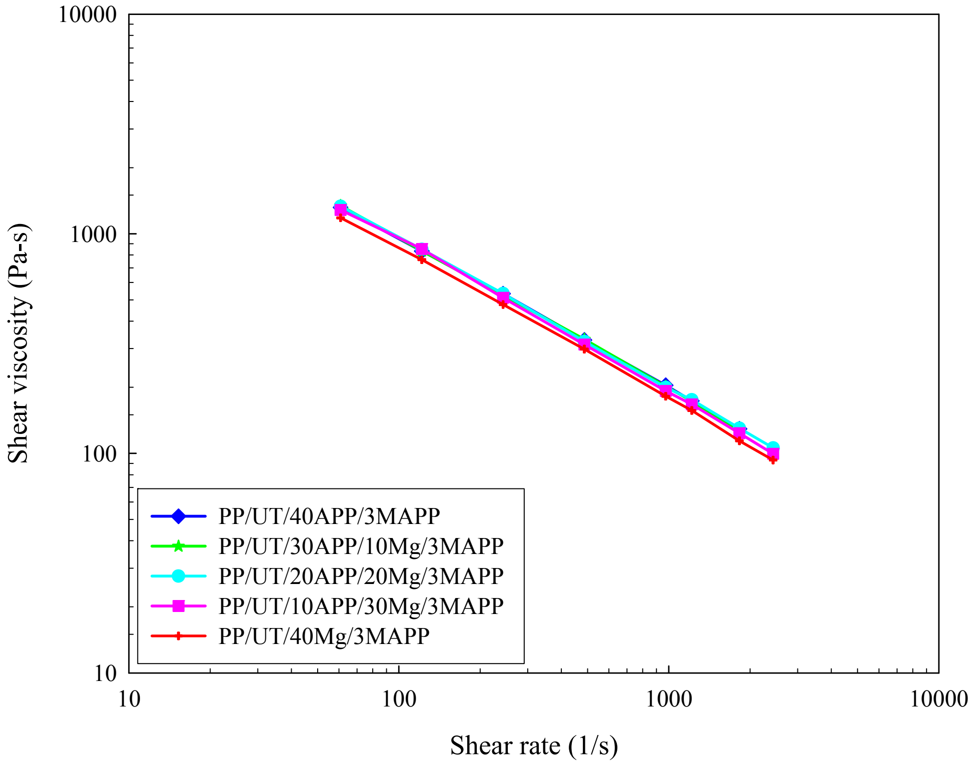


Figure 4.26 Shear viscosity of PP composites with combination of APP and $Mg(OH)_2$.

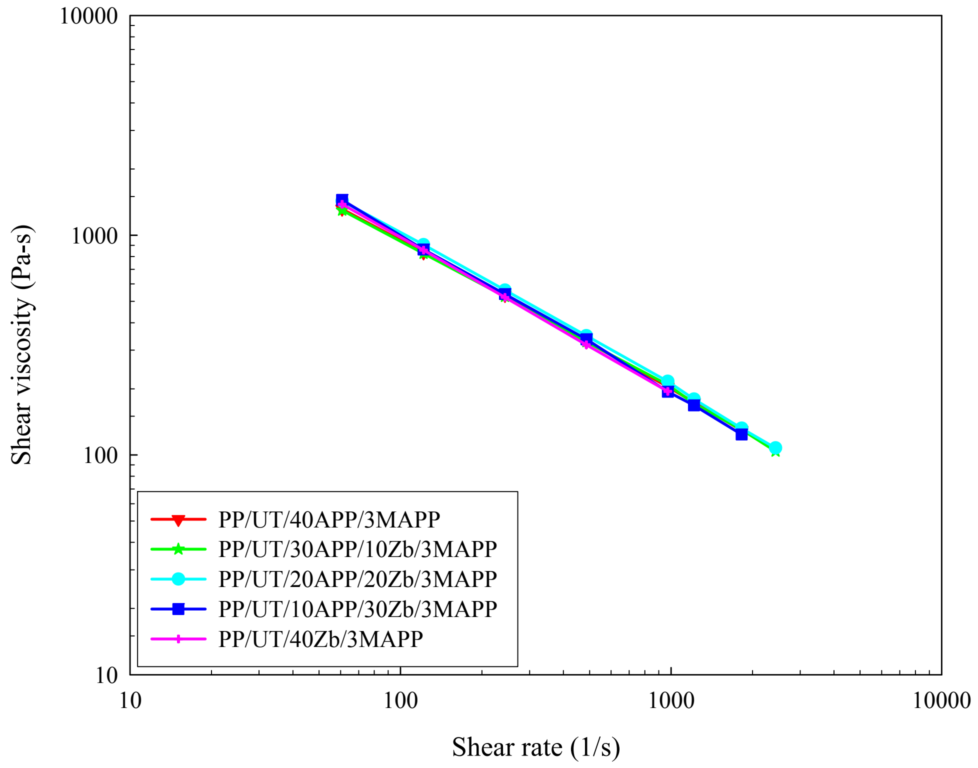


Figure 4.27 Shear viscosity of PP composites with combination of APP and Zb.

Table 4.12 Melt flow index of PP composites with combination of flame retardants.

Designation	**MFI (g/10min)**
PP/UT/40APP/3MAPP	0.97 ± 0.01
PP/UT/30APP/10Mg/3MAPP	1.21 ± 0.01
PP/UT/20APP/20Mg/3MAPP	1.34 ± 0.09
PP/UT/10APP/30Mg/3MAPP	1.62 ± 0.05
PP/UT/40Mg/3MAPP	1.85 ± 0.09
PP/UT/30APP/10Zb/3MAPP	1.33 ± 0.09
PP/UT/20APP/20Zb/3MAPP	1.43 ± 0.07
PP/UT/10APP/30Zb/3MAPP	1.50 ± 0.04
PP/UT/40Zb/3MAPP	1.80 ± 0.04

CHAPTER V

CONCLUSIONS

Incorporating APP into sisal fiber/PP composites resulted in improved flame retardancy and thermal decomposition temperature of the composites. With increasing APP content, the flame retardancy and thermal stability of the composites were improved while their tensile strength and flexural strength slightly decreased. The sisal fiber/PP composite containing 40 phr of APP gave the highest flame retardancy and thermal stability. SEM micrographs revealed poor distribution of APP in PP matrix since PP and APP were not compatible. All sisal fiber/PP composites exhibited insignificant difference in shear viscosity. Alkalization showed no remarkable effect on the properties of the composites.

Adhesion between PP matrix and sisal fibers or APP was enhanced with addition of MAPP leading to the improvement of tensile strength and flexural strength of the PP/UT/40APP composites. On the other hand, flammability and thermal property of the composites were not much affected by the incorporation of MAPP. There was no significant change of the tensile properties and flexural properties of the composites with adding more than 3 phr of MAPP. SEM micrographs of the composites containing MAPP exhibited good adhesion and good distribution of flame retardant and sisal fiber in PP matrix. MAPP showed no influence on the shear viscosity of the composites. This suggested that MAPP did not affect the processability of the composites.

The combination of APP and $Mg(OH)_2$ showed a negative impact on flame retardant property of the PP/UT/3MAPP composites. However, the composite with 30 phr of APP and 10 phr of Zb exhibited the highest flame retardancy. PP composite containing $Mg(OH)_2$ showed the highest thermal stability when compared to PP composites with APP and those with combination of APP and $Mg(OH)_2$. In case of adding 40 phr of Zb into PP composite, this composite exhibited the lowest thermal stability. Combination of APP with $Mg(OH)_2$ or Zb showed slight effect on thermal behaviors of PP composites. Adding a combination of flame retardants exhibited insignificant change in tensile properties, flexural properties, impact strength, and viscosity of the composites. SEM micrographs of the composites revealed good distribution of flame retardants and sisal fiber in PP matrix.

REFERENCES

Abu Bakar, M. B., Mohd Ishak, Z. A., Mat Taib, R., Rozman, H. D., and Mohamad Jani, S. (2010). Flammability and mechanical properties of wood flour filled polypropylene composites. **J. Appl. Polym. Sci.** 116: 2714-2722.

Allen, N. S. (1983). **Degradation and Stability of Polyolefins.** London: Applied Science Publishers.

Andreas, M. and Hartmut, W. (2001). Injection molding of natural fiber reinforced thermoplastics. **Kunstst. Plast. Eur.** 91: 25–27.

Arbelaiz, A., Fernandez, B., Ramos, J. A., Retegi, A., Liano Ponte, R., and Mongrsgon, I. (2005). Mechanical properties of short flax fibre bundle/ polypropylene compositess: Influence of matrix/fibre modification, fibre content, water uptake and recycling. **Comp. Sci. Tech.** 65: 1582-1592.

Ashton, H. C. (2005). Fire retardants. In M. Xanthos (Ed.). **Functional Fillers for Plastics.** Weinheim: Wiley-VCH.

Ballice, L. and Reimerta, R. (2002). Classification of volatile products from the temperature programmed pyrolysis of polypropylene (PP), atactic-polypropylene (APP) and thermogravimetrically derived kinetics of pyrolysis. **Chem. Eng. Proc.** 41: 289-296.

Bledzki, A. K. and Gassan, J. (1999). Compositess reinforced with cellulose based fibres. **Prog. Polym. Sci.** 24: 221-274.

Carpentier, F., Bourbigot, S., Bras, M. L., and Delobel, R. (2000). Rheological investigations in fire retardancy: Application to ethylene-vinyl-acetate copolymer/ magnesium hydroxide/zinc borate formulations. **Polym. Int.** 49: 1216-1221.

Chaigneau, M., and, Le Moan, G. (1982). Toxicity of products resulting from the cold combustion of polypropylene. Comptes Rendus des Seances de l' Academie des Sciences. Serie III. **Sciences de la Vie.** 295: 223-225.

Doan, T. T. L., Gao, S. L., and Madar, E. (2006). Jute/polypropylene composites: Part I. Effect of matrix modification. **Comp. Sci. Tech.** 66: 952-963.

Einsele, U., Koch, W., and Herlinger, H. (1984). Investigations into the development of heat when textiles burn in air. **Melliand Textilber.** 65**:** 200-206.

Frye, R. B., and Zembayashi, M. (1985). Flame retardant thermoplastic compositions. **US Patent 4,536,529.**

Gu, H. (2009). Tensile behaviours of the coir fibre and related composites after NaOH treatment. **Mater. Design.** 30: 3931-3934.

Hendrickson, L and Connole, K. B. (1995). Review of stabilization of polyolefin insulated conductors. I: Theory and factors affecting stability. **Polym. Eng. Sci.** 35: 211-217.

Jang, J. and Lee, E. (2001) Improvement of the flame retardancy of paper sluge/polypropylene composites. **Polym. Test.** 20: 7-13.

Jeencham, R., Suppakarn, N., and Jarukumjorn, K. (2009) Effect of flame retardant on flammability and mechanical properties of polypropylene composites. In **Proceeding of Pure and Applied Chemistry International Conference** 2009. (pp 314-316). Phitsanulok, Thailand: Naresaun University.

Jenssens, M. (1991). Rate of heat release of wood products. **Fire Safety.** 17: 217-238.

Jha, N. K., Misra, A. C., and Bajai, P. (1984). Flame-retardant additives for polypropylene. **Macromol. Sci. Chem.** 24:69-116.

Kozlowski, R. and Wladka-Przybylak, M. (2001). In A.R. Horrocks and D. Price (ed.). **Fire Retardant Materials.** New York: CRC Press.

Le Bras, M., Duquesne, S., Fois, M., Grisel, M., and Poutch, F. (2005). Intumescent polypropylene/flax blends: A preliminary study. **Polym. Degrad. Stab.** 88: 80-84.

Lee, S. Y., Kang, L. A., and Wu, Q. (2008). Thermal, mechanical and morphological properties of polypropylene/clay/wood flour nanocomposites. **Polym. Lett.** 2: 78-87.

Lu., S. Y. and Hamerton, I. (2002). Recent developments in the chemistry of halogen-free flame retardant polymers. **Prog. Polym. Sci.** 27:1661-1712.

Maclaury, M. R. and Holub, F. F. (1981). Flame retardant compositions and coated article. **US Patent 4,273,691.**

Mareri, P., Bastide, S., Binda, N., and Crespy, A. (1998). Mechanical behaviour of polypropylene composites containing fine mineral filler: Effect of filler surface treatment. **Comp. Sci. Tech.** 58:747-752.

Matko, S., Toldy, A., Keszei, S., Anna, P., Bertalan, G., and Marosi, G. (2005). Flame retardancy of biodegradable polymer and biocomposites. **Polym. Dregrad. Stab.** 88: 138-145.

Montezin, F., Lopez Cuesta, J. M., Crespy, A., and Georlette, P. (1997). Flame retardant and mechanical properties of a copolymer PP/PE containing brominated compounds/antimony trioxide blends and magnesium hydroxide or talc. **Fire. Mater.** 21: 245-252.

Obi, R. K., Uma, M. C., Jeevan, P. R. D., and Varada, R. A. (2009). Thermal properties of Napier grass fibers**. Mater. Lett.** 63: 2390-2392.

Paul, S. A., Boudenne, A., Ibos, L., Candau, Y., Joseph, K., and Thomas, S. (2008) Effect of fiber loading and chemical treatments on thermophysical properties of banana fiber/polypropylene commingled composite materials. **Compos. Part A.** 39: 1582-1588.

Rana, A. K., Mandal, A., Mitra, B. C., Jacobson, R., Rowell, R., and Banerjee, A. N. (1998). Short jute fiber-reinforced polypropylene composites: Effect of compatibilizer. **J. Appl. Polym. Sci.** 69: 329-338.

Rothon, R. (1990). **The Emergence of Magnesium Hydroxide as a Fire Retardant Additive**. London: Elsevier.

Sain, M., Park, S. H., Suhara, F., and Law, S. (2004). Fame retardant and mechanical properties of natural fibre-PP composites containing magnesium hydroxide. **Polym. Dregrad. Stab.** 83: 363-367.

Samyn, F., Bourbigot, S., Duquesne, S., and Delobel, R. (2007). Effect of zinc borate on the thermal degradation of ammonium polyphosphate. **Therm. Acta.** 456: 134-144.

Schartel, B., Braun, U., Schwarz, U., and Reinmann, S. (2003). Fire retardancy of polypropylene/flax blends. **Polymer.** 44: 6241-6250.

Schwarz, U., Pflug, G., and Reinemann, S. (2002). Polypropylen-Flachs-Compounds. **Kunststt. Plast. Eur.** 92: 93-94.

Saheb, D. N. and Jog, J. P. (1999). Natural fiber polymer composites: a review. **Adv. Polym. Technol.** 18: 351-363.

Sen, A. K., Mukherjee, B., and Bhowmick, K. (1991). Preparation and characterization of low halogen and nonhalogen fire resistant low smoke (FRLS) cable sheathing compound from blends of functionalized polyolefins and PVC. **J. Appl. Polym. Sci.** 43:1674-1684.

Shehata, A. B. (2004). A new cobalt chelate as flame retardant for polypropylene filled with magnesium hydroxide. **Polym. Degrad. Stab.** 85:577-582.

Suppakarn, N. and Jarukumjorn, K. (2009). Mechanical properties and flammability of sisal/PP composites: Effect of flame retardant type and content. **Compos. Part B.** 40: 613-618.

Suppakarn, N., Jarukumjorn, K., and Tananimit, S. (2008). Effect of flame retardant on mechanical properties and flammability of sisal/PP composites. **Adv. Mater. Res.** 47-50: 403-406.

Wang, Z. Y., Liu, Y., and Wang, Q. (2010). Flame retardant polyoxymethylene with aluminium hydroxide/melamine/novolac resin synergistic system. **Polym. Degrad. Stab.** 95: 945-954.

Yang, H. S., Kim, H. J., Park, H. J., Lee B. J., and Hwang, T. S. (2007). Effect of compatibilizing agents on rice-husk flour reinforced polypropylene composites. **Compstruct.** 77: 45-55.

Zanetti, M., Camino, G., and Wilkie, C. A. (2002). Fire retardant halogen-antimony-clay synergism in polypropylene layered silicate nanocomposites. **Chem. Mater.** 14: 189-193.

Zhang, S. and Horrocks, A. R. (2003). A review of flame retardant polypropylene fibres. **Prog. Polym. Sci.** 28: 1517-1538.

Zhou, S., Song, L., Wang, Z., Hu, Y., and Xing, W. (2008). Flame retardation and char formation mechanism of intumescent flame retarded polypropylene composites containing melamine phosphate and pentaerythritol phosphate. **Polym. Degrad. Stab**. 93: 1793-1806.

APPENDIX A

COST CALCULATION FOR SISAL FIBER/ POLYPROPYLENE COMPOSITES

Cost analysis of sisal fiber/polypropylene composites containing flame retardants

1. Cost of material for preparing sisal fiber/polypropylene composites containing flame retardants

Untreated sisal fiber was used as a reinforcing filler for PP. APP and Zb were used as flame retardants. MAPP was used a compatibilizer. Total cost of materials for preparing PP/UT/40APP/3MAPP and PP/UT/30APP/10Zb/3MAPP composites based on 1 kg of PP are shown in Table A.1 and A.2 respectively.

Table A.1 Cost of materials for preparing PP/UT/40APP/3MAPP composite based on 1 kg of PP.

Materials	Contents (kg)	Price/Unit (baht/kg)	Price (baht)
PP	1.00	50.00	50.00
UT	0.30	120.00*	36.00
APP	0.40	800.00	320.00
MAPP	0.03	250.00	7.50
Total	1.73		413.50

Remark : * Expense for fiber cutting = 800 baht/kg

Table A.2 Cost of material for preparing PP/UT/30APP/10Zb/3MAPP composite based on 1 kg of PP.

Materials	**Contents (kg)**	**Price/Unit (baht/kg)**	**Price (baht)**
PP	1.00	50.00	50.00
UT	0.30	120.00*	36.00
APP	0.30	800.00	240.00
Zb	0.10	80.00	8.00
MAPP	0.03	250.00	7.50
Total	1.73		341.50

Remark : * Expense for fiber cutting = 800 baht/kg

2. Cost analysis summary

Cost analysis summary of PP/UT/40APP/3MAPP and PP/UT/30APP/10Zb/3MAPP composites are shown in Table A.3. Using a combination of 30 phr of APP and 10 phr of Zb resulted in a cost reduction (17.41%) when compared to PP/UT/40APP/3MAPP composite. In addition, adding combination of 30 phr of APP and 10 phr of Zb into sisal fiber/PP composite not only reduced the cost of the composites but also gave comparable mechanical properties and flame retardancy of PP/UT/40APP/3MAPP composite.

Table A.3 Cost comparison for PP/UT/40APP/3MAPP composite versus PP/UT/30APP/10Zb/3MAPP composite.

Designation	**Contents (kg)**	**Price (baht)**
PP/UT/40APP/3MAPP	1.73	413.5
PP/UT/30APP/10Zb/3MAPP	1.73	341.5

APPENDIX B

LIST OF PUBLICATIONS

List of publication

Jeencham, R., Suppakarn., N, and Jarukumjorn., K. (2009). Effect of flame retardant on flame retardancy and mechanical properties of glass fiber/polypropylene composites. In **Proceeding of Advances in Materials and Processing Technologies** 2009. (p 86). Kuala Lumpur, Malaysia.

Jeencham, R., Suppakarn., N, and Jarukumjorn., K. (2009). Effect of flame retardant on flammability and mechanical properties of polypropylene composites. In **Proceeding of Pure and Applied Chemistry International Conference** 2009. (pp 314-316). Phitsanulok, Thailand.

Jeencham, R., Suppakarn., N, and Jarukumjorn., K. (2009). Effect of ammonium polyphosphate on flammability and mechanical properties of polypropylene/ sisal fiber composites. In **Proceeding of the 11th Pacific Polymer Conference** 2009. (p 53). Cairns, Australia.

Jeencham, R., Suppakarn., N, and Jarukumjorn., K. (2010). Flammability and mechanical properties of sisal fiber/polypropylene composites: Effect of combination of flame retardants. **Adv. Mater. Res.** 123-125: 85-88.

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EFFECT OF FLAME RETARDANT ON FLAME RETARDANCY AND MECHANICAL PROPERTIES OF GLASS FIBER/POLYPROPYLENE COMPOSITES

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ABSTRACT

Composites based on polypropylene and glass fiber were prepared by melt mixing. The effect of magnesium hydroxide as a flame retardant on flammability and thermal behavior of glass fiber/polypropylene composites was studied. Ratio of glass fiber to magnesium hydroxide in each composite sample was varied. Maleic anhydride grafted polypropylene (MAPP) was used to improve the interfacial adhesion between polypropylene and fillers. Flammability and thermal behavior of the composites were examined using a horizontal burning test and a thermogravimetric analyzer, respectively. Morphology and mechanical properties of the composites were also investigated. Magnesium hydroxide reduced the flammability while improved thermal decomposition temperature of the polypropylene composites. However, magnesium hydroxide showed a negative impact on the tensile strength of the polypropylene composites.

KEYWORDS: (Flammability, Mechanical properties, Glass fiber, Magnesium hydroxide)

EFFECT OF FLAME RETARDANT ON FLAMMABILITY AND MECHANICAL PROPERTIES OF POLYPROPYLENE COMPOSITES

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Abstract: Polypropylene (PP) is used worldwide for many applications, e.g. housing, wire and cables, electronic devices and automobiles. However, high flammability of PP limits its uses in some areas. Ammonium polyphosphate (APP) is very efficient halogen-free flame retardant mainly used in polyolefins. APP is a non toxic, environmentally friendly additive and it does not generate additional quantities of smoke. In this work, APP as a flame retardant was added in to PP. Flammability of the PP and PP composites were measured using a horizontal burning test. Synergistic effect was also investigated when APP was used in combination with zinc borate (Zb). In addition, tensile and impact properties of the PP and PP composites were examined.

Introduction

Polypropylene (PP) is one of the most popular polymers used in many applications. The advantages of PP are low cost, low density, low processing temperature, easy processibility and corrosion resistance [1]. However, PP is flammable and cause a serious problem in practical uses [2]. Addition of flame retardant is a solution to reduce flammability of PP. Phosphorus compounds e.g. ammonium polyphosphate, pentaerythritol phosphates and melamine phosphate are very efficient halogen-free flame retardant mainly used in polyolefins [3,4]. APP is a non toxic, environmentally friendly flame retardant and it does not generate additional quantities of smoke [5]. The mode of action is based on the decomposition of APP to polyphosphoric acid and ammonia. A charred surface layer is formed from the thermal degradation products of APP and the flame retarded polymer which prevents further flame spread [6]. Moreover, addition of synergistic agent e.g. aluminum hydroxide and zinc borate into flame retardants could improve flame retardancy and mechanical properties of polymer [7-11]. Previous studies have demonstrated that there are major advantages in using a combination of zinc borate with halogen free flame retardants in several kinds of polymers [8-10]. It can be mentioned they act as smoke suppressant, afterglow suppressant, corrosion inhibitor, anti tracking agent and synergistic agent [9]. Serge et al. [10] found that zinc borate may act as a synergistic agent and smoke suppressant in ethylene vinyl acetate based formulations flame retardants such as aluminium trihydroxide or magnesium hydroxide. Pi et al. [11] reported that combination of zinc borate with aluminum trihydrate remarkably enhanced flame retardant properties and increased impact and yield strengths and elongation at break of polyvinyl chloride.

The objective of this research was to investigate the effect of ammonium polyphosphate on the flammability and mechanical properties of PP. In addition, effect of zinc borate in combination with ammonium polyphosphate on the properties of PP was also studied.

Materials and Methods

Materials: Isotactic PP (700J) was supplied by Thai Polypropylene Co., Ltd. Maleic anhydride grafted polypropylene (MAPP, Fusabond® P MZ 109D, DuPont) was used as a compatibilizer. Ammonium polyphosphate (Exolit AP 766, Clariant) and zinc borate (Firebrake®ZB) were use as flame retardants.

Preparation of composites: The composites were prepared using an internal mixer (Hakke Rheomix). The rotor speed was 50 rpm and mixing temperature was 170°C. The total mixing time was 13 min. The test specimens were molded by an injection molding (Chuan Lih Fa, CLF 80T). Compositions of composites and their designation are shown in Table 1.

Flammability tests: Flammability of each composite was studied by a horizontal burning test according to ASTM D635. The specimen was held horizontally and a flame was applied to one end of the specimen. The time for the flame to reach from the first reference mark (25 mm from the end) to the second reference mark, which is at 100 mm from the end, was measured. Five specimens from each composite were tested. Then, burning rates of the composites were calculated.

Mechanical tests: Tensile properties of PP and PP composites were tested according to ASTM D638. using Instron universal testing machine (model 5569) with load cell of 5 kN and a crosshead speed of 50 mm/min. Izod impact tests were performed on unnotched PP composites according to ASTM D256.

Table 1: Compositions and designation of materials used

Designation	PP [a](phr)	APP [a](phr)	Zb [a](phr)	MAPP [a](phr)
PP	100	-	-	-
PP/10APP	100	10	-	3
PP/20APP	100	20	-	3
PP/30APP	100	30	-	3
PP/10APP/5Zb	100	10	5	3
PP/10APP/10Zb	100	10	10	3
PP/10Zb	100	-	10	3

[a] parts per hundred of polypropylene

Results and Discussion

Table 2: Horizontal burning rate of PP and PP composites

Designation	Horizontal Burning Rate (mm/min)
PP	20.99 ± 0.98
PP/10APP	15.66 ± 0.44
PP/20APP	6.96 ± 1.58
PP/30APP	No burning
PP/10APP/5Zb	16.85 ± 0.63
PP/10APP/10Zb	22.75 ± 1.16
PP/10Zb	20.66 ± 0.76

Burning rate of PP and PP composites measured by horizontal burning test are listed in Table 2. The burning rate of PP decreased with increasing APP contents. PP filled with 30 phr of APP did not burn under the testing condition. Since APP is quite expensive, zinc borate was selected to investigate the synergistic effect on flammability of PP. However, combination of APP and zinc borate gave a higher burning rate compared to PP filled with APP. This suggested that zinc borate showed a negative effect on flame retardant properties when used with APP.

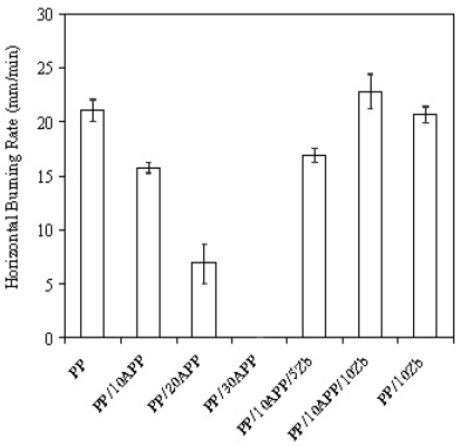

Figure 1. Horizontal burning rate of PP and PP composites

Mechanical properties of PP and PP composites are reported in Table 3. No significant change of tensile modulus was found when APP or zinc borate was added into PP. However, all PP composites exhibited higher tensile strength compared to PP. This indicated that flame retardants acted as fillers for PP. In addition, adding MAPP into PP composites promoted the adhesion between PP and flame retardants. There was an increase in tensile strength of PP/10APP with the addition of zinc borate. PP showed the highest impact strength. However, adding APP or zinc borate into PP yielded negative impact on the impact strength of PP. Impact strength further decreased with increasing APP contents. It was interesting to note that incorporation of 10 phr zinc borate into PP/10APP significantly improved impact strength. This indicated that the combination of APP and zinc borate exhibited the synergistic effect on tensile and impact strength of PP.

Table 3: Mechanical properties of PP and PP composites

Designation	Tensile Modulus (GPa)	Tensile Strength (MPa)	Impact Strength (kJ/m^2)
PP	1.02 ± 0.08	16.95 ± 1.68	69.26 ± 0.28
PP/10APP	1.16 ± 0.04	26.65 ± 0.38	33.41 ± 0.93
PP/20APP	1.28 ± 1.28	26.16 ± 0.43	24.23 ± 0.76
PP/30APP	1.35 ± 0.11	24.77 ± 1.24	19.70 ± 0.57
PP/10APP/5Zb	1.18 ± 0.05	28.28 ± 0.60	32.61 ± 1.32
PP/10APP/10Zb	1.02 ± 0.06	32.27 ± 0.64	58.23 ± 1.23
PP/10Zb	1.18 ± 0.01	22.90 ± 3.52	32.78 ± 0.64

Conclusions

The addition of ammonium polyphosphate led to an improvement of fire retardancy of PP. With increasing APP contents the flammability of PP decreased. Antagonism effect on flame retardant properties was observed when APP was used in combination with zinc borate. All PP composites showed better tensile strength compared to that of PP. Tensile modulus were not much affected by the incorporation of flame retardants. When APP was used in combination with zinc borate the impact and tensile strength of PP composites were increased.

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References

[1] C.H. Hong, Y.B. Lee and T.W. Hwang, *J. Ind. Eng.* **11** (2005), pp. 76-82.

[2] J. Green In: M Lewin, S.M. Atlas and E.M. Peace (Eds.), *Flame Retardant Polymeric Materials*, Plenum Press, New York (1982), pp. 97-153.

[3] G. Camino and L. Trossarelli, *Polym. Degrad. Stab.* **7** (1984), pp 203–221.

[4] G. Bertelli, L. Costa and R. Locatelli, *Polym. Degrad. Stab.* **20** (1988), pp 295-314.

[5] H.C. Ashton In: M. Xanthos (Eds.), *Functional Fillers for Plastics*, Wiley-VCH, Weinheim (2005), pp 305.

[6] E. Schmitt, *Plast. Addit. Comp.* **9** (2007), pp. 26-30.

[7] S.A. Ahmad Ramazani, A. Rahimi and S. Radman, *Mater. Design.* **29** (2008), pp. 1051-1056.

[8] G. Fontaine, S. Bourbigot and S. Duquesne, *Polym. Degrad. Stab.* **93** (2008), pp. 68-76.

[9] F. Carpentier, S. Bourbigot and R. Delobel, *Polym. Inter.* **49** (2000), pp. 1216 – 1221.

[10] B. Serge, L.B. Michel and K. Shenc, *Polym. Degrad. Stab.* **64** (1999), pp. 419-425.

[11] H. Pi, S. Guo and Y. Ning , *J. Appl. Polym. Sci.* **89** (2003), pp. 753-762.

Effect of Ammonium Polyphosphate on Flammability and Mechanical Properties of Polypropylene/Sisal Fiber Composites

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Introduction

Nowadays, polypropylene/natural fiber composites are used worldwide for many applications, *e.g.* automotive components, building materials, and electronic devices. Various types of natural fibers such as flax, hemp, jute, and sisal are used as fillers for thermoplastic composites since they are low cost, biodegradability, renewability, and non toxic by products. Among those types of natural fibers, sisal fiber is one of the interesting plants for reinforcing polypropylene (PP) due to its high tensile strength and stiffness.[1] Moreover, sisal fiber has grown in a wide range of areas in Thailand. However, the compatibility between PP and sisal fiber is poor. This leads to a decrease in mechanical properties of the composites. Maleic anhydride grafted polypropylene (MAPP) has been known to be an effective compatibilizer for the PP/natural fiber composites.[2] Since PP and sisal fiber are flammable, this limits their applications in automotive and electric industries. Addition of flame retardants is a solution to reduce flammability of polymers. Ammonium polyphosphate (APP) is well known as flame retardant for polymers because it is non toxic, environmentally friendly and being a smoke suppressant.[3] The degradation mechanism of APP can be explained as follows. First at about 250 °C, APP decomposes to yield polyphosphoric acid and evolving ammonia. Between 360 and 420 °C, the polyphosphoric acid reacts with the carbonaceous compound to form the char as insulating protective layer.[4] In a previous study, Matko et al.[5] found that APP decreased flammability of PP/wood flakes composites. The objective of this study is to investigate the effect of APP on the flammability and mechanical properties of PP/sisal fiber composites.

Experimental

A commercial grade of isotactic PP (700J) was supplied by Thai Polypropylene Co., Ltd. Sisal fiber with an average length of 2 mm was purchased from Sisal-Handicraft OTOP Group, Tambon Ban Kao, Amphur Dan Khun Thod, Nakhon Ratchasima, Thailand. The composites were prepared using an internal mixer (Hakke Rheomix, 3000p). Sisal fiber content was 30 phr. Maleic anhydride grafted polypropylene (MAPP, Fusabond® P MZ 109D, DuPont) loading was 3 phr. Ammonium polyphosphate (APP, Exolit AP 765, Clariant) contents were varied as 10, 20, 30 phr. The rotor speed was 50 rpm and mixing temperature was 170°C. The total mixing time was 13 min. The test specimens were molded by an injection molding. Flammability of the composites was examined using a horizontal burning test. Mechanical properties of the composites were also investigated.

Results and Discussion

Burning rates of PP and PP composites measured by horizontal burning tests are shown in Table 1. PP/sisal fiber composites showed the highest burning rate compared to that of the PP and other composites. The burning rate of PP/sisal fiber composites decreased with increasing APP content. This indicated that APP enhanced flame retardancy of PP/sisal fiber composites.

Generally, flame retardants are added to polymers to reduce the flammability of the systems. However, they can adversely affect the mechanical properties of the polymer as found by Sain et al.[6] They observed that the addition of magnesium hydroxide ($Mg(OH)_2$) showed a negative impact on tensile and flexural strength of PP/sawdust and PP/rice husk composites. Additionally, Jang and Lee[7] reported that adding flame retardants, *i.e.* ethylenebispentabromodiphenylethane (Saytex8010) and triphenyphosphate (TPP) decreased flexural strength of PP/paper sludge composites. Their results were in contrast to ours.

Mechanical properties of PP and PP composites are listed in Table 2. PP/sisal fiber composites exhibited higher tensile strength and modulus than PP. This indicated that sisal fiber is a good reinforcing filler for PP. However, adding sisal fiber decreased impact strength of PP. This is because the filler disturbs matrix continuity and each fiber is a site of stress concentration, which can act as a microcrack initiator.[8] In comparison between PP/sisal fiber composites and PP/sisal fiber composites containing APP, there was no significant change of tensile properties and impact strength. This result implied that APP improved flame retardancy of PP/sisal fiber composites without deterioration of the mechanical properties of PP/sisal fiber composites.

Table 1: Horizontal burning rate of PP and PP composites

Material	Horizontal burning rate (mm/min)
PP	21.13 ± 1.65
PP/Sisal/MAPP	28.11 ± 1.85
PP/Sisal/MAPP/10APP	21.97 ± 1.05
PP/Sisal/MAPP/20APP	18.03 ± 0.54
PP/Sisal/MAPP/30APP	14.37 ± 0.41

Table 2: Mechanical properties of PP and PP composites

Material	Tensile modulus (GPa)	Tensile strength (MPa)	Impact strength (kJ/ m^2)
PP	1.02 ± 0.08	16.95 ± 1.68	72.05 ± 1.43
PP/Sisal/MAPP	2.17 ± 0.03	30.13 ± 0.30	13.72 ± 0.47
PP/Sisal/MAPP/10APP	2.24 ± 0.06	29.65 ± 0.33	13.77 ± 0.43
PP/Sisal/MAPP/20APP	2.27 ± 0.29	28.62 ± 0.13	11.13 ± 0.48
PP/Sisal/MAPP/30APP	2.32 ± 0.04	27.58 ± 0.24	10.91 ± 0.50

Conclusions

The addition of ammonium polyphosphate led to an improvement in fire retardancy of PP/sisal fiber composites. The flammability of PP/sisal fiber composites decreased with increasing APP content. Tensile properties and impact strength of PP/sisal fiber composites were not much affected by the incorporation of flame retardant.

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References

[1] Bledzki, A. K. and Gassan, J. *Prog. Polym. Sci.* **1999**, *24*, 221-274.
[2] Van den Oever, M., and Peijs, T. *Appl. Sci. Manuf.* **1998**, 29, 227-239.
[3] Ashton, H.C. In: Xanthos, M. (Eds.), *Functional Fillers for Plastics*, Willey, Weinheim (2005), pp 305.
[4] Marchal, A., Delobel, R., Le Bras, M., Leroy, J.M., and Price, D. *Polym. Degrad. Stab.* **1994**, *44*, 263-272.
[5] Matko, Sz., Toldy, A., Keszei, S., Anna, P., Bertalan, Gy., and Marosi, Gy. *Polym. Degrad. Stab.* **2005**, *88*, 138-145.
[6] Sain, M., Park, S.H., Suhara, F., and Law, S. *Polym. Degrad. Stab.* **2004**, *83*, 363-367.
[7] Jang, J. and Lee, E. *Polym. Test.* **2001**, *20*, 7-13.
[8] Mareri, P., Bastide, S., Binda, N., and Crespy, A. *Compos. Sci. Technol.* **1998**, *58*, 747-752.

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Flammability and Mechanical Properties of Sisal Fiber/Polypropylene Composites: Effect of Combination of Flame Retardants

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Keywords: Flammability, Mechanical properties, Sisal fiber, Polypropylene, Ammonium polyphosphate, Zinc borate

Abstract. Ammonium polyphosphate (APP) and zinc borate (Zb), as flame retardants were incorporated into sisal fiber/polypropylene (PP) composites. Ratios of APP to Zb were varied. Maleic anhydride grafted polypropylene (MAPP) was used to improve the interfacial adhesion between polypropylene and fillers. Flammability of the composites was examined using a horizontal burning test, a vertical burning test, and a limiting oxygen index test. Morphology and mechanical properties of the composites were also investigated. The composite containing 30 phr of APP and 10 phr of Zb exhibited better flame retardancy than the composites containing other ratios of APP to Zb. The combination of APP and Zb insignificantly changed mechanical properties of the composites. In addition, SEM micrographs of the composites revealed good distribution of flame retardants and sisal fiber in PP matrix.

Introduction

Nowadays, natural fiber/PP composites are used worldwide for many applications, e.g. automotive components, building materials, and electronic devices. Sisal fiber is one of the interesting plants for reinforcing PP due to its high tensile strength and stiffness [1]. However, the compatibility between PP and sisal fiber is poor leading to a decrease in mechanical properties of the composites. Maleic anhydride grafted polypropylene (MAPP) has been known to be an effective compatibilizer for the natural fiber/PP composites [2]. In addition, PP and sisal fiber are flammable. This limits their applications in automotive and electric industries. Addition of flame retardants is a solution to reduce flammability of polymers. Ammonium polyphosphate (APP) is well known as a flame retardant for polymers because it is nontoxic, environmentally friendly and being a smoke suppressant [3]. At about 250 °C, APP decomposes to yield polyphosphoric acid and evolving ammonia. Between 360 and 420 °C, the polyphosphoric acid reacts with the carbonaceous compound to form the char as insulating protective layer [4]. Matko et al. [5] found that APP decreased flammability of wood flakes/PP composites. Moreover, many researchers have reported that a combination of two types of flame retardants exhibited the synergistic effect on flame retardancy and mechanical properties of polymer [4,6]. Zinc borate (Zb) is one of the flame retardant to use in combination with halogen free flame retardants in polymers resulting in the polymers with enhanced flame retardancy and mechanical properties [6]. Zb starts to decompose endothermically at about 360 °C and releases water [4].

The objective of this study is to investigate the effect of Zb in combination with APP on the flammability and mechanical properties of sisal fiber/PP composites.

Experimental

A commercial grade isotactic PP (700J) was supplied by Thai Polypropylene Co., Ltd. Sisal fibers were purchased from Sisal-Handicraft OTOP Group, Nakhon Ratchasima, Thailand. The fibers were cut into an approximate length of 2 mm then dried in an oven at 60°C overnight. The composites were prepared using an internal mixer (Hakke Rheomix, 3000p). Sisal fiber content was 30 phr. MAPP (Fusabond® P MZ 109D, DuPont) content was 3 phr. APP (Exolit AP 765, average diameter of 8 μm) was supplied from Clariant Chemical (Thailand), Co., Ltd. Zb (Firebrake®ZB, average diameter of 9 μm) was pherchased from Global Connections Public Co., Ltd. The rotor speed was 50 rpm and the mixing temperature was 170°C. The total mixing time was 13 min. The test specimens were molded by an injection molding machine (Chuan Lih Fa, CLF 80T). Designation and composition of PP composites are shown in Table 1. Flammability of the composites was examined using a horizontal burning test, a vertical burning test, and a limiting oxygen index (LOI) test. Morphologies, tensile properties, and impact strength of the composites were also investigated.

Table 1: Designation and composition of PP composites

Designation	PP [phr]	Sisal fiber [phr]	APP [phr]	Zb [phr]	MAPP [phr]
PP/Sisal	100	30	-	-	-
PP/Sisal/40APP	100	30	40	-	3
PP/Sisal/30APP/10Zb	100	30	30	10	3
PP/Sisal/20APP/20Zb	100	30	20	20	3
PP/Sisal/10APP/30Zb	100	30	10	30	3
PP/Sisal/40Zb	100	30	-	40	3

Results and Discussion

Horizontal burning rate, vertical burning range, and LOI of PP composites are shown in Table 2. PP/Sisal composites showed the highest burning rate among all composites. PP/Sisal/40APP and PP/Sisal/30APP/10Zb composites did not burn under the horizontal test condition and gave afterflame time less than 10 s. These composites were classified as V-0. In addition, they showed higher LOI than other composites. Adding 40 phr of Zb and the combination of APP and Zb (>10 phr) into the PP/Sisal composites slightly decreased the burning rate of the composites. For vertical burning test, PP/Sisal, PP/Sisal/20APP/20Zb, PP/Sisal/10APP/30Zb, and PP/Sisal/40Zb showed complete combustion (NC). PP/Sisal composite showed the lowest LOI. From results of the flammability tests, this suggested that incorporating 40 phr of APP and combination of 30 phr of APP and 10 phr of Zb into PP/Sisal composite enhanced flame retardancy of the composites. Samyn et al. [4] found that adding combination of APP and Zb into PP resulted in a synergistic effect of two flame retardants. This was believed to occur by a reaction to produce zinc pyrophosphate ($Zn_2P_2O_7$) under high temperature of the fire environment. The zinc pyrophosphate is believed to serve as an efficient intumescent char which could act as a physical barrier and a glassy cage for polymer chains. However, it was found in this study that adding more than 10 phr of Zb into the composites gave a negative effect on flame retardancy. This was caused by the unbalance of stoichiometry between APP and Zb.

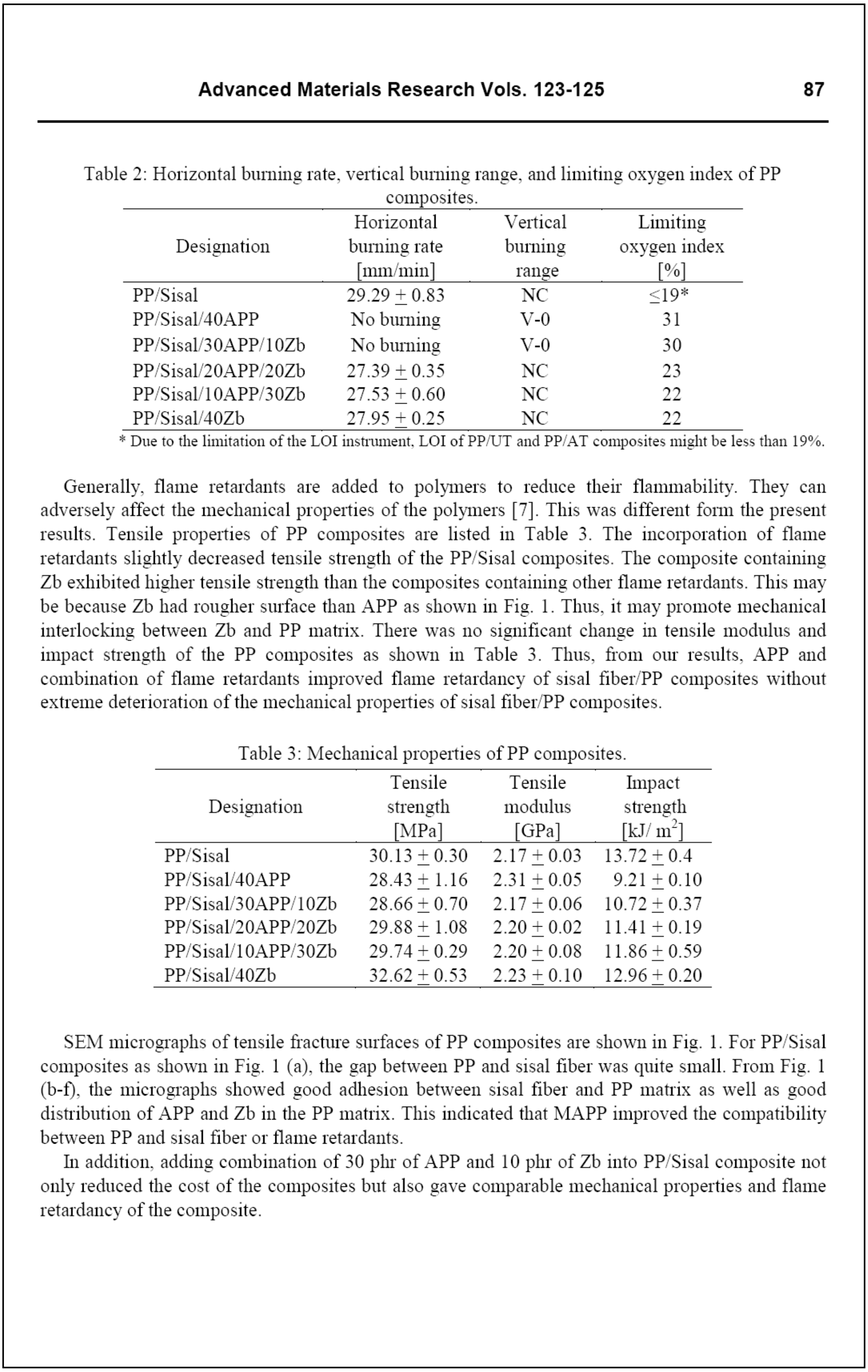


Table 2: Horizontal burning rate, vertical burning range, and limiting oxygen index of PP composites.

Designation	Horizontal burning rate [mm/min]	Vertical burning range	Limiting oxygen index [%]
PP/Sisal	29.29 ± 0.83	NC	$\leq$19*
PP/Sisal/40APP	No burning	V-0	31
PP/Sisal/30APP/10Zb	No burning	V-0	30
PP/Sisal/20APP/20Zb	27.39 ± 0.35	NC	23
PP/Sisal/10APP/30Zb	27.53 ± 0.60	NC	22
PP/Sisal/40Zb	27.95 ± 0.25	NC	22

* Due to the limitation of the LOI instrument, LOI of PP/UT and PP/AT composites might be less than 19%.

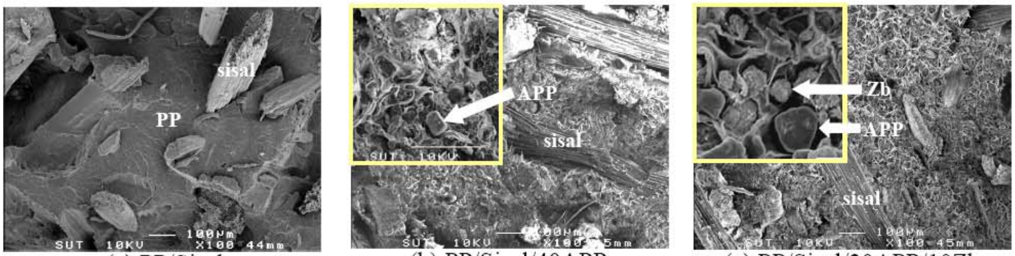
Generally, flame retardants are added to polymers to reduce their flammability. They can adversely affect the mechanical properties of the polymers [7]. This was different form the present results. Tensile properties of PP composites are listed in Table 3. The incorporation of flame retardants slightly decreased tensile strength of the PP/Sisal composites. The composite containing Zb exhibited higher tensile strength than the composites containing other flame retardants. This may be because Zb had rougher surface than APP as shown in Fig. 1. Thus, it may promote mechanical interlocking between Zb and PP matrix. There was no significant change in tensile modulus and impact strength of the PP composites as shown in Table 3. Thus, from our results, APP and combination of flame retardants improved flame retardancy of sisal fiber/PP composites without extreme deterioration of the mechanical properties of sisal fiber/PP composites.

Table 3: Mechanical properties of PP composites.

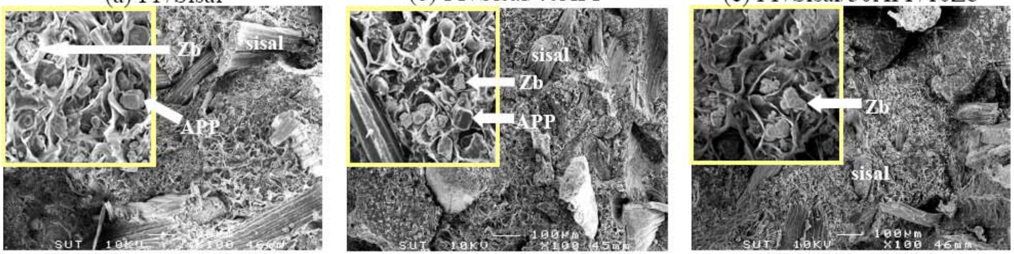
Designation	Tensile strength [MPa]	Tensile modulus [GPa]	Impact strength [kJ/ m^2]
PP/Sisal	30.13 ± 0.30	2.17 ± 0.03	13.72 ± 0.4
PP/Sisal/40APP	28.43 ± 1.16	2.31 ± 0.05	9.21 ± 0.10
PP/Sisal/30APP/10Zb	28.66 ± 0.70	2.17 ± 0.06	10.72 ± 0.37
PP/Sisal/20APP/20Zb	29.88 ± 1.08	2.20 ± 0.02	11.41 ± 0.19
PP/Sisal/10APP/30Zb	29.74 ± 0.29	2.20 ± 0.08	11.86 ± 0.59
PP/Sisal/40Zb	32.62 ± 0.53	2.23 ± 0.10	12.96 ± 0.20

SEM micrographs of tensile fracture surfaces of PP composites are shown in Fig. 1. For PP/Sisal composites as shown in Fig. 1 (a), the gap between PP and sisal fiber was quite small. From Fig. 1 (b-f), the micrographs showed good adhesion between sisal fiber and PP matrix as well as good distribution of APP and Zb in the PP matrix. This indicated that MAPP improved the compatibility between PP and sisal fiber or flame retardants.

In addition, adding combination of 30 phr of APP and 10 phr of Zb into PP/Sisal composite not only reduced the cost of the composites but also gave comparable mechanical properties and flame retardancy of the composite.



(a) PP/Sisal (b) PP/Sisal/40APP (c) PP/Sisal/30APP/10Zb



(d) PP/Sisal/20APP/20Zb (e) PP/Sisal/10APP/30Zb (f) PP/Sisal/40Zb

Figure 1: SEM micrographs of PP composites with combination of flame retardants: (a) PP/Sisal, (b) PP/Sisal/40APP, (c) PP/Sisal/30APP/10Zb, (d) PP/sisal/20APP/20Zb, (e) PP/sisal/10APP/30Zb, (f) PP/sisal/40Zb

Conclusions

The combination of APP and Zb enhanced flame retardancy of sisal fiber/PP composites without deterioration their mechanical properties. In addition, SEM micrographs of the composites revealed good distribution of flame retardants and sisal fiber in PP matrix.

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References

[1] A.K. Bledzki and J. Gassan: Prog. Polym. Sci Vol. 24 (1999), p. 221-274

[2] M. Van den Oever and T. Peijs: Appl. Sci. Manuf Vol. 29 (1998), p. 227-239

[3] H.C. Ashton, in: *Functional Fillers for Plastics*, edtied by M. Xanthos Willey Publications, Weinheim, NY (2005).

[4] F. Samyn, S. Duquesne, and R. Delobel: Therm. Acta Vol. 456 (2007), p. 134-144

[5] Sz. Matko, A. Toldy, S. Keszei, P. Anna, Gy. Bertalan and Gy. Marosi: Polym. Degrad. Stab Vol. 88 (2005), p. 138-145

[6] F. Carpenter, S. Bourbigot, M.L. Bras and R. Delobel: Polym. Degrad. Stab Vol. 49 (2007), p. 1216-1221

[7] M. Sain, S.H. Park, F. Suhara and S. Low: Polym. Degrad. Stab Vol 83 (2004), p. 363-367

BIOGRAPHY

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