

Effect of recycling on properties of rice husk-filled-polypropylene

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Abstract

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This research concerned with the use of rice husk (*Oryza sativa*) as a filler for polypropylene and its recycle ability. Rice husk (200 mesh and 40% by weight) and polypropylene were compounded in a twin-screw extruder and injection moulding technique was applied in order to obtain testing specimens. It was found that tensile, flexural and impact properties as well as % water absorption of the rice husk-filled polypropylene were only slightly dropped upon recycling process, presenting the ability of the rice husk-filled-polypropylene samples to recycle. The increase in melt flow index of the samples was also obtained. In addition, SEM micrographs revealed the reduction of rice husk particle size by the recycling process. Moreover, FTIR spectroscopy and TGA technique were performed for characterizing the filled specimens.

Key words : rice husk, polypropylene, mechanical properties, reuse

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บทคัดย่อ

จุฑารัตน์ ปรัชญาวรรณ และ นิรชา แยมบุญยิ่ง
ผลของการนำกลับมาใช้ใหม่ที่มีต่อสมบัติต่าง ๆ ของพอลิพรอพิลีนที่มีแกลบเป็นสารตัวเติม
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งานวิจัยนี้เกี่ยวข้องกับกระบวนการนำแกลบมาใช้เป็นสารตัวเติมสำหรับพอลิพรอพิลีนและความสามารถในการนำกลับมาใช้ใหม่ของวัสดุนี้ แกลบ (200 เมช ในปริมาณ 40%) และพอลิพรอพิลีนถูกนำมาคอมพาวนในเครื่องอัดรีดชนิดเกลียวหนอนคู่และขึ้นรูปโดยเทคนิคการฉีดขึ้นรูปเพื่อใช้เป็นชิ้นงานสำหรับทดสอบ จากการศึกษาพบว่าสมบัติทางแรงดึง การโค้งงอและความทนทานต่อแรงกระแทกรวมถึงร้อยละการดูดซึมน้ำของพอลิพรอพิลีนที่มีแกลบ เป็นสารตัวเติมมีค่าลดลงเพียงเล็กน้อยเมื่อผ่านกระบวนการนำกลับมาใช้ใหม่ ซึ่งแสดงให้เห็นถึงการนำกลับมาใช้ใหม่ของพอลิพรอพิลีนที่มีแกลบเป็นสารตัวเติม สำหรับชิ้นงานตัวอย่างยังมีดัชนีการหลอมไหลที่เพิ่มขึ้น และภาพถ่ายจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงให้เห็นถึงการลดลงของขนาดของแกลบเนื่องจากการนำกลับมาใช้ใหม่ นอกจากนี้ได้นำเทคนิคของ FTIR และ TGA มาใช้เพื่อตรวจสอบสมบัติของชิ้นงานตัวอย่าง

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Composites based on thermoplastic resins are now becoming popular because of their processing advantages. In recent years, cellulosic fillers have attracted considerable interest for the reinforcement of thermoplastics such as polypropylene and polyethylene, which melt or soften relatively at low temperatures. Among organic filler, wood and cellulose fibres offer a number of benefits as reinforcements for synthetic polymers because of their high specific strength and stiffness, relatively low density, biodegradability and low cost on a unit volume basis (Bledski and Gassan, 1999).

In terms of organic fillers, rice husk obtained from milling process of rice, *Oryza sativa*, one of the major food crops in the world, can be used as an organic filler because of its availability. Disposal of rice husk is a particularly serious problem, which requires special attention due to the large quantities. It is estimated that rice husk of approximately 20% is obtained from the total rice by the milling process. Rice husk roughly contains 35% cellulose, 35% hemicellulose, 20% lignin and 10% ash (94% silica), by dry weight basis (Luh, 1980).

From previous research, rice husk ash, obtained from burning rice husk in an opened area,

was reported to be applied as a filler for rubber such as natural rubber (Costa *et al.*, 2000) and for thermoplastic elastomers, such as, natural rubber/linear low density polyethylene blend (Siriwasdena *et al.*, 2001 and Ismail *et al.*, 2001). In addition, rice husk was also used for thermoplastics i.e. polypropylene (Yang *et al.*, 2004; Prachayawarakorn and Yaemboonying, 2004 and Ishak *et al.*, 2001). The effects of rice husk particle sizes, contents and crosshead speeds on the mechanical properties were investigated (Yang *et al.*, 2004 and Prachayawarakorn and Yaemboonying, 2004). It was found that tensile modulus was improved with increasing filler loadings and the specimen became brittle at higher crosshead speeds. Moreover, hygrothermal aging behaviour of rice husk-filled polypropylene was investigated (Ishak *et al.*, 2001). It was stated that the diffusion coefficient and the maximum moisture content were depended on the filler volume fractions and the immersion temperatures.

From an environmental point of view, the ability to reuse rice husk-filled-polypropylene specimen is of importance, therefore, in this present study, the effect of recycle ability of rice husk-filled polypropylene on properties, i.e. mechanical, morphological and thermal properties was carried

out. In addition, melt flow index and FTIR spectroscopic study were investigated.

Materials and Methods

1. Materials

Commercial polypropylene homopolymer (PP), Profax Z30S from HMC Polymers, Thailand, was used as the polymer matrix. The density of the PP was 0.90 g/cm³. Rice husk, obtained from local rice mill, belongs to the species of *Oryza sativa* of which abundantly grows in Thailand.

2. Preparation of Rice Husk-Filled PP and Recycling Process

The rice husk was ground and screen to 200 mesh size, corresponded to the filler lengths of 75 µm. It should be noted that the amount of the filler of 40% by weight was maintained. The sieved rice husk was firstly dried in an oven at 90°C for 24 hours. Then, the mixture of the ground rice husk and PP were compounded by a co-rotating and intermeshing twin-screw extruder (Axon Plasma) with a screw speed of 25 rpm using the temperature range of 165-190°C. After that, the extrudate was ground and injection-moulded (Weltec Industrial Equipment) into testing specimens, using the temperature range of 170-190°C from the feed section to the metering section. In addition, rice husk-filled polypropylene was recycled for 4 times under the same processing condition in order to study the effect of recycling on properties of rice husk-filled polypropylene.

3. Testing

3.1 FTIR Spectroscopic Study

Samples with the thickness of 10-100 µm were used for FTIR measurements. The FTIR spectra were recorded on a Spectrum 2000 GX spectrometer (Perkin-Elmer) using the KBr disc technique for 16 scans. The resolution was 4 cm⁻¹ and the spectral scanned range was 4000-650 cm⁻¹.

3.2 Thermal Properties

Thermal characterisation of the materials was carried out using thermal gravimetry TGA

(Perkin Elmer, Pyris 1). The specimen was under nitrogen atmosphere using the temperature range of 35-700°C and heating rate of 10°C/min.

3.3 Melt Flow Index Testing

Melt flow index was performed in a melt flow indexer (CREAST 6841) with the temperature of 230°C and the constant weight of 2.16 kg. The extrudate was cut at the time of 30 sec and then it was weighed. The melt flow index was reported as g/10 min.

3.4 Scanning Electron Microscopy

A LEO 1455 VP scanning electron microscope was employed to study the filler dispersion of the rice-husk-filled polypropylene. The filled samples were firstly immersed in liquid N₂, and then broken. After that, the samples were mounted on an aluminium stub and sputter coated with a thin layer of gold to prevent electrical charging during the observation.

3.5 Mechanical Test

All mechanical tests was carried out at the temperature of 23±1°C and relative humidity of 50±5%. Tensile test was conducted according to ASTM D-638. The tensile property measurements (tensile strength, % elongation at yield and Young's modulus) from dumbbell specimens were carried out in a Universal Testing Machine fitted with 5 kN load cell and crosshead speed of 5 mm/min. For flexural property, ASTM D-790 was used as a reference. Three-point bending test was set up in the Universal Testing Machine. The length of support span was 40 mm and compression speed was 5 mm/min using 5 kN load cell. Izod impact type was selected to obtain the specimen impact strength. The notched testing specimens used followed the ASTM D-256. It should be noted that 12 specimens were used for each mechanical test in order to obtain average values of the mechanical properties.

3.6 Water absorption

% water absorption was conducted according to ASTM D-570. The samples were weighed, immersed in water for prolonged period and reweighed every 3 days. It should be noted that 3 samples were used for each measurement.

Results and Discussion

1. FTIR spectroscopy

In general, vibrational frequencies are shown to be characteristic of particular functional groups in molecules. FTIR spectra of polypropylene, rice husk and rice husk-filled-polypropylene specimen are presented in Figure 1. The spectrum of polypropylene in Figure 1(a) presents the wave numbers

in the region of 2600-3100 cm^{-1} and 1300-1400 cm^{-1} , illustrating C-H stretching of aliphatic carbon and CH_2 and/or CH_3 deformation, respectively (Chuai *et al.*, 2001 and Khali *et al.*, 2001). In addition, peak positions obtained from rice husk component in Figure 1(b) are at 3250-3500 cm^{-1} , 1700-1750 cm^{-1} and 1400-1600 cm^{-1} , assigned to O-H stretching, C=O stretching of hemicellulose and lignin and C=C stretching of aromatic carbon,

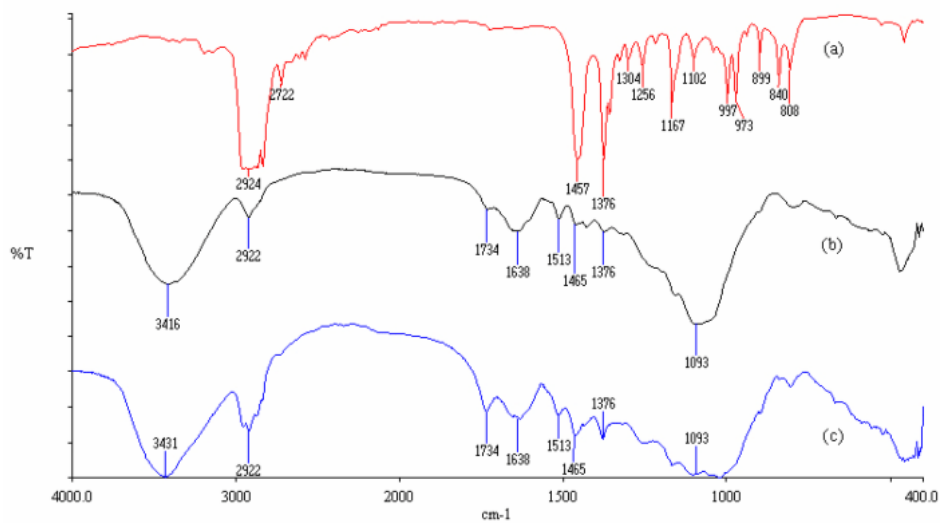


Figure 1. FTIR spectra for (a) polypropylene (b) rice husk and (c) rice husk-filled polypropylene.

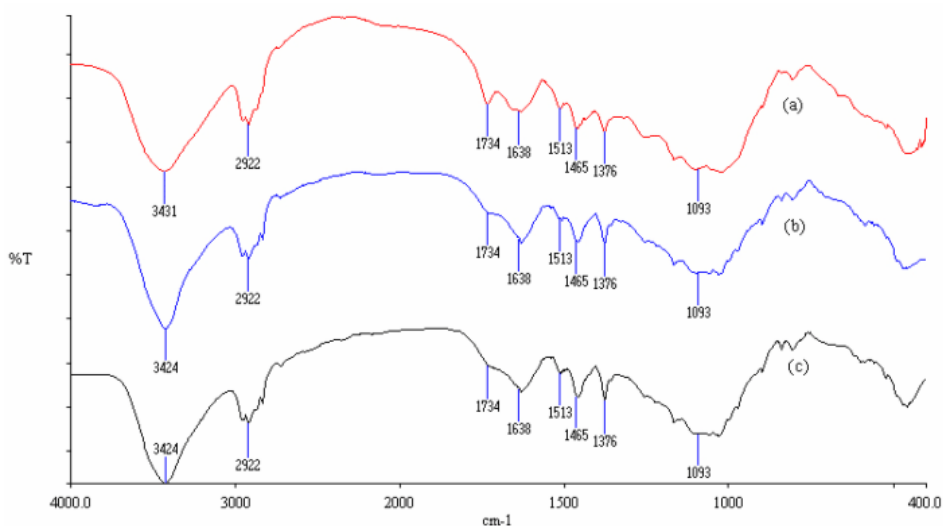


Figure 2. FTIR spectra for rice husk-filled polypropylene upon recycling (a) before recycling (b) the 2nd recycled time and (c) the 4th recycled time.

respectively (Chuai *et al.*, 2001 and Khali *et al.*, 2001). The FTIR spectrum in Figure 1(C) clearly shows the vibrational bands of both compositions from polypropylene and rice husk.

When recycling effect is considered, it is found in Figure 2 that no dramatic change in FTIR spectra can be observed with the 2nd and 4th recycled times, indicating that the major chemical structure of rice husk-filled-polypropylene samples is still unaffected by recycling process. It should be noted that the intensity at 1734 cm⁻¹ seems to be slightly dropped, suggesting that the amount of C=O groups obtained from hemicellulose and lignin of rice husk tends to be decreased with increasing recycled time.

2. Thermal properties

Weight loss of polymer samples as a function of temperature is commonly determined by TGA technique and is an irreversible process due to thermal degradation. The results from TGA thermograms in Figure 3 show that polypropylene possesses thermal degradation temperature of 390-440°C; whereas rice husk presents thermal degradation temperatures in 2 different ranges, i.e. 270-330°C and 330-650°C (Figure 3). The first and second transition temperature ranges correspond to thermal degradation temperatures of cellulose/hemicellulose and lignin, respectively (Mansaray and Ghaly, 1998).

For rice husk-filled polypropylene specimen, it can also be seen in Figure 3 that the initial degradation temperature appears at the tempera-

ture range of 260-370°C. The result implies that rice husk-filled-polypropylene specimen shows lower initial degradation temperature than that of polypropylene due to the cellulose and hemicellulose components in rice husk. Besides, the second degradation temperature is found at 390-480°C due to lignin and polypropylene components. The shift of the second transition temperature toward higher temperature is probably due to some physical interaction between rice husk and polypropylene.

When rice husk-filled-polypropylene samples are reprocessed (Figure 4), TGA thermograms of the specimens present slightly lower thermal degradation temperatures, suggesting that thermal degradation temperature of the compounded specimen is slightly affected by recycling process. Besides, the trace of partial removal of cellulose and hemicellulose is observed from the reduction of % weight loss of the sample upon recycling.

3. Melt Flow Index

Melt flow index values of polypropylene and rice husk-filled-polypropylene specimens are shown in Table 1. It can be seen that melt flow index of polypropylene shows greater value than those of the rice husk-filled-polypropylene specimens. This is because the rice husk particle can interrupt the molten polymer to be extruded from the capillary rheometer. The lower MFI value also indicates greater melt viscosity in the filled samples. Moreover, melt flow index of rice husk-filled polypropylene is slightly increased with the

Table 1. Melt flow index values (MFI) of polypropylene and rice husk-filled polypropylene upon recycling.

Samples	MFI (g/10 min)
Polypropylene	27.4
Polypropylene + Rice husk	10.6
Polypropylene + Rice husk (1 st Recycled)	11.1
Polypropylene + Rice husk (2 nd Recycled)	11.9
Polypropylene + Rice husk (3 rd Recycled)	12.5
Polypropylene + Rice husk (4 th Recycled)	13.9

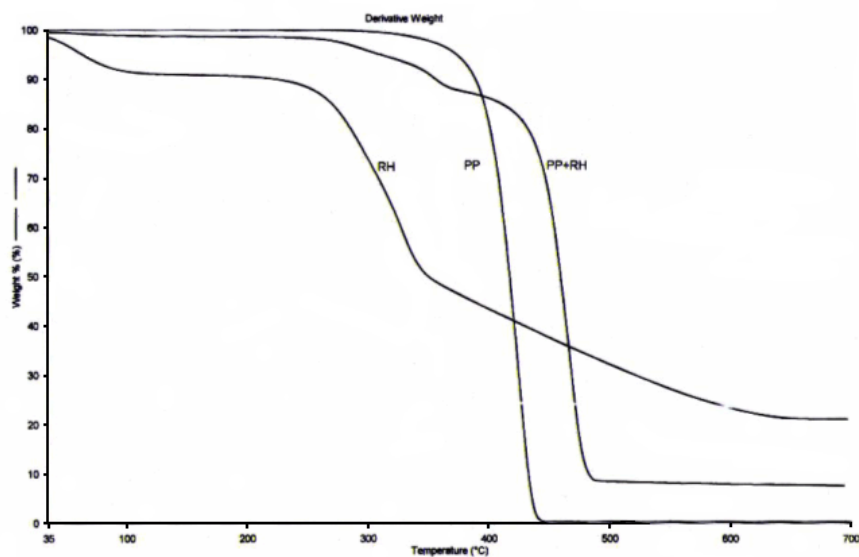


Figure 3. TGA thermograms for polypropylene (PP) rice husk (RH) and rice husk filled polypropylene (PP+RH).

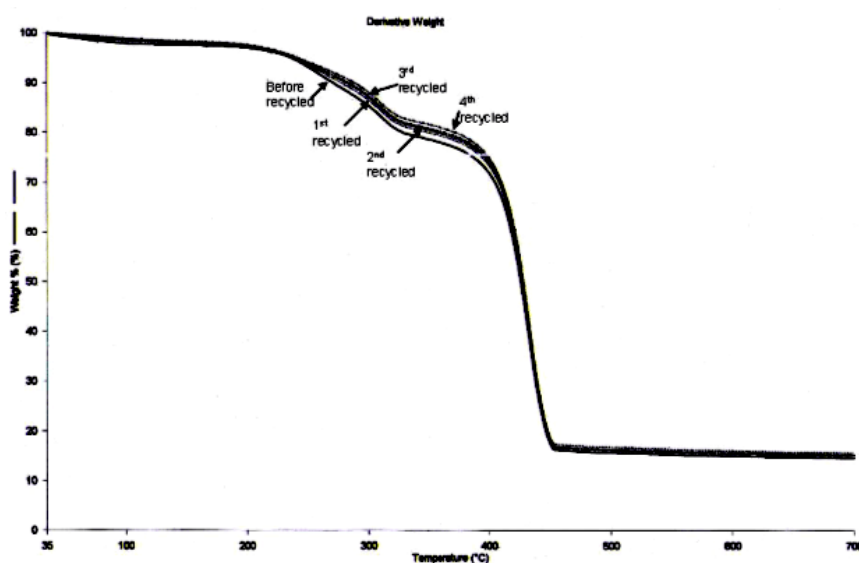


Figure 4. TGA thermograms for rice husk-filled polypropylene upon recycling.

increasing number of recycled times, indicating that the melt viscosity of polypropylene is slightly reduced in the specimen, especially in the 4th recycled time. This is probably due to the breakdown of polypropylene chains upon recycling; however, the effect is not evident.

4. Morphology

SEM produces the clearest images of the surface topography. The morphology of the rice husk-filled specimens is illustrated in Figure 5. It can be seen in Figure 5(a) that rice husk particles dispersed in polypropylene matrix. Some voids in

the interfacial boundary are also observed in the SEM micrographs because of the pull out of the rice husk particle from polypropylene as a result of the difference in polarity between the hydrophilic rice husk and the hydrophobic polypropylene.

When the filled specimens are recycled, it is clearly seen in Figures 5(b)-5(e) that rice husk particle size seems to be reduced upon recycling, leading to better phase compatibility between rice husk and polypropylene. It should be noted that

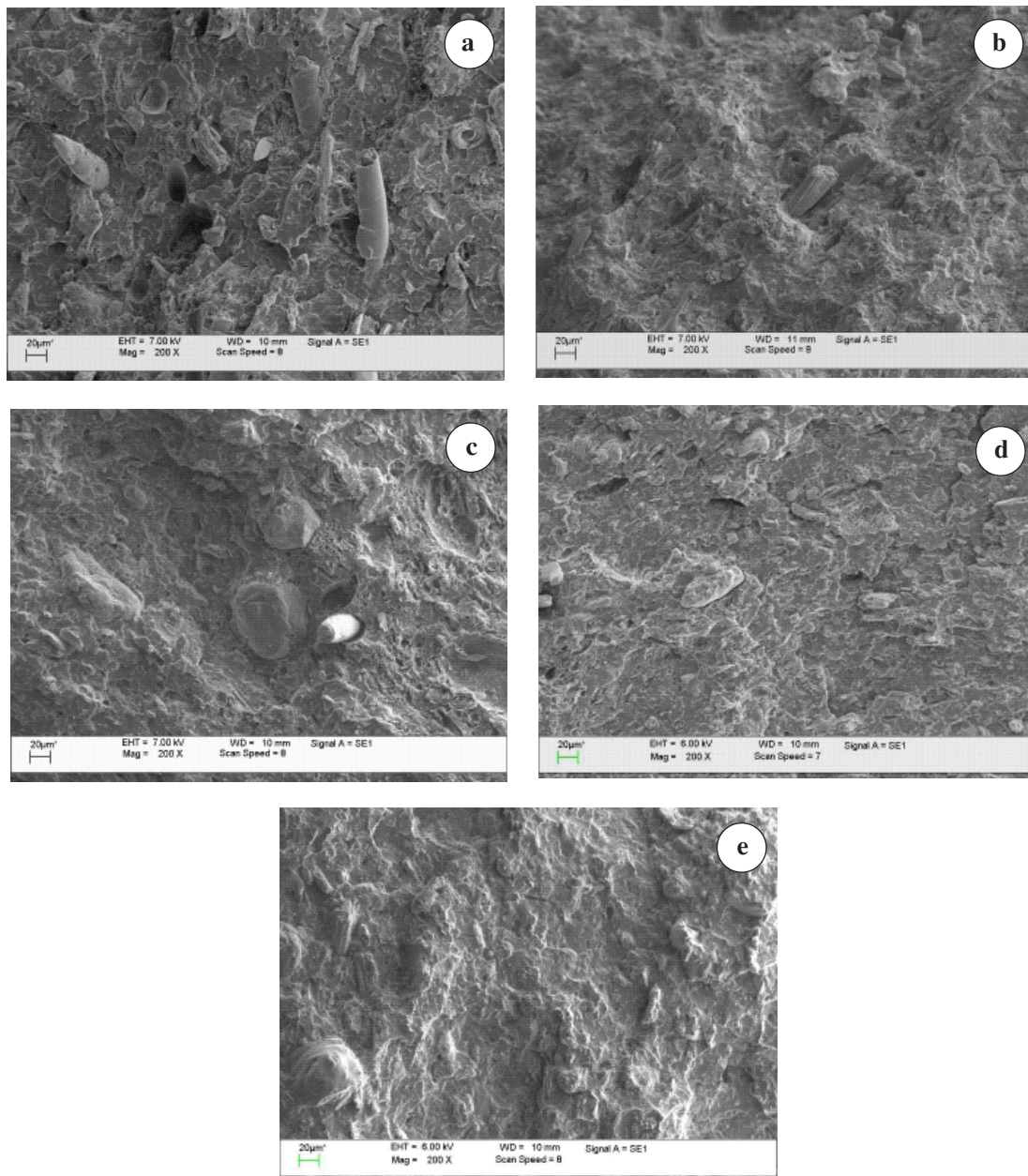


Figure 5. SEM micrographs of rice husk-filled polypropylene upon recycling (a) before recycling (b) the 1st recycled time and (c) the 2nd recycled time (d) the 3rd recycled time and (e) the 4th recycled time.

Table 2. Mechanical properties of rice husk-filled polypropylene upon recycling.

Samples	Tensile strength (MPa)	Elongation at yield (%)	Young's modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (kJ/m ²)
Polypropylene	30.5±0.1	14.9±0.4	421±26	52.6±0.3	1378±61	2.76±0.13
Polypropylene + Rice husk	21.5±0.2	4.7±0.2	709±17	48.7±0.8	2057±63	3.17±0.07
Polypropylene + Rice husk (1 st Recycled)	20.5±0.3	4.8±0.3	718±30	47.0±1.2	2053±67	3.04±0.18
Polypropylene + Rice husk (2 nd Recycled)	20.5±0.6	5.3±0.4	716±19	46.8±1.5	2001±57	2.88±0.13
Polypropylene + Rice husk (3 rd Recycled)	20.6±0.5	5.4±0.4	687±22	45.9±1.1	1954±68	2.82±0.14
Polypropylene + Rice husk (4 th Recycled)	20.3±0.4	5.9±0.3	636±19	43.4±0.9	1832±71	2.61±0.10

the decline in rice husk particle size of the recycling sample, resulting in the greater ability of polypropylene to flow, confirms the increment in melt flow index results.

5. Mechanical Testing

When rice husk is incorporated into polypropylene, it can be seen in Table 2 that tensile strength, % elongation at yield and flexural strength are slightly dropped due to the immiscibility between rice husk and polypropylene phases, causing voids or weak points inside the specimens. On the other hand, because of the greater stiffness of rice husk than that of polypropylene, this brings about the improvement in specimen Young's modulus and flexural modulus that determine stiffness of the specimen. For impact strength, the addition of rice husk into polypropylene matrix can increase impact strength of the sample since rice husk can absorb and transfer impact force.

The mechanical properties i.e. tensile, flexural and impact properties of rice husk-filled polypropylene with the numbers of recycled times is also shown in Table 2. It is found that tensile strength, Young's modulus, flexural strength, flexural modulus and impact strength are found to be slightly decreased, whereas % elongation at yield seems to be slightly extended when the recycled time is increased. The effect is more pronounced with the 4th recycled time. In general, mechanical behaviour of a polymer is a function of its microstructure or morphology. The drop in the sample mechanical properties is because the specimens experience repeated thermal processes, leading to the deterioration of rice husk component as seen from FTIR spectra, TGA thermograms and SEM micrographs. Nevertheless, % change in mechanical properties presented in Table 3, is approximately in the range of 5-25%, showing the ability of the rice husk-filled-polypropylene

Table 3. % difference in mechanical properties of rice husk-filled-polypropylene specimens comparing between before recycling and the 4th recycled time.

Mechanical properties	% alteration
Tensile strength	-5.6
% Elongation at yield	+25.5
Young's modulus	-10.3
Flexural strength	-10.9
Flexural modulus	-10.9
Impact strength	-17.7

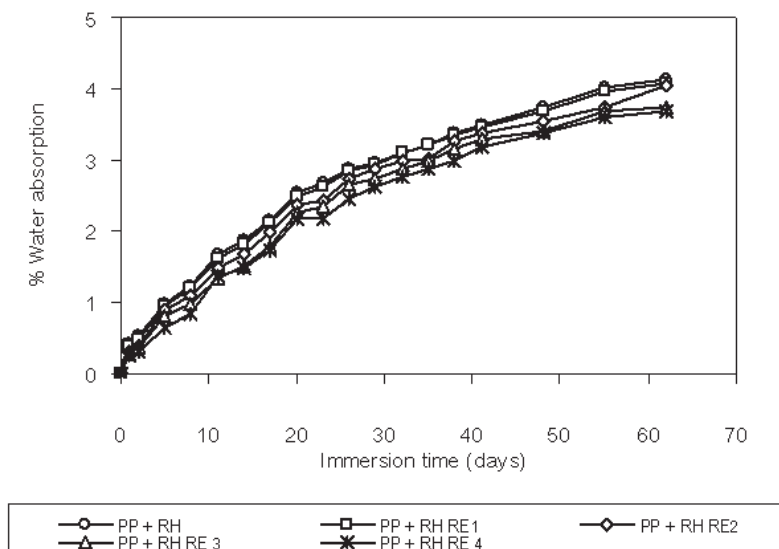


Figure 6. % water absorption rice husk-filled polypropylene with water immersion time upon recycling.

samples to be reused.

6. Water absorption

Generally, polypropylene hardly absorbs water due to its hydrophobic structure; however, rice husk can absorb water significantly because of its hydrophilic characteristics. Rice husk-filled-polypropylene specimens can absorb water by three different boundaries, i.e. lumen and cell wall of rice husk, and finally the interfacial area between rice husk and polypropylene that appears to be voids inside the specimens as observed in SEM micrographs in Figure 5.

The influence of % water absorption with immersion time of rice husk-filled polypropylene upon recycling is represented in Figure 6. Rice husk-filled polypropylene presents the increasing trend with extended water immersion time. When the rice husk specimen is recycled, % water absorption of the specimen seems to be reduced with increasing numbers of recycled times due to the partial removal of cellulose and hemicellulose (as observed from FTIR and TGA technique), major components in rice husk, bringing about the reduction of hydrophilicity of rice husk, the main source for absorbing water.

Conclusions

Rice husk-filled-polypropylene samples using 200 mesh and 40% by weight rice husk were recycled in order to study the influence of recycling. The rice husk was compounded with polypropylene in a twin-screw extruder and the compound was injected into testing specimens. The result from FTIR and TGA techniques revealed that the structure of the filled specimens was slightly changed with the increasing recycled time due to the rice husk component. Besides, SEM micrographs presented the reduction in rice husk particle sizes upon recycling. Tensile, flexural and impact properties including % water absorption of the rice husk-filled polypropylene was found to be slightly decreased as the result of the increase in melt flow index by the recycling process.

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