Effects of Wheat Straw Fiber Content and Characteristics, and Coupling Agent Concentration on the Mechanical Properties of Wheat Straw Fiber-Polypropylene Composites

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ABSTRACT: Wheat straw fiber-polypropylene (PP) composites were prepared to investigate the effects of wheat straw fiber content (10, 20, 30, 40, and 50 wt %), fiber size (9, 28, and 35 mesh), and maleic anhydride grafted polypropylene (MAPP) concentration (1, 2, 5, and 10 wt %) on the static and dynamic mechanical properties of the wheat straw fiber-PP composites in this study. The tensile modulus and strength of the composites increased linearly with increasing wheat straw fiber content up to 40%, whereas the elongation at break decreased dramatically to 3.78%. Compared with the composites made of the longer wheat straw fiber, the composites made of the fines (>35 mesh) had a slightly higher tensile strength of 31.2 MPa and tensile elongation of 5.39% at break. With increasing MAPP concentration, the composites showed an increase in tensile strength, and the highest tensile strength of 34.0 MPa occurred when the MAPP concentration reached 10 wt %. As wheat straw fiber content increased from 0 to 40%, the flexural modulus of the composites increased gradually from 1335 to 3437 MPa. The MAPP concentration and wheat straw fiber size distribution had no appreciable effect on the static flexural modulus of the composites. The storage flexural modulus of the composites increased with increasing wheat straw fiber content. The scanning electron microscopy (SEM) observation on the fracture surface of the composites indicated that a high wheat straw fiber content (>30 wt %) resulted in fiber agglomeration and a reduction in interfacial bonding strength. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1000–1007, 2009

Key words: composites; fibers; mechanical properties; morphology; poly(propylene) (PP)

INTRODUCTION

In recent years, polymer composites reinforced with natural fiber such as wood, corn stalk, flax, hemp, and wheat straw have become popular thanks to their renewable, recyclable, and biodegradability.[1–3] These composite products are characterized by a unique combination of excellent durability, superior dimensional stability, high rigidity, and relatively low density.[4] Natural fibers have been widely used for the polymer composite manufacturing in the form of pellets or powder form rather than in the fibrous form.[5,6] Wood fiber has traditionally been the major natural fiber used for the manufacturing of natural fiber-reinforced plastic composites. In recent years, other types of natural fiber such as wheat straw, corn stalk, flax, and hemp have also been used as fillers for the manufacturing of thermoplastic composites. The utilization of agriculture fibers as an alternative to wood fiber for natural fiber plastic composites can reduce the consumption of wood fiber, and thus, help protect forest and environment.

During the manufacturing of natural fiber and polymer composites, the use of natural fiber is limited mainly by the poor interfacial adhesion between the hydrophilic fiber and the hydrophobic polymer. To improve the interfacial adhesion between natural fiber and the polymer, coupling agents such as maleic anhydride grafted polyethylene (MAPE), styrene-ethylene-butylene-styrene grafted with maleic anhydride (SEBS-g-MA), and maleated ethylene-propylene-diene (EPDM-g-MA) have been introduced to the natural fiber and polymer system. The most commonly used is maleic anhydride grafted polypropylene (MAPP), which is attributed to esterification reaction between hydroxyl groups of natural fiber and anhydride functionality of MAPP. A study[7] has shown that the tensile strength was

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significantly increased with the addition of MAPP in the wood flour-PP composites. Furthermore, it was reported that the MAPP concentration in the composites and the grafting level of MA on the PP backbone affected the mechanical properties of the composites.[8,9] The recommended MAPP as a coupling agent should possess a high wt % MA-grafting level and high molecular weight of PP copolymer.

The mechanical properties of the natural fiber-polymer composites are influenced by natural fiber content. Rana et al.[10] reported a remarkable improvement in all mechanical properties of jute fiber-PP composites when 60 wt % jute fiber was added. Zaini et al.[11] also reported that with increasing fiber content, the flexural modulus of the composites increased, whereas the elongation at break of the composites decreased due to the decreased deformability of a rigid interphase between the fiber and the matrix material. The impact strength of the composites increased initially with the addition of natural fiber, and then started to decrease with further increase in fiber content.

The properties of the polymer composites are also influenced by fiber characteristics such as fiber size. It was reported that the fines had a slightly higher tensile elongation at break and tensile strength than the larger size of fibers. However, the reinforcement of long fiber couldn't be observed in the polymer composites, because of fiber breakage during the extrusion and injection processing.[12,13] It is interesting to note that small wood powder particles lead to improved properties, even without addition of MAPP. For example, the PP composite containing 20 wt % wood powder (<38 μm) had Young's modulus and elongation at break similar to those of the pure PP, but a higher stress at break than the pure PP.[14]

So far, very limited studies[13,15,16] have examined the effects of wheat straw fiber content and size distribution on the properties of the wheat straw fiber-PP composites. The objectives of this study are to investigate the relationships of the tensile and flexural properties, dynamic-mechanical properties and surface morphology of the wheat straw fiber-PP composites with the following variables: (1) the wheat straw fiber content (10, 20, 30, 40, and 50 wt %); (2) the concentration of MAPP as a coupling agent (1, 2, 5, and 10 wt %); and (3) morphology and size distribution of the wheat straw fiber (<9, 9–28, 28–35, and >35 mesh).

EXPERIMENTAL

Materials

Wheat straw fiber samples for this study were obtained from the MDF refining facility at Forintek under the following refining conditions: steam pressure of 8 bar, refining speed of 2500 rpm, and moisture content of 5.0–7.5%. The length of refined wheat straw fiber ranges from 0.04 mm to 6.29 mm with an average length of 0.30 mm, measured with a HiRes fiber quality analyzer (mode-LDA02). Wheat straw fiber samples with four different sizes were produced with the Tyler screen system equipped with 9, 28, and 35 mesh screens.

TABLE I
Composition of the Wheat Straw Fiber-PP Composites

Sample code	PP (wt %)	Wheat straw fibre (wt %)	MAPP (wt %)	Size distribution
PP	100	0	0	–
PPF10M2	88	10	2	–
PPF20M2	78	20	2	–
PPF30M2	68	30	2	–
PPF40M2	58	40	2	–
PPF50M2	48	50	2	–
PPF20	80	20	0	–
PPF20M1	79	20	1	–
PPF20M5	75	20	5	–
PPF20M10	70	20	10	–
<9 mesh	78	20	2	<9 mesh
9–28 mesh	78	20	2	9–28 mesh
28–35 mesh	78	20	2	28–35 mesh
>35 mesh	78	20	2	>35 mesh

The polypropylene (PP) used in this study was a homopolymer pellet, "Pro-fax" PDC, $\rho = 0.90$ g/cm^3, melt flow index (MFI) 12.0 g/10 min (230°C/2.16 kg), supplied from Basell (Canada). MAPP Polybond®3000, supplied from Crompton Company was used as compatibilizer. Polybond®3000 has 1.2 wt % MA, 0.91 g/cm^3 density at 23°C, and MFI of 400 g/10 min (190°C/2.16 kg).

Processing of wheat straw fiber-PP composites

The wheat straw fiber was dried at 105°C to constant weight before mixing process. Polymer and the wheat straw fiber were blended in a batch mixer (Thermo Haake Rheomix) at 170°C for 7 min at 55 rpm. After mixing, the compounds were removed from the mixer, and cooled to room temperature, and then compression—molded at 180°C for 4 min to produce specimens for various mechanical tests. Compositions of the wheat straw fiber-PP composites prepared are summarized in Table I.

Testing of tensile properties

Tensile properties of the wheat straw fiber-PP composites were performed with a hydraulic Instron 88215 tester. The tensile properties were determined in accordance with the ASTM D638 procedure at a cross head rate of 2 mm/min. The specimen size for the tensile tests was 55 mm (L) × 7 mm (W) × 1.5 mm (T). Eight specimens were tested in each run.

Testing of flexural properties

Flexural properties of the wheat straw fiber-PP composites were also performed with a hydraulic Instron 88215 tester. The flexural properties were determined according to the ASTM D790 in the three point bending mode at a cross head speed of 5 mm/min and with a span of 67 mm. The specimen size for the flexural tests was 100 mm (L) $\times$ 15 mm (W) $\times$ 1.5 mm (T). Six specimens were tested in each run. All the tests were performed at 25°C $\pm$ 2°C.

Dynamic mechanical analysis of the composites

Dynamic mechanical properties of the wheat straw fiber-PP composites were carried out on a Rheometrics scientific analyzer (RSA) in the dual cantilever bending mode. The specimen size for the DMA tests was 55 mm (L) $\times$ 7 mm (W) $\times$ 1.5 mm (T). The storage flexural modulus was measured at the frequency of 1 Hz with the strain amplitude of 0.021%, and in a temperature ranging from 25 to 150°C with a heating rate of 1°C/min.

Scanning electron microscopy

To better understand the interfacial adhesion between the wheat straw fiber and matrix, the fracture surfaces of the tested samples were observed using a JEOL JSM-840A SEM at an accelerating voltage of 15 kV. The surfaces were firstly fractured in liquid nitrogen, and then coated with palladium and gold before examination.

RESULTS AND DISCUSSION

Tensile properties

Effect of wheat straw fiber content

The tensile properties of the wheat straw fiber-PP composites were influenced by wheat straw fiber content. Figure 1 showed the tensile modulus, strength, and elongation at break of the wheat straw fiber-PP composites in relation to wheat straw fiber content. With increasing wheat straw fiber content up to 50 wt %, the tensile modulus of the PP composites increased linearly to as high as 2711 MPa, which was approximately four times higher than that of pure PP material. The tensile strength of the wheat straw fiber as a rigid material was higher than that of pure PP, addition of the wheat straw fiber thus led to a higher tensile strength of the wheat fiber-PP composites. Furthermore, the wheat straw fiber had a higher stiffness than the matrix, and thus resulted in a dramatic decrease in the elongation at break. As the wheat straw fiber content increased, the overall elongation at break of the composites decreased significantly. Reduction in tensile elongation may be due to the decreased deformability of a rigid interphase between the wheat straw fiber and the matrix. It was found that the tensile

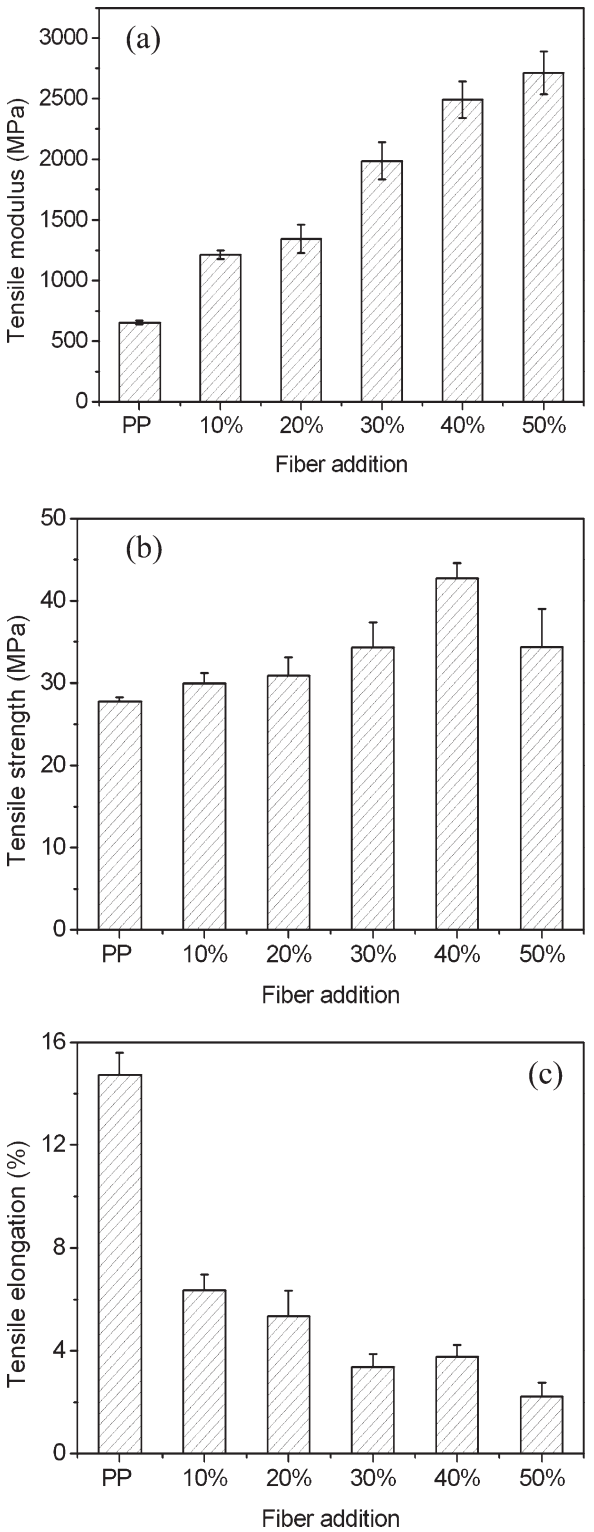

Figure 1 Effects of wheat straw fiber content on the tensile properties of the composites: (a) modulus, (b) strength, and (c) elongation.

strength of the PP composites decreased slightly with 50 wt % wheat straw fiber content. The reason for this could be that the probability of the wheat straw fiber agglomeration increased with such a high wheat straw fiber content. This created regions of stress concentration that required less stress to initiate or propagate a crack. In addition, yield stress rarely occurred in the wheat straw fiber-PP composites, unlike PP system, especially in the PP composites filled with a high wheat straw fiber content.

Effect of MAPP concentration

To improve the mechanical properties of the wheat straw fiber-PP composites, coupling agents such as commonly used MAPP were recommended to add to the system.[5,17–20] The PP composites containing 20 wt % wheat straw fiber were selected to investigate the effects of the MAPP concentration on tensile properties of the PP composites. Figure 2(a,b,c) showed the effect of MAPP concentration on tensile properties of the wheat straw fiber-PP composites. With increasing MAPP concentration, tensile strength of the PP composites increased, and with 10 wt % MAPP, the composites had the highest tensile strength of 34.0 MPa, which represents an increase by 54% as compared with the wheat straw fiber-PP composites without MAPP. The addition of MAPP led to the formation of interfacial bonding between the PP and wheat straw fiber. This was also associated with the ester linkages formed by the chemical reactions of the wheat straw fiber and MAPP, and the physical entanglement of PP molecule for the matrix and MAPP.

The optimum concentration (around 2 wt % MAPP), which gave high tensile modulus and tensile strength in the PP composites indicated the high interfacial adhesion between the wheat straw fiber and PP matrix. It is noted that a low MA concentration in the MAPP leads to the creation of a thin and irregular polymer layer, which facilitates the formation of plastic deformation zone around the wheat straw fiber during the tensile testing. A higher concentration of MA in the MAPP resulted in stronger interaction between the PP matrix and wheat straw fiber, which caused brittle fracture and reduced ductility of the PP matrix.[5] In this study, the MAPP with a slightly higher concentration of MA explained the decrease in tensile elongation after 2 wt % MAPP addition despite an increase in the tensile strength and modulus. The stronger interfacial bonding between the PP matrix and wheat straw fiber reduced the ductility of the PP matrix and thus the tensile elongation of the wheat straw fiber-PP composites at break.

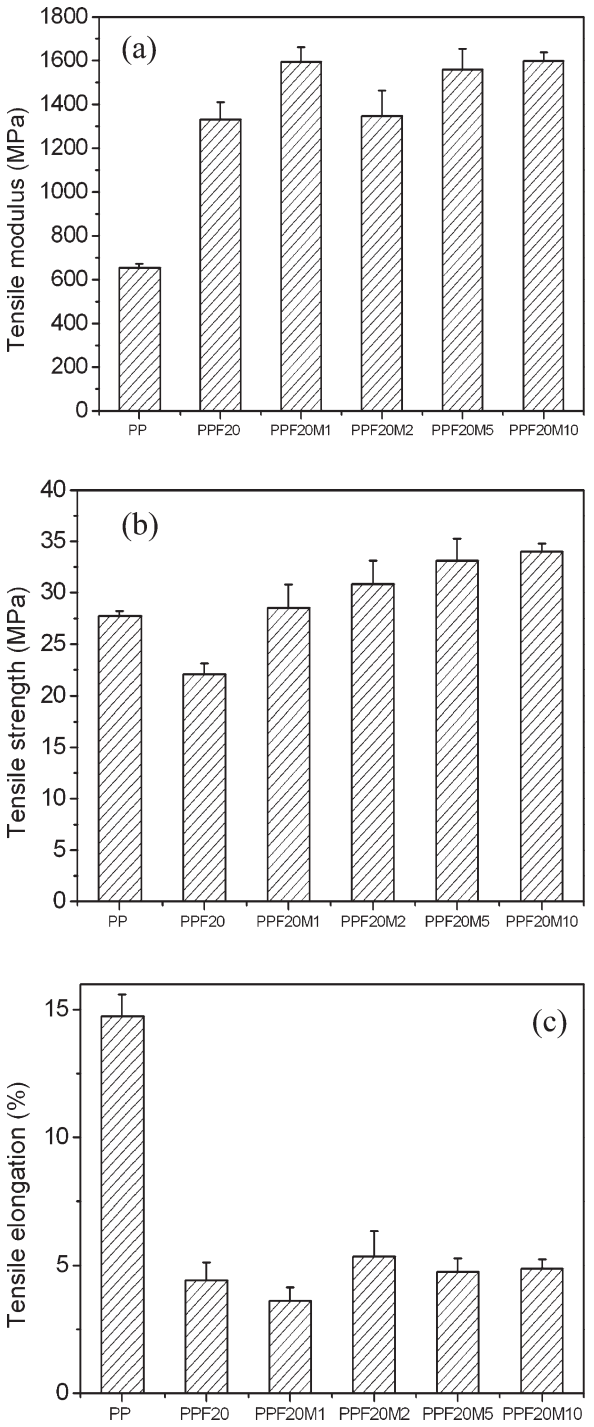

Figure 2 Effects of MAPP concentration on the tensile properties of the composites: (a) modulus, (b) strength, and (c) elongation.

Effect of size distribution

The morphology and size of the wheat straw fiber affect the tensile modulus and strength of the wheat straw fiber-PP composites. The PP composites containing 20 wt % wheat straw fiber and 2 wt % MAPP were selected to investigate the effects of size distribution of the wheat straw fiber on tensile

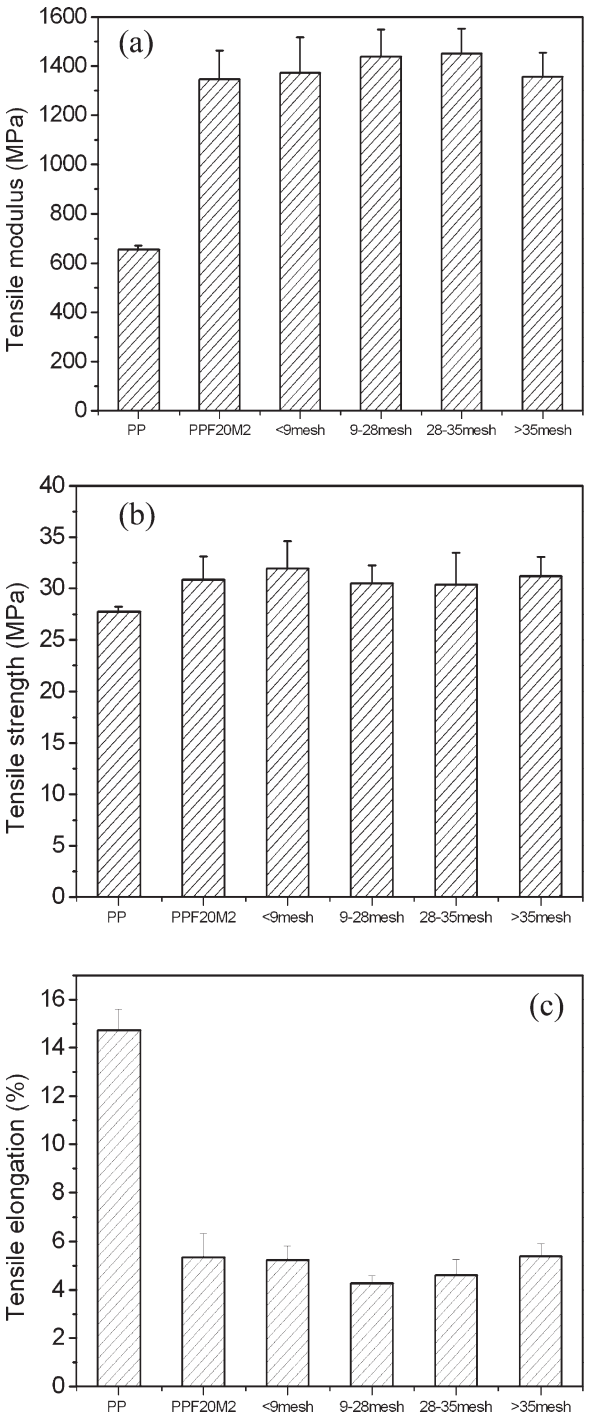

Figure 3 Effects of size distribution on the tensile properties of the composites: (a) modulus, (b) strength, and (c) elongation.

properties of the PP composites. As shown in Figure 3, composites made of the fines (>35 mesh, including short wheat straw fiber and powders), corresponding to the low aspect ratio, had a slightly higher tensile elongation at break of 5.39% and tensile strength of 31.2 MPa than those made of the longer fiber, whereas the tensile modulus of 1355 MPa was lower as the result of a decrease in stiffness. This result is consistent with a previous study.[12] The improvement in tensile properties of the PP composites reinforced with longer fiber (<9 mesh, including fiber bundles and agglomerated fiber) couldn't be observed in this study, most likely because of the wheat straw fiber breakage during the mixing process.

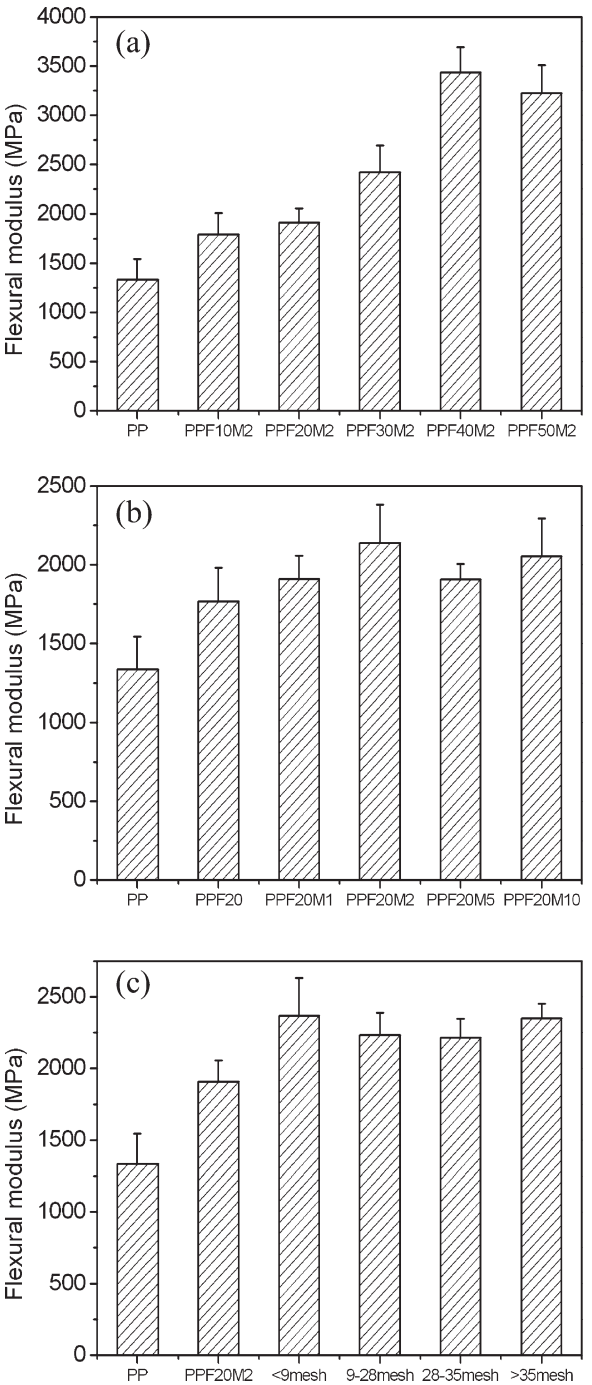

Figure 4 Flexural modulus of the composites in relation to: (a) wheat straw fiber content, (b) MAPP concentration, and (c) size distribution.

Static flexural properties

Figure 4(a) showed the flexural properties of the wheat straw fiber-PP composites in relation to wheat straw fiber content. Similar to the tensile modulus, the flexural modulus of the PP composite increased with addition of the wheat straw fiber to PP matrix. As wheat straw fiber content increased from 0 to 40%, the flexural modulus of the PP composites increased gradually from 1335 to 3437 MPa. The increased flexural modulus may result from the fact that the stiffness of the wheat straw fiber is higher than that of the PP matrix and the reinforcement introduced by the wheat straw fiber enables stress to be transferred from the matrix to the wheat straw fiber.[21] The PP composites containing a high wheat straw fiber content (50 wt %), however, had a decreased flexural modulus (3225 MPa) because of the agglomeration of the wheat straw fiber and a weak interfacial impartibility between the wheat straw fiber and matrix. Figure 4(b) showed the effect of MAPP concentration on the flexural modulus of the PP composites with 20 wt % wheat straw fiber. The optimum concentration (2 wt % MAPP) giving the best flexural modulus in the PP composites indicated the highest interfacial adhesion between the wheat straw fiber and PP matrix. Figure 4(c) presented the morphology and size of the wheat straw fiber affecting the flexural property of the composites. The composites filled with the fines and long fibers both showed higher flexural modulus values of 2349 and 2368 MPa, respectively. This study indicated that the mechanical properties of the wheat straw fiber-PP composites could be manipulated through those variables such as wheat straw fiber content and coupling agent concentration.

Dynamic flexural properties

The dynamic mechanical properties of the wheat straw fiber-PP composites were analyzed on DMA in a temperature ranging from 25 to 150°C. The storage flexural modulus (E') and damping factor (Tan δ) were presented in Table II.

Figure 5 showed the storage flexural modulus (E') of the composites reinforced with different wheat straw fiber contents in relation to temperature. The storage flexural modulus of all composites increased with increasing wheat straw fiber content from 10 to 50 wt % over the entire temperature range. This could be attributed to the higher stiffness of the wheat straw fiber. It is worth noting that the values of E' and the slope of the curve decreased with increasing temperature, because the polymer chains become more flexible and mobile with increasing temperature. The results from the static flexural testing and DMA testing exhibited a little difference, because of the different testing specimen sizes and different testing methods. The relationship between these two methods will be discussed in the next article.

Figure 6 presented the effect of wheat straw fiber content on the damping factor (Tan δ) of the composites. Tan δ, the ratio of loss modulus to storage modulus, is used to describe the flexibility of the composites.[22] As shown in Figure 6, pure PP showed a higher Tan δ over the entire temperature range. In contrary, the composites had a lower Tan δ, which indicated that the composite formulations exhibited more elasticity. Moreover, Tan δ value of the composite decreased linearly with increasing wheat straw fiber content from 10 to 50 wt %. This clearly indicated a remarkable decrease in the mobility of

TABLE II
Dynamic Mechanical Properties of the Composites

	E' (GPa)			Tan δ		
Sample code	25°C	100°C	150°C	25°C	100°C	150°C
PP	1.55	0.4	0.09	0.045	0.09	0.086
MAPP	–	–	–	–	–	–
PPF10M2	2.08	0.7	0.22	0.039	0.08	0.09
PPF20M2	2.26	0.86	0.34	0.038	0.075	0.089
PPF30M2	2.6	1.08	0.41	0.015	0.073	0.095
PPF40M2	3.6	1.78	0.76	0.032	0.068	0.096
PPF50M2	4.12	2.31	1.08	0.03	0.066	0.101
PPF20	2.24	0.9	0.36	0.038	0.074	0.101
PPF20M1	2.57	1.08	0.39	0.035	0.073	0.09
PPF20M5	2.59	1.08	0.41	0.034	0.072	0.088
PPF20M10	2.31	0.95	0.4	0.034	0.073	0.086
<9 mesh	2.35	0.88	0.32	0.036	0.075	0.075
9–28 mesh	2.86	1.17	0.45	0.033	0.074	0.092
28–35 mesh	2.43	0.93	0.36	0.036	0.075	0.088
>35 mesh	2.72	1.03	0.36	0.036	0.077	0.092

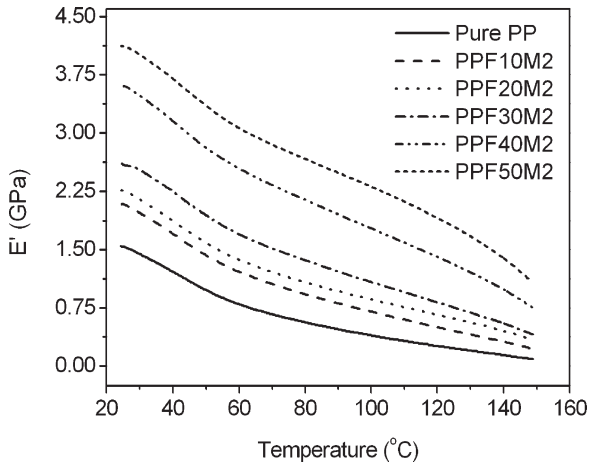

Figure 5 Storage modulus of the composites in relation to wheat straw fiber addition.

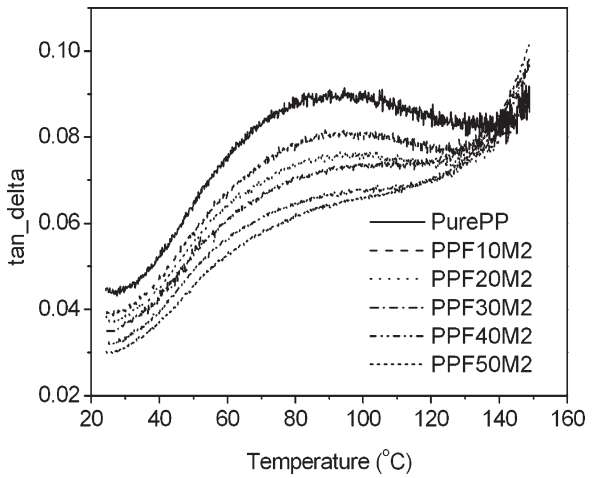

Figure 6 Tan δ of the wheat straw fiber-PP composites in relation to wheat straw fiber addition.

the polymer because of the addition of the wheat straw fiber to the PP system. The reduction in the deformability of the composites led to a lower mobility of the polymer chains, constrained by the wheat straw fiber. This result is in agreement with a previous study.[23]

Scanning electron microscopy

The morphology of the fracture surface of the wheat straw fiber-PP composites made of different wheat straw fiber contents were presented in Figure 7(a,b,c,d). From Figure 7(a), the wheat straw fiber could be embedded in the matrix at a low content of

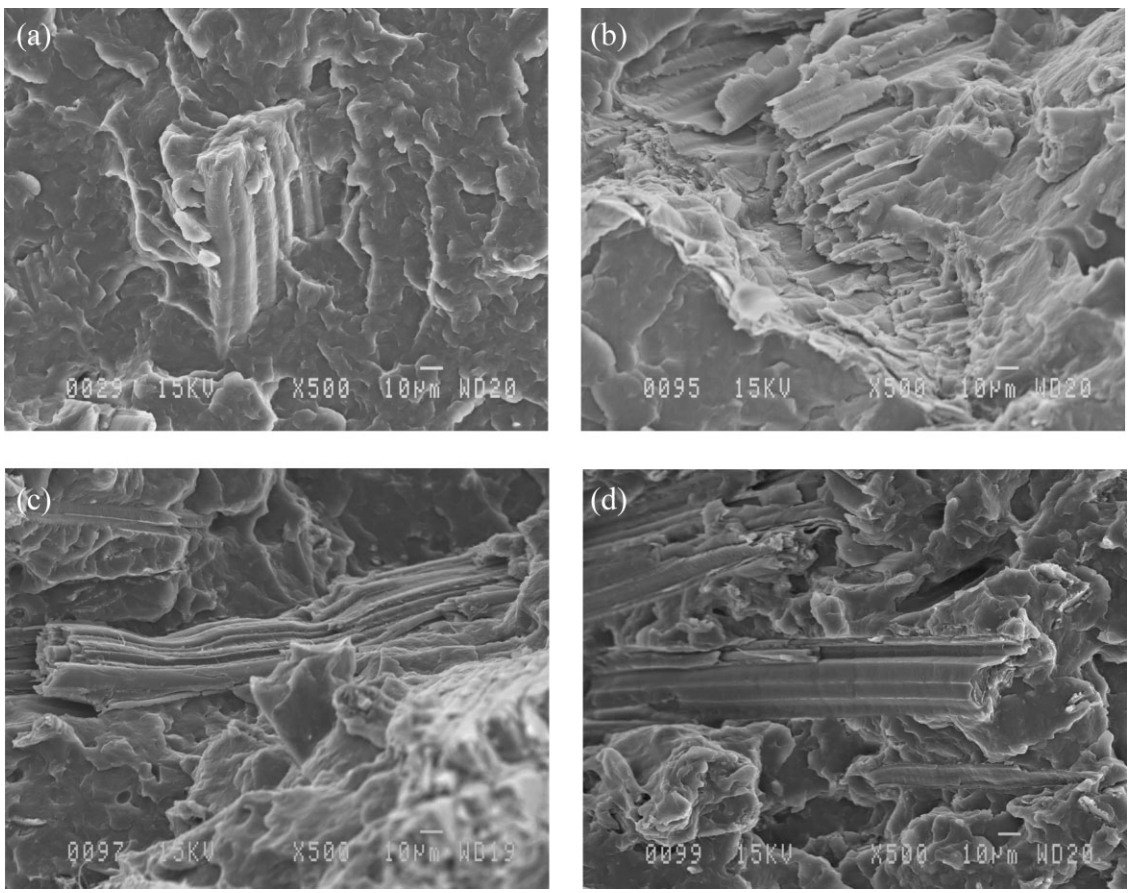

Figure 7 SEM observations of the composites: (a) PPF10M2, (b) PPF20M2, (c) PPF30M2, and (d) PPF40M2.

10 wt %. From Figure 7(b,c), the wheat straw fiber were uniformly coated by layers of PP matrix, and fiber breakage increased considerably. Figure 7(d) clearly showed the wheat straw fiber pullouts in the composites filled with 40 wt % wheat straw fiber. This indicated that a high wheat straw fiber content resulted in fiber agglomeration, difficulty in dispersion, and a reduction in interfacial bonding strength, all of which led to an increase in fiber pull-out.

CONCLUSIONS

The tensile, static, and dynamic flexural mechanical properties of the wheat straw fiber-PP composites have been investigated in this study. By adding wheat straw fiber into PP matrix, the tensile modulus and strength of the composites increased gradually, whereas the tensile elongation at break decreased because of the stiffness of the wheat straw fiber. With increasing MAPP concentration, the PP composites showed an increase in tensile strength, the highest tensile strength occurred with the concentration of MAPP up to 10 wt %. Composites made of the fines had a slightly higher tensile elongation at break and tensile strength than those made of the longer fiber. As wheat straw fiber content increased to 40%, the flexural modulus of the PP composites increased gradually. The MAPP concentration and fiber size distribution had no obvious effect on the flexural modulus of the wheat straw fiber-PP composites. The dynamic storage flexural modulus of the composites tended to increase with increasing wheat straw fiber content. The SEM observation on the fracture surface of the composites indicated that a high wheat straw fiber content (>30 wt %) resulted in fiber agglomeration and difficulty in dispersion.

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