Sunflower Seed Cake as Reinforcing Filler in Thermoplastic Composites

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ABSTRACT: Dimensional stability, mechanical properties, and melting and crystallization behavior of polypropylene composites filled with sunflower seed cake (SSC) were investigated. Injection molded composites were prepared from the SSC flour and polypropylene with and without maleic anhydride-grafted polypropylene (MAPP) at 30, 40, 50, and 60 wt % contents of the SSC flour. Twenty-eight days thickness swelling and water absorption values of the specimens increased by 43 and 56% as the filler content increased from 30 to 60 wt %, respectively. The flexural modulus of the polypropylene composites increased from 3157 to 4363 MPa as the SSC flour increased from 30 to 60 wt %. The maximum flexural strength 38.4 MPa was observed for 40 wt % SSC flour filled specimens. However, further increment in the SCC flour decreased the flexural strength to 31.4 MPa. The tensile strength of the specimens decreased from 22.5 to 14 MPa while the tensile modulus increased from 3023 to 3677 MPa as the SSC flour increased from 30 to 60 wt %. The dimensional stability and mechanical properties of the composites were significantly improved by the incorporation of the coupling agent (MAPP). The effect of the MAPP addition was more pronounced for the strength than for the modulus. The melting temperature and degree of crystallinity of the neat polypropylene decreased with increasing content of the SSC flour. The degree of crystallinity of filled composites considerably increased with the incorporation of the MAPP. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1170–1178, 2013

INTRODUCTION

Interest in using lignocellulosic materials, which predominantly consist of cellulose, lignin, and hemicellulose, in the production of thermoplastic composites has gained momentum in recent years.[1] The use of such materials in composites has increased due to their low cost, their ability to recycle and for the fact that they can compete well in terms of strength per weight of material. The impetus to use such fibrous materials is dictated further by environmental pressure groups and stringent environmental laws. One of the materials of this category that is of great relevance to the world in particular is sunflower (*Helianthus annuus L.*) seed cake (SSC) generated by sunflower oil industry in a large quantity. The SSC is the residue left after the pressing of sunflower seeds to extract their oil. In 2011, total world production of sunflower oil was more than 4.81 million tons, and about 13.99 million tons were SSC. Ukraina is the main world producer of the SSC with 8000 m^3 followed by European Union, Russia, Argentina, China, USA, and Turkey.[2] However, the oil production represents only 30% of the total biomass produced by the industry, of which the remaining 70% (by weight) consists of lignocellulosic material.[3]

The SSC, the residue of the oil extraction of the seed, consists of ∼ 40% lignocellulosic fibers and ∼ 35% protein.[4] The full composition and main features of the SSC is presented in Table I. The SSC can be an interesting raw material in the manufacture of filled thermoplastic composites due to its lignocellulosic fibers. Turkish sunflower oil industry generates 800,000 tons of SSC per annum.[5] It has few outlets in cattle feeding because of lower nutritional properties than those of its competitors, rapeseed and soybean oil cake.[6] The high fiber content and its deficiency of lysine are responsible for the limited use of SSC in poultry diets. It is thus available in large amounts on a small number of sites and is particularly cheap. The oil (1.5–2.5%) in the SSC can act as a natural lubricant for the compound, improving and speeding up subsequent processing in the extruder. The use of SSC as a replacement for commercial fillers in thermoplastic composites will thus be of great interest.

A growing demand for wood plastic composites has led to continuous efforts to find new resources as alternative to wood. One of these residuals is SSC, which are produced in high quantities in the sunflower oil industry. It does not require any

Table I. Composition of SSC[4]

Sunflower seed cake (SSC) composition	Value + standard deviation (%)
Moisture	8.0 ± %0.5
Total protein	31.4 ± 1.6
Fats	1.7 ± 0.1
Carbohydrates	58.7 ± 2.6
Hemicellulose	9.2 ± 0.5
Cellulose	21.7 ± 1.1
Lignin	9.5 ± 0.4
Total solids	93.4 ± 1.9
Mineral solids	6.6 ± 0.1
Volatile solids	86.5 ±1.3
C	43.6 ± 0.3
H	6.2 ± 0.1
O	45.6 ± 0.5
N	4.6 ± 0.6

additional cost for collecting and chipping in thermoplastic composite industry. Lignocellulosic filled thermoplastic composite industry has recently increased in Turkey. The SSC generated in massive quantities by sunflower-oil extraction in the sunflower oil mill can play an important role in the manufacture of lignocellulosic filled thermoplastic composites, thereby reducing the demand for wood material. Thermoplastic composites are commonly used in applications requiring a high dimensional stability such as swimming pool decking and garden decking. In this study, the potential utilization of SSC flour as a source of reinforcing fillers in polypropylene composites used in outdoor applications was investigated. For this aim, the dimensional stability, mechanical properties, and melting and crystallization behavior of the thermoplastic composites prepared from the SSC flour and polypropylene with and without maleic anhydride-grafted polypropylene (MAPP) at 30, 40, 50, and 60 wt % contents of the SSC flour were studied.

EXPERIMENTAL

Materials

The SSC, the biomass remaining as a byproduct of industrial processes after removal of oil by press, was used in this study. The SSC was supplied from sunflower oil factory in the city of Ordu, North-East Turkey. Prior to the use, the SSC sample was air-dried and then grounded with a high-speed rotary cutting mill to pass a 35-mesh screen and retained by an 80-mesh screen. The SSC flour with an average particle size of 0.18 mm was then dried in a laboratory oven at 100°C for 24 h to about moisture content of 1%.

The polypropylene (MFI/230°C/2.16 kg = 5.5 g/10 min) supplied by a Petrochemical Company in Ukraine, was used as the polymeric material. The MAPP (Optim®P-425, MFI/190°C, 2.16 kg = 120 g/10 min) as the coupling agent was supplied by Pluss Polymers, India.

Preparation of Injection Molded Thermoplastic Composites

The SSC, polypropylene, and MAPP granulates were processed in a 30 mm corotating twin-screw extruder with a length-to-diameter (L/D) ratio of 30:1. The eight barrel temperature zones of the extruder were controlled at 175 and 190°C. The extruded strand passed through a water bath and was subsequently pelletized. The pellets were stored in a sealed container and then dried to the moisture content of 1% in a laboratory oven before the injection molding. The pellets were injection molded into tensile test using the 60-ton capacity injection-molding machine at a barrel temperature of between 180 and 200°C, an injection pressure of 5–6 MPa with 20 s holding time.

To avoid thermal degradation (above 200°C) of the lignocellulosics, the barrel temperature in the injection machine was set to 180–200°C in all experimental runs. A thermoplastic compound with a high content of filler (that is, low content of thermoplastic) is difficult to mold in the injection machine due to increasing viscosity of the compound. For the molten compound containing the filler to flow easily into the mold cavities, the large-diameter flow channel was used in the production of SSC flour filled polypropylene composites. This is important because the molten compound containing could not easily flow into the mold cavities if traditional flow channels used for neat polypropylene are used. The filled and unfilled polypropylene composites were produced using the same flow channel. The oil (1.5–2.5%) in the SSC acted as a natural lubricant for the compound, which improved the flow of molten compound.

The test specimens were conditioned at a temperature of 23°C and relative humidity of 50% according to ASTM D 618.[7] Air-dry density values of the specimens varied from 1010 to 1050 kg/m³. The raw material formulations used for the composites are presented in Table II.

Determination of Dimensional Stability. The thickness swelling (TS) and water absorption (WA) tests were carried out according to ASTM D 570[8] specifications. The TS and WA tests were performed on the same specimen. The test specimens were in the form of a disk 50.8 mm in diameter and 3.2 mm in thickness. The conditioned specimens were entirely immersed

Table II. Compositions of the Injection Molded Composites

Composite type	Composite compositon		
	SSC flour (wt %)	Polypropylene (wt %)	Coupling agent (MAPP) content (wt %)
A	30	70	–
B	40	60	–
C	50	50	–
D	60	40	–
E	30	67	3
F	40	57	3
G	50	47	3
H	60	37	3
I	0	100	–

Table III. The Physical Properties of Unfilled and SSC Flour Filled Polypropylene Composites

Composite type[a]	Density (kg/m^3)	Water absorption (WA) (%)			Thickness swelling (TS) (%)		
		1-day	7-days	28-days	1-day	7-days	28-days
A	1010 (40) a	0.27 (0.02) ab	0.49 (0.03) a	1.52 (0.05) ab	0.67 (0.03) ab	1.13 (0.06) a	1.47 (0.06) ab
B	1020 (40) a	0.44 (0.07) c	0.71 (0.05) bc	1.64 (0.07) be	0.75 (0.10) abcd	1.30 (0.06) ab	1.57 (0.12) c
C	1030 (30) a	0.48 (0.04) cd	0.83 (0.11) cd	2.04 (0.13) c	0.84 (0.12) bcd	1.52 (0.09) c	1.83 (0.05) d
D	1040 (10) a	0.73 (0.10) e	1.08 (0.08) e	2.37 (0.14) d	0.93 (0.03) d	1.62 (0.10) c	2.10 (0.09) e
E	1010 (10) a	0.21 (0.03) a	0.42 (0.04) a	1.43 (0.08) a	0.61 (0.06) a	1.11 (0.06) a	1.39 (0.05) a
F	1030 (10) a	0.27 (0.01) ab	0.62 (0.08) b	1.56 (0.14) ab	0.71 (0.11) abc	1.20 (0.09) a	1.52 (0.06) bc
G	1040 (10) a	0.32 (0.04) a	0.71 (0.07) bc	1.75 (0.12) e	0.75 (0.09) abcd	1.21 (0.11) a	1.60 (0.05) c
H	1050 (20) a	0.50 (0.04) d	0.94 (0.09) d	2.18 (0.13) c	0.88 (0.10) cd	1.46 (0.12) bc	1.93 (0.13) f
I	876 (10) b	0.06 (0.02) f	0.10 (0.01) f	0.18 (0.02) f	0.12 (0.01) e	0.14 (0.01) d	0.24 (0.01) g

[a]See Table II for composite formulation. Groups with same letters in column indicate that there is no statistical difference ($P < 0.01$) between the specimens according Duncan's multiply range test.
The values in the parentheses are standard deviations.

for 1-day, 7-days, and 28-days in a container of water at 23 ± 2°C. At the end of each immersion time, the specimens were taken out from water and all surface water was removed with a clean dry cloth. The specimens for the WA test were weighed to the nearest 0.01 g. After the weight measurements, the thickness of the same specimens for the TS test was measured to the nearest 0.001 mm immediately. Ten replicate specimens were tested for each composite formulation.

Determination of Mechanical Properties. The flexural properties of the specimens with dimensions of 127 × 12.7 × 3.2 (thickness) mm^3, flexural modulus and strength, were measured in three-point bending test using a standard material testing system (Lloyd) at a crosshead speed of 1.3 mm/min in accordance with ASTM D 790.[9] Tensile strength and modulus of the specimens [dogbone shape (Type III)] were tested with a crosshead speed of 5 mm/min in accordance with ASTM D 638.[10] Ten replicate specimens were tested for the tensile and flexural properties of each composite formulation.

Differential Scanning Calorimetry (DSC) Analysis. Melting and crystallization behavior of the specimens were studied in a heat-flux type differential scanning calorimeter (DSC, Perkin Elmer-DSC 8000) according to ASTM D3418.[11] Temperature and heat flow calibration of the instrument were performed with high purity indium (In), tin (Sn), and zinc (Zn) metals. The test specimens weighing about 9 to 10 mg in an aluminum crucible were heated up to 200 °C with the heating rate of 10°C/min and kept at this temperature for 2 min to remove thermal history. Then the specimens were cooled down to 0°C with the cooling rate of 10°C/min by an electrical cooling device to allow the sample crystallize dynamically and kept at this temperature for 2 min. Subsequently, the nonisothermally crystallized specimens were reheated to 200°C with the heating rate of 10°C/min. All heating-cooling runs in melting and crystallization studies were carried out under nitrogen (N$_2$) atmosphere at a flow rate of 50 mL/min to prevent oxidation of the specimens. Degree of crystallinity (X_c%)

was determined from the second melting enthalpy values using the following equation:

$$X_c = \frac{\Delta H_m}{(1 - \alpha)\Delta H_m^o} \times 100$$

where, ΔH_m is melting enthalpy of the samples (J/g), ΔH_m^o is the enthalpy value of melting of a 100% crystalline form of polypropylene (209 J/g) and $(1 - \alpha)$ is the weight fraction of polymer into the composite material.

Interfacial Morphological Analysis. The morphology of tensile fracture surfaces was studied by means of scanning electron microscopy (SEM, JEOL Neo Scope JSM-5000) under an acceleration voltage of 10 KV. The test specimens were attached to an aluminum stub and sputtered with gold to eliminate the electron charging effects. The objective was to get some information regarding the filler dispersion and bonding quality between filler and polymer matrix and to detect the presence of micro defects.

Statistical Analysis. An analysis of variance, ANOVA, was conducted ($P < 0.01$) to evaluate the effect of the SSC flour content on the dimensional stability and mechanical properties of the composites. Significant differences among the average values of the composite types were determined using Duncan's multiple range test.

RESULTS AND DISCUSSION

Dimensional Stability
The TS and WA values of the SSC flour filled polypropylene composites are presented in Table III. The incorporation of the SSC flour into the polypropylene resulted in high TS and WA values due to the hydrophilic property of the SSC, particularly beyond 50 wt % (Table III). The water residence sites in the composite increased with increasing content of the SSC flour. This can explain why the composites containing large amounts of the SSC flour absorbed more water. The specimens containing higher polypropylene content showed lower WA. 28-days TS and WA values of the specimens increased by 43 and 56% as
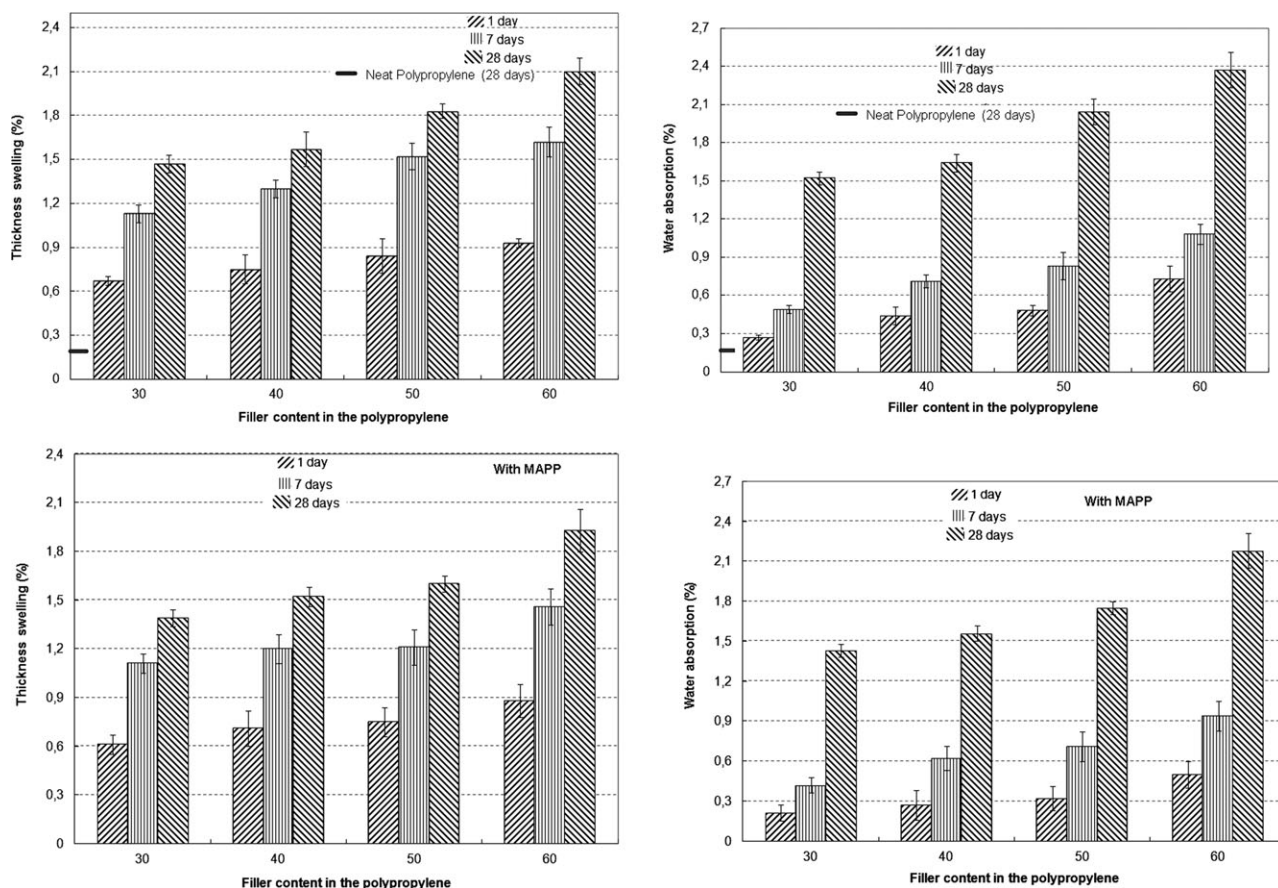
Figure 1. Dimensional stability of polypropylene composites unfilled and filled with SSC flour.

the filler content increased from 30 to 60 wt %, respectively. However, the dimensional stability of the specimens was significantly improved by the incorporation of the compatibilizer MAPP. At the constant content of the SSC flour, the TS and WA values of the specimens coupled with the MAPP were significantly lower than those of the specimens without the MAPP. For example, 28 days TS and WA values of the coupled specimens at the 50 wt % content of the SSC flour decreased by 13 and 14% as compared with the noncoupled specimens. The largest increment in the swelling of the specimens' occurred in the first 7 days. The WA values of the specimens considerably increased as the immersion time was increased to 28 days (Figure 1). Significant differences ($P < 0.01$) among some group averages for the TS and WA values are shown in Table III.

The rates of the WA and TS of the specimens increased with increasing content of the SSC flour. The reason behind this was higher possibility of WA by hydrophilic nature of the SSC flour. Polypropylene has very negligible or no WA[12] and hence, it can be assumed that 99.9% of water is absorbed by SSC flour. 24 h WA of the neat polypropylene used in this study was found to be 0.06% (Table III). The increment in the filler content increases total surface area of the filler in the composite. This causes more water intrusion into the cell walls of the SSC component in polymer matrix.

Although the WA of the polypropylene composites decreased with increasing content of the SSC flour, it was lower than that of the polypropylene composites filled with wood and various lignocellulosic wastes such as wheat-straw, bagasse stalk, rice hull, and pine cone.[13–16] For example, San et al.[13] reported that TS and WA values (1-day) of polypropylene composites filled with 60 wt % wood flour and 3 wt % MAPP were 1.82 and 0.84% but the same properties were found to be 0.88 and 0.50% for polypropylene composites containing 60 wt % SSC and 3 wt % MAPP, respectively. The lower TS and WA of the polypropylene composites filled with the SSC flour as compared with those of the above-mentioned studies were mainly attributed to lower amounts of the hygroscopic materials, cellulose, and hemicelluloses, in the cell walls of the SSC flour (Table I). Heat and shear induced aggregation of proteins involving hydrophobic interactions and disulfide bridges results in the formation of a three dimensional network. This essential property makes the injection molded SSC products water-resistant.[17]

The dimensional stability of the specimens was significantly improved by the incorporation of the MAPP. However, the positive effect of the MAPP on the dimensional stability of the specimens decreased at higher contents of the SSC flour, in particular beyond 50 wt %. The MAPP improves the interfacial adhesion between the SSC flour and polymer matrix, leading to less microvoids and fiber-polypropylene debondings in the interphase region. The chemical reaction of the hydrophilic hydroxyl groups of the lignocellulosics and acid anhydride groups of the MAPP, thus forming ester linkages reduce the
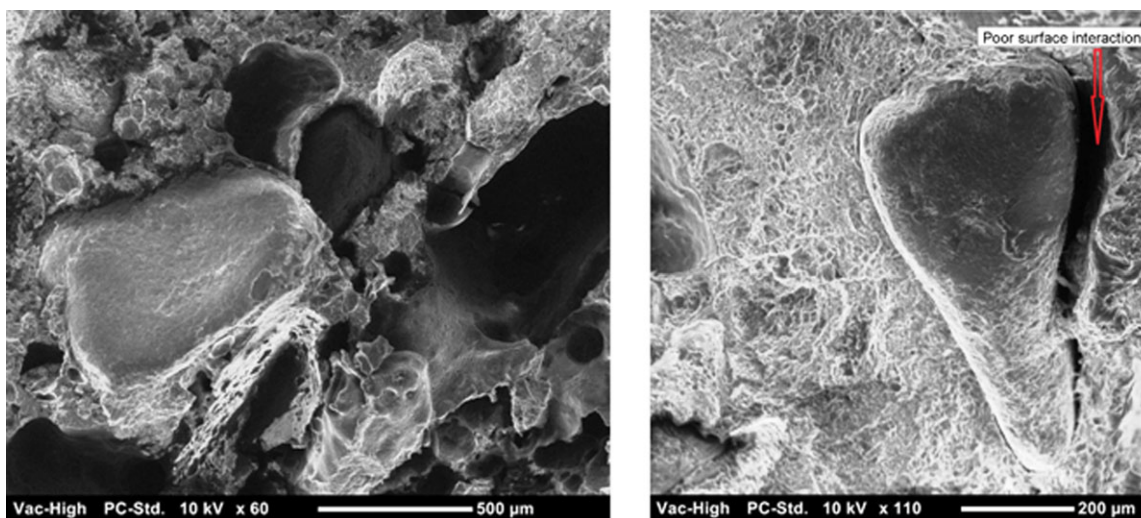
Figure 2. SEM micrographs of the uncoupled polypropylene composite at 60 wt % loading of SSC (fiber pullout and poor surface interaction). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

number of free hydrophilic groups.[1] This indicates that chemical bonding of hydroxyl groups of the SSC with functional groups of the MAPP at the interface reduces water uptake of the specimens. The improvement in water resistance of the specimens by the introduction of the compatibilizer MAPP was also due to the tortuous path formed for the penetrating water. Efficient dispersion of the SSC flour within the polymer matrix due to the addition of the MAPP forms more tortuous path for penetrating water, slowing down the whole process. Decreased efficiency in WA of the composites without the MAPP was most likely due to the decreased tortuousity in the composite. This was caused by the poor dispersion of the SSC flour in the polymer matrix.

Adding the SSC flour to the polypropylene increased its density. This was expected, because the cell density of the cellulose (average 1.3 g/cm^3 after extrusion and injection molding) is much higher than injection molded polypropylene density (0.876 g/cm^3) and is in accordance with previous reports.[18,19]

The results of the analysis of variance indicated that filler loading did not significantly affect the composite density (Table III). The WA of the composites was significantly affected by the presence of voids and defects mainly located in the filler/matrix interface. This was due to the poor dispersion of the filler in the polymer matrix. The SEM images of the fracture surfaces confirmed a loss of interfacial bonding between the filler and the polymer matrix (Figure 2). The number of the voids and defects in the polypropylene composite increased with increasing content of the filler. However, the voids and defects in the composite decreased with the incorporation of the compatibilizer MAPP.

Mechanical Properties

Flexural Properties. The flexural properties of the polypropylene composites as a function of the SSC flour content are presented in Table IV. The flexural modulus of the specimens significantly improved with increasing content of the SSC flour.

Table IV. The Mechanical Properties of Unfilled and SSC Flour Filled Polypropylene Composites

Composite type[a]	Mechanical properties				
	Flexural strength (MPa)	Flexural modulus (MPa)	Tensile strength (MPa)	Tensile modulus (MPa)	Tensile Elongation at break (%)
A	37.6 (1.9) ab[b]	3157 (129) a	22.5 (1.6) ab	3023 (121) a	1.54 (0.23) a
B	38.4 (2.2) ab	3409 (150) ac	19.3 (1.3) cd	3305 (172) abc	1.50 (0.13) a
C	35.7 (2.0) a	3822 (145) abcd	17.5 (1.9) de	3475 (131) bcd	1.40 (0.09) a
D	31.9 (1.1) c	4363 (178) bd	14.0 (1.5) f	3677 (147) cd	1.60 (0.22) b
E	39.3 (1.6) ab	3356 (154) a	24.5 (0.9) a	3205 (178) ab	1.60 (0.11) a
F	43.4 (1.8) d	3665 (177) abc	22.0 (2.0) ab	3417 (59) bcd	1.56 (0.03) a
G	40.4 (2.1) bd	4144 (184) bd	21.6 (1.6) bc	3566 (132) bcd	1.46 (0.05) a
H	35.9 (1.3) a	4455 (202) d	15.5 (1.1) ef	3712 (94) d	1.69 (0.31) b
I	28.3 (0.4) e	652 (73) e	27.8 (0.7) g	1709 (92) e	8.59 (0.32) c

[a]See Table II for composite formulation. [b]Groups with same letters in column indicate that there is no statistical difference ($P < 0.01$) between the specimens according Duncan's multiply range test. The values in the parentheses are standard deviations.
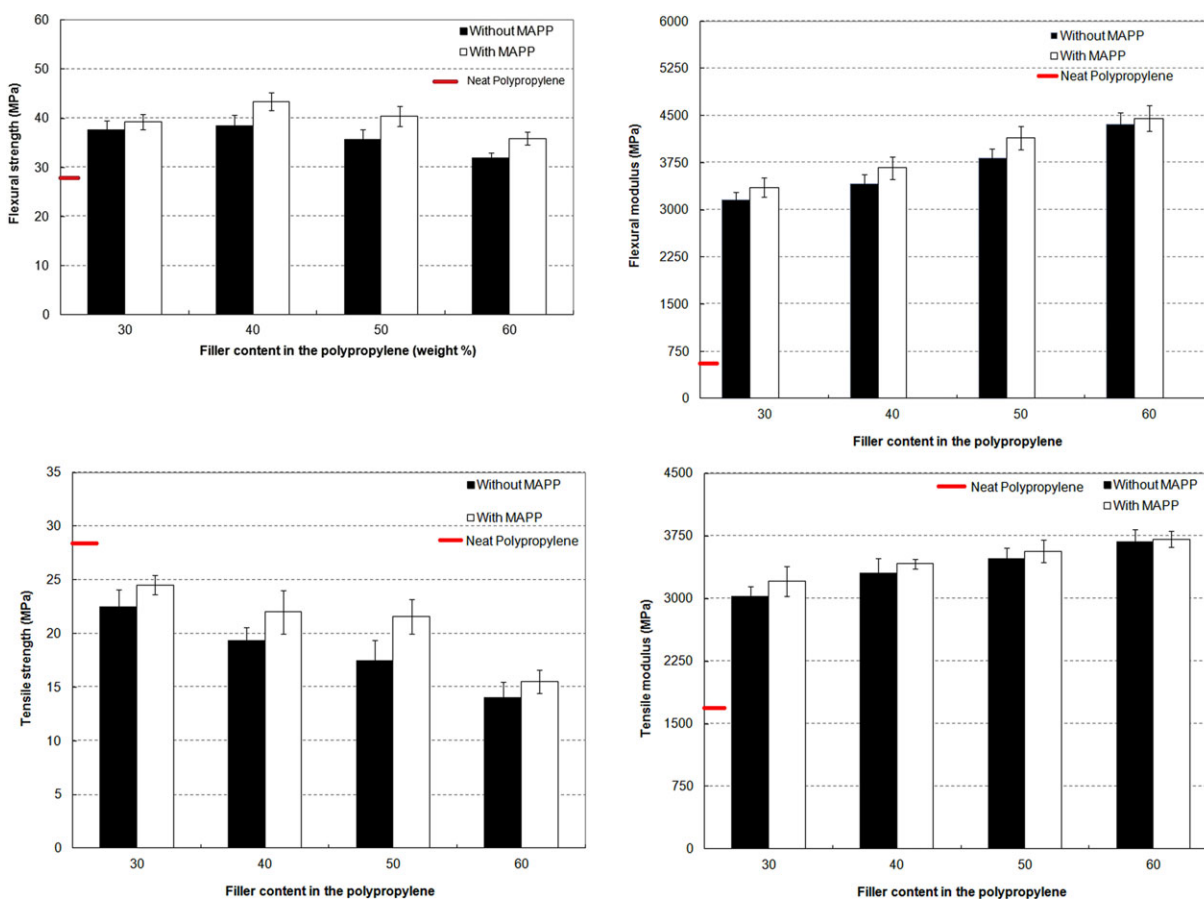
Figure 3. Mechanical properties of polypropylene composites unfilled and filled with SSC flour. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The modulus of the specimens' increased from 3157 to 4363 MPa as the SSC flour increased from 30 to 60 wt %. The highest increment in the flexural modulus was observed as the SSC flour content increased from 50 to 60 wt %. The maximum flexural strength was found to be 38.4 MPa (35.7% of neat polypropylene) for 40 wt % SSC flour filled specimens. However, further increment (60 wt %) in the SSC flour content decreased the flexural strength to 31.9 MPa. All the polypropylene composites filled with SSC flour showed higher flexural modulus and flexural strength than the neat polypropylene, which were 652 and 28.3 MPa. As compared with the neat polypropylene, the flexural modulus of the filled polypropylene increased by 569% as the SSC flour content increased to 60 wt %. Significant differences ($P < 0.01$) among some group averages for the mechanical properties are shown in Table IV.

The flexural modulus of the composites increased with increasing content of the SSC flour (Figure 3). This was because the lignocellulosic fillers were more rigid compared to the polypropylene.[20] The composite material became stiffer with the addition of SSC flour; however, the corresponding strain at failure was decreased. In thermoplastic composites the cellulose fiber is the main load-bearing component, and the more the fibers are oriented along the flow, the higher are the flexural properties of the material.[21] As compared with the neat polypropylene, higher flexural properties of the polypropylene composites filled with the SSC flour was also caused by the orientation of the cellulose fibers of the SCC flour in the matrix.

The flexural modulus and strength of the SSC filled polypropylene composites were good compared with thermoplastic composites filled with various lignocellulosic wastes such as olive mill sludge, pine cone, corn stalk, oilseed stalk, and reed stalk.[16,22,23] For example, Ayrilmis and Buyuksari[16] found that flexural strength and modulus of polypropylene composites filled with 40 wt % olive mill sludge were 37.5 and 3125 MPa, respectively. In other study, Nourbakhsh and Ashori[23] found that flexural strength and modulus of 2 wt % MAPP coupled polypropylene composites filled with 45 wt % oilseed stalk flour were about 30 and 3500 MPa, respectively.

The reduction in the flexural strength of the specimens as a function of the SSC flour content was mainly attributed to the poor compatibility between polar SSC and nonpolar polypropylene, which forms the weak interfacial regions. As other lignocellulosic materials, the SSC surface is covered by polar hydroxyl groups contributed by cellulose, hemicellulose, and lignin. As more filler is incorporated in the composite, more incompatible interfacial regions between polar lignocellulosic and nonpolar polypropylene are created. The weak interfacial region results in

Table V. The Results of Differential Scanning Calorimetry (DSC) Analysis

Composite type[a]	First melting peak temperature (°C)	Crystallization peak temperature (°C)	Second melting enthalpy (J/g)	Second melting temperature (peak) (°C)	Crystallization enthalpy (J/g)	X_c Degree of crystallinity (%)
A	167.8	120.4	53.2	165.9	66.7	36.4
B	167.2	119.4	44.6	165.2	60.7	35.6
C	166.4	118.5	37.1	164.5	47.2	35.5
D	165.7	117.4	27.8	164.9	44.7	33.3
E	166.2	121.6	74.5	167.2	78.2	50.9
F	166.1	120.4	62.3	166.0	72.0	49.7
G	164.9	119.0	50.8	163.4	61.7	48.6
H	163.9	118.5	31.7	162.9	35.1	37.9
I	167.2	115.2	78.8	166.9	91.8	37.7

[a]See Table II for composite formulation.

low stress-transferring efficiency from the matrix to the reinforcement component.[1] This results in a lower flexural strength as the amount of filler was increased in the composite.

The composites coupled with the MAPP showed better mechanical properties than the composites without the MAPP (Figure 3). For example, at the constant content of the SSC flour (50 wt %), the coupled composites had the flexural strength and modulus values of 13.1 and 8.4% higher than the noncoupled composites, respectively. The presence of MAPP reduces the voids sizes and turns the surface more homogeneous confirming its effect on promoting adhesion in the interfacial region.[1] The improvement in the interfacial adhesion and stress transfer from the polymer matrix to the stiffer SSC flour caused the increases in the flexural modulus and strength. A higher mechanical interlocking can increase the interfacial frictional sliding. If the interface is weak, the effective load distribution is not achieved and thus the mechanical properties of the composites are impaired. The effect of the MAPP addition was more pronounced for the flexural strength than for the flexural modulus.

Tensile Properties

Significant improvement in the tensile modulus was observed with increasing content of the SSC flour. As the filler loading increased, a positive correlation with modulus was observed for both the tensile and flexural properties. The MAPP coupled composites with a high content of the SSC flour had better the tensile modulus and strength than the noncoupled ones. As compared with the neat polypropylene, the tensile modulus increased by 115% as the amount of the SSC flour increased to 60 wt % in the polypropylene whereas the tensile strength decreased by 98.6%. The results of the tensile modulus showed that the presence of the SSC filler reduced the ductility of the polypropylene and increased its modulus. This is true for lignocellulosic filled thermoplastic composites in which filler added to a thermoplastic restrains the movement of its chains, thereby increasing its modulus.[1] This was also because the SSC lignocellulosic filler was more rigid that the neat polypropylene.

The tensile strength of the specimens decreased gradually with increasing content of the SSC flour. The tensile strength values of the specimens filled with 40 or 50 wt % SSC flour were similar

each other (Table IV). The decrease in the tensile strength was associated with the poor dispersion and adhesion of the SSC flour in the polymer matrix. The poor adhesion between the SSC flour and polymer matrix creates weak interfacial regions (Figure 2). The effect of the MAPP addition was more pronounced for the tensile strength than for the tensile modulus. For example, at the constant content of the SSC flour (50 wt %), the tensile strength and modulus of the specimens increased by 23.4 and 2.6%, respectively, as the MAPP (3 wt %) was incorporated into the composite. The improvement in the tensile properties of the coupled specimens was due to the improvement of the interfacial adhesion between the SSC flour and polymer matrix. This was good agreement with previous studies.[24,25]

The tensile elongation at break values declined sharply with the addition of the SSC flour (Table III). This result was good consistent with previous studies.[26–28] The most reduction in the elongation at break was observed for the composites filled with 60 wt % SSC flour (437% of the neat polypropylene) because the composite became stiffer when the amount of lignocellulosic filler was increased. Although the coupling agent had no significant effect on the elongation at break, the coupled composites showed higher elongation at break than ones without MAPP. For example, at the constant content of the SSC flour (60 wt %), the elongation at break values of the specimens increased by 5.6%, as the MAPP (3 wt %) was incorporated into the composite. This could be explained by the good dispersion of the SSC flour in the polymer matrix.

DSC Analysis

All filled polypropylene composites with and without MAPP, except for 30 wt % filler content, had a slightly higher first melting temperature than the neat polypropylene (Table V). Neat polypropylene had the highest melting temperature (167.2 °C), while the polypropylene composites filled with 60 wt % SSC four had the highest melting temperature (165.7°C). The increment in the filler content decreased the melting temperature of the polypropylene, representing that less energy was needed to melt the composites. A similar trend was also observed for the second melting temperature. This result could be due to the fact that the amount of polypropylene decreased as the SSC flour increased. In other words, a smaller amount of
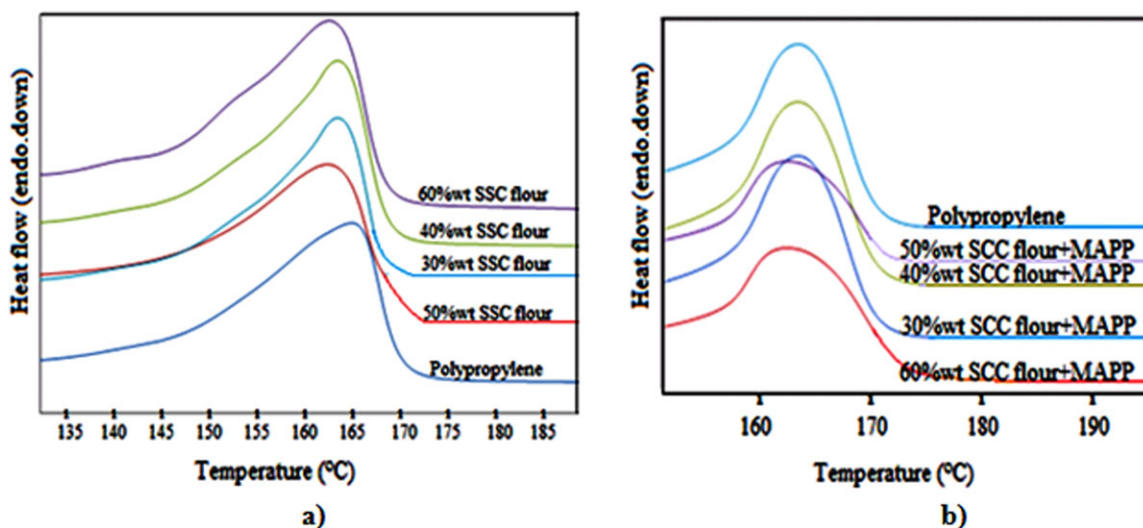
Figure 4. Second melting (peak) temperatures of unfilled and SSC flour filled polypropylene composites. (a) Without MAPP. (b) With MAPP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polypropylene in the composite requires less heat to melt. The incorporation of the MAPP into the formulation slightly decreased first melting temperature of the filled composites.

The second melting enthalpy of the polypropylene composites considerably decreased with increasing content of the SSC flour [Figure 4(a)]. As compared to the neat polypropylene (78.8 J/g), the second melting enthalpy of the filled composited decreased from 53.2 to 27.8 J/g. This result indicates that SSC flour absorbed more heat energy in the melting of the composites. The MAPP coupled specimens showed higher melting enthalpy than unfilled specimens [Figure 4(b)]. However, the effect of the MAPP on the melting enthalpy of the composites decreased beyond 50 wt % filler content (Table V).

The crystalline peak temperatures of the filled polypropylene composites decreased with increasing content of the SSC filler [Figure 5(a)]. The crystalline peak temperature of the neat polypropylene was found to be 115.2°C, and it decreased from 120.4 to 117.4°C as the filler content increased from 30 to 60 wt %. The MAPP slightly increased the crystalline peak temperatures of the filled composites [Figure 5(b)]. The MAPP acts as nucleating agents, which increase the crystallization temperature of polypropylene.[29] As shown in Table V, the crystallinity (X_c) of the neat polypropylene (37.7%) decreased with increasing content of the SSC flour. The X_c of the filled polypropylene composites decreased from 36.4 to 33.3% as the amount of the SSC flour increased from 30 to 60 wt %. The MAPP coupled composites had higher X_c as compared with uncoupled composites (Table V). For example, with the addition of 3 wt % MAPP in the composite filled with 30 wt % SSC flour, X_c was increased from 36.4 to 50.9%. The effect of the MAPP on the X_c of the composites decreased as the SSC content reached to 60 wt%. The X_c of the coupled specimens was higher than that of the neat polypropylene.
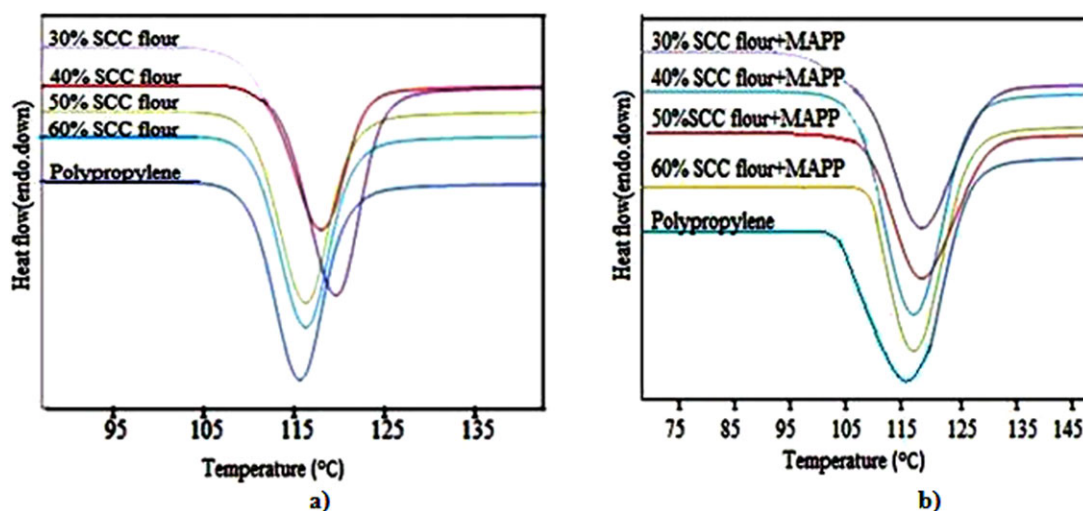

Figure 5. Crystallization peak temperatures of unfilled and SSC flour filled polypropylene composites. (a) Without MAPP. (b) With MAPP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The TS and WA of the polypropylene composites increased gradually with increasing content of the SSC flour but these increments were less than those of wood flour filled polypropylene composites. This was mainly attributed to lower amounts of the hygroscopic materials, cellulose and hemicelluloses, in the cell walls of the SSC flour. The flexural and tensile modulus of the composites significantly improved with increasing content of the SSC flour, in particular beyond 50 wt %. The maximum flexural strength was observed for 40 wt % the SSC flour filled specimens whereas further increment decreased the flexural strength. Tensile strength of the composites significantly decreased with increasing content of the SSC flour. Dimensional stability and mechanical properties of the composites were significantly improved by the coupling agent, which was the MAPP. The increment in the amount of the SSC flour decreased the melting temperature and degree of crystallinity of the neat polypropylene. The incorporation of the MAPP into the composites increased the melting temperature of the composites while the degree of crystallinity was decreased. Based on the findings obtained from this study, the SSC can be efficiently used as reinforcing filler for polypropylene composites used in applications requiring a high dimensional stability such as swimming pool decking and garden decking.

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