Thermal, Mechanical, and Morphological Properties of Maleated Polypropylene Compatibilized *Borassus* Fruit Fiber/Polypropylene Composites

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ABSTRACT: With a view of exploring the potential use of natural recourses, we made an attempt to fabricate new *Borassus* fruit fiber/ polypropylene composites by melt mixing method using 5 wt % of fiber. Fibers were chemically modified by alkali treatment using maleated PP (MAPP) as compatibilizer to improve the adhesion between fibers and matrix. Thermal, mechanical, and morphological properties of untreated, alkali treated, and MAPP modified fiber reinforced composites were explored by thermogravimetric analysis, differential scanning calorimetry, universal testing machine, and scanning electron microscopy (SEM), respectively. Thermal stability of the composites was enhanced to some extent on alkali treatment and addition of MAPP. The tensile strength and modulus, flexural strength and modulus, and impact strength were increased for alkali treated/MAPP composites by 4.5%, 17%, 17.2 %, 9%, and 10% respectively. SEM studies on tensile fractured specimens of unmodified composites reveal the poor fiber-matrix interaction, whereas the interaction is strong with enhanced mechanical properties for modified fiber composites. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Composite materials based on the natural-fiber reinforcement have been the subject of extensive research and development worldwide. The advantages associated with the use of natural fibers as reinforcement in plastics are their biodegradability, low energy consumption, low cost, low density, and high specific properties. Natural fibers like jute, flax, hemp coir, and sisal have all proved to be good reinforcement in thermoset and thermoplastic matrices and are being used in automotive applications, construction as well as in packaging industries.[1–11]

Borassus (Palmyra Palm) is a genus of six species of fan palms, native of tropical regions of Africa, Asia, and New Guinea, economically useful and widely cultivated. The Palmyra palm has been one of the most important trees of Cambodia and India, where it is used in over 800 different ways. The fruits are eaten either roasted or raw, and the young, jellylike seeds are also edi-

ble.[12] These fruits consist coarse and fine fibers. Recently, a significant study on morphology, mechanical, and thermal properties of these fibers was carried out by Obireddy et al. and suggested that these fibers can potentially be utilized as reinforcement component in green composite manufacturing.[13] In an attempt, we recently developed natural fiber reinforced thermosetting (diglycidylphenylphosphate/diglycidylepoxy of bisphenol-A based epoxy) composites, using *Borassus* fruit fiber (BFF) as reinforcement.[14] However, no reports on BFF reinforced thermoplastic composites are available in the literature.

One of the most often used thermoplastics for obtaining composites is polypropylene (PP), but the adhesion of these matrices with natural fibers is rather low due to its hydrophobic nature.[15] On the other hand, the natural fibers have hydroxyl groups in their structure, which promote the polarity to the materials with more hydrophilic character. The combination of hydrophobic and hydrophilic components involves poor
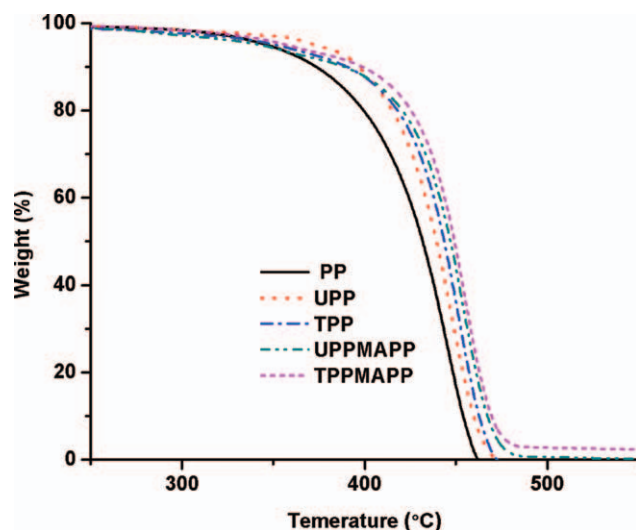
Figure 1. TGA thermograms of PP and composites with untreated, alkali treated fibers, with and without compatibilizer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dispersion and incompatibility between natural fiber and polymer matrix.[16] Though there are many ways to improve the adhesion at the interface of the fiber and matrix,[17,18] addition of maleated PP (MAPP) [grafting of maleic anhydride (MA) on polypropylene (PP)] coupling agent is one of the popular methods to enhance the interface interaction between the fiber and the matrix.[16,19] The coupling agent has polar functional groups, which are able to react with the hydroxyl groups on the surface of the fiber to form ester bonds.[20–24] These bonds induce the compatibilization and the transference of stresses from the polymer to the fiber, promoting better mechanical properties to the material. Literature reveals that the 5 wt % of MAPP is the optimum concentration in the PP matrix.[1,16,25,26] Surface modification of the fibers with NaOH and the addition of MAPP to the matrix lead to considerable improvement in the fiber–ma-
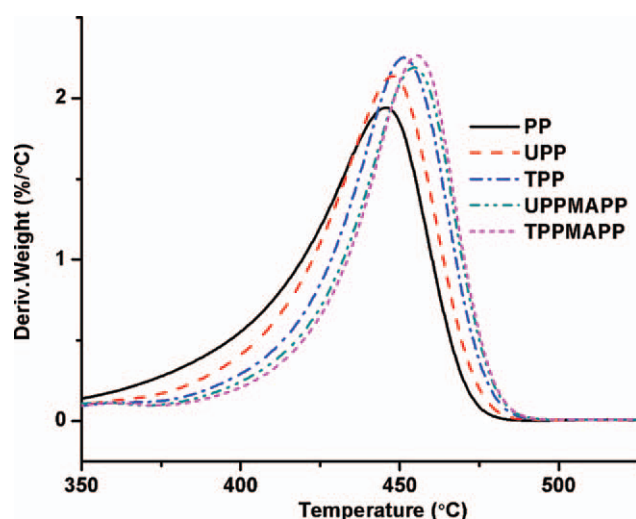

Figure 2. DTG thermograms of PP and composites with untreated, alkali treated fibers, with and without compatibilizer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. DSC thermograms of PP and composites with untreated, alkali treated fibers, with and without compatibilizer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
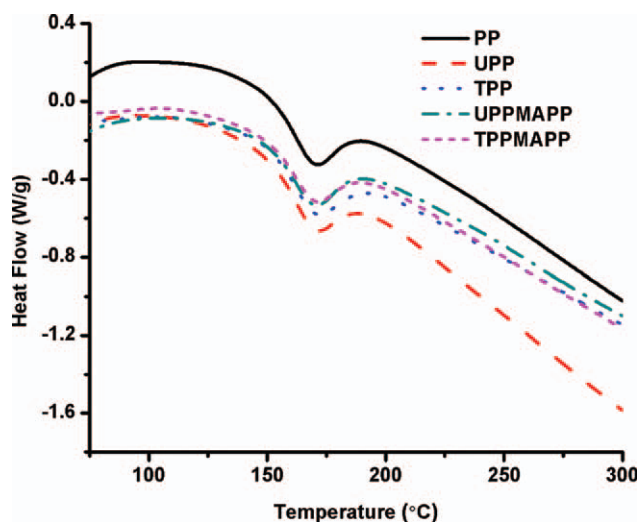
trix adhesion and physicomechanical properties of the resulting composites.[1,25]

This study deals with the investigation of mechanical, thermal, and morphological properties of both alkali treated and untreated *Borassus* fruit fine fiber-PP composites using 5 wt % of MAPP as a compatibilizer while maintaining 5 wt % of fiber loading.

EXPERIMENTAL

Materials

BFF (BFF can be referred as *Borassus* fruit fiber or *Borassus* fruit fine fiber in this paper) were extracted from the dried fruits, as per procedure explained elsewhere[13] and used as reinforcement. The coupling agent, PP-graft-MA (MAPP; Aldrich) and sodium hydroxide (NaOH; Dae-Jung Chemicals) were purchased and used as received. PP (injection grade) was obtained from Honam Petrochemical corporation, South Korea.
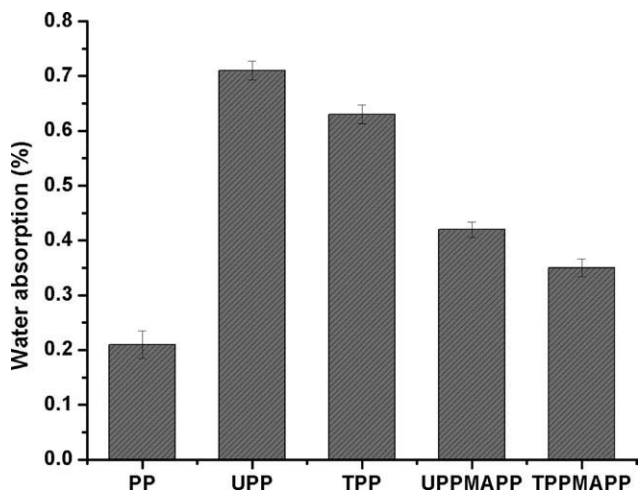

Figure 4. Water absorption properties of PP and composites with untreated, alkali treated fibers, with and without compatibilizer.
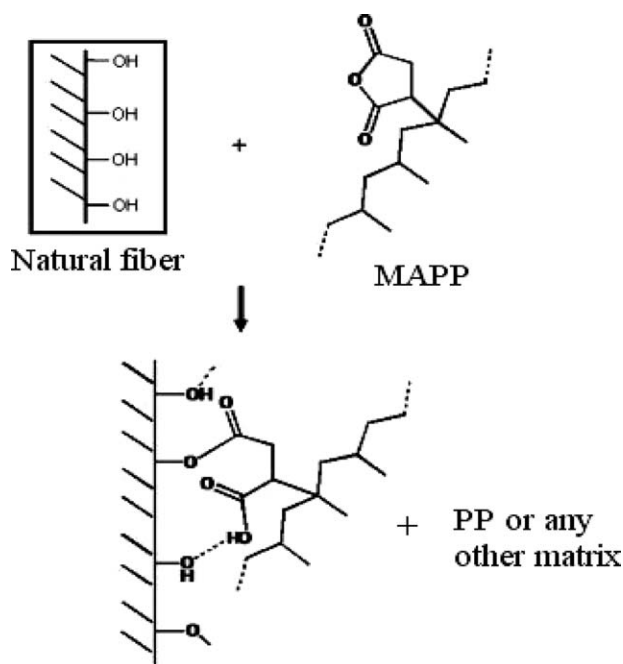
Figure 5. Mechanism of interactions between coupling agent (MAPP) and the hydroxyl groups on the surface of natural fibers.

Fiber Surface Modification

The BFF were treated with 4% NaOH for 5 h at room temperature maintaining the liquid ratio of 1 : 20 and washed with distilled water until the fibers showed no residual NaOH (neutral pH) and dried in a vacuum oven at 70°C for 24 h. For the comparison, fiber without alkali treatment was prepared by immersing them in water for 12 h to remove the dust, and allowed to dry at 70°C for 12 h. The dried alkali treated and untreated fibers were chopped into 5–10 mm, stored in a sealed plastic bag for further processing.

Composites Fabrication

PP, short fine fiber and MAPP (for modified composites) were mixed first by melt-compounding using twin-screw extruder
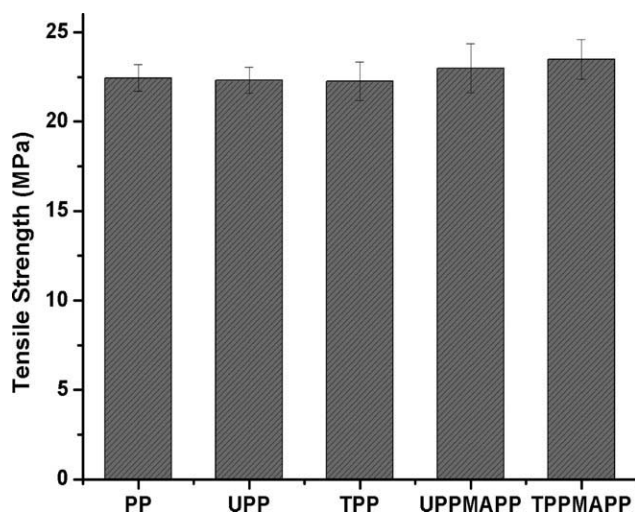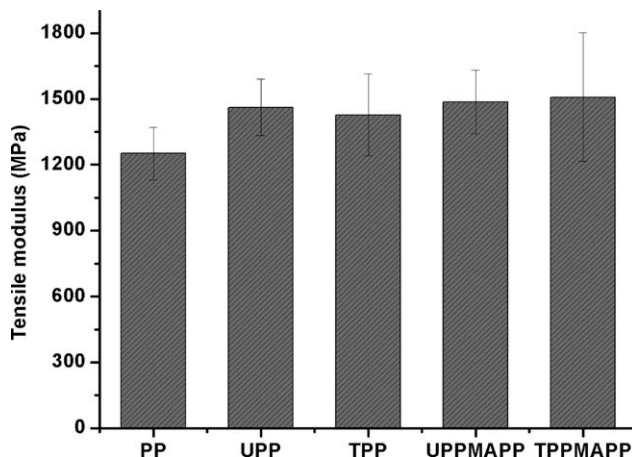

Figure 7. Tensile modulus of PP and its composites with untreated, alkali treated fibers, with and without compatibilizer.

(PRISM, TSE 16TC, Thermoelectron Corporation). The temperatures of barrel and the die were maintained at 190°C during extrusion and the screw speed was 120 rpm. Subsequently, the extrudate was palletized, dried, and injection molded (WOOJIN, SELXR CO. LT) into standard specimens for mechanical properties testing. The injection-molding temperature and pressure were 200°C and 60 MPa, respectively. Before the preparation of the composites, all the components were first dried in an oven at 80°C for at least 24 h.

Characterization

Thermal Properties. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on untreated and alkali-treated BFF/PP/MAPP and virgin PP composites using simultaneous Mettler TA 3000 thermal analyzer in nitrogen atmosphere with a heating rate of 20°C/min (weight of the sample 3–5 mg) in the temperature range of 35–700°C.

Water Absorption. Moisture uptake was determined as per the ASTM D570-98. For each test, three test specimens (80 × 24.6

Figure 6. Tensile strengths of PP and its composites with untreated, alkali treated fibers, with and without compatibilizer.
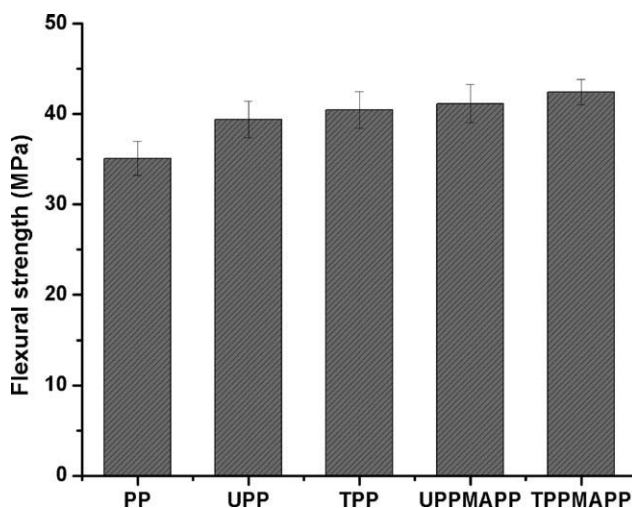

Figure 8. Flexural strengths of PP and its composites with untreated, alkali treated fibers, with and without compatibilizer.
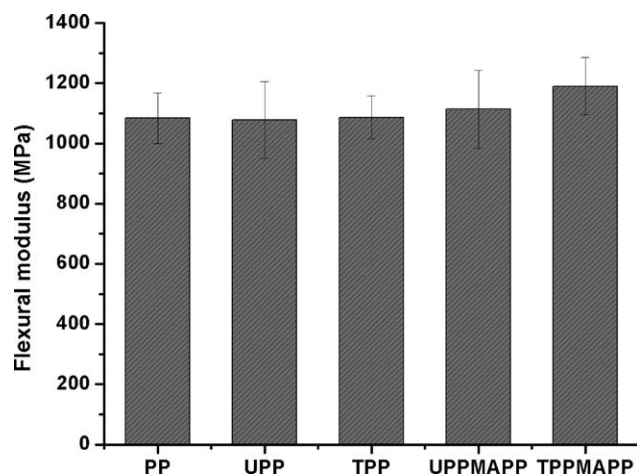
Figure 9. Flexural modulus of PP and its composites with untreated, alkali treated fibers, with and without compatibilizer.
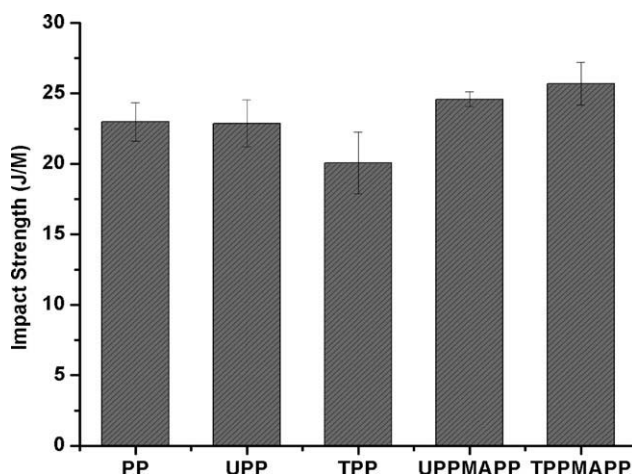

Figure 10. Impact strength of PP and its composites with untreated, alkali treated fibers, with and without compatibilizer.

× 3.2 mm³) were used. Prior to absorption experiments, the samples were dried in an oven at 50°C and then allowed them to cool to room temperature in a desiccator until the weight (dry weight) stabilized before weighing them to the nearest 0.001 g. The specimens were then immersed in distilled water at room temperature for 24 h. The specimens were taken out from the water and all surface water was removed with a clean dry cloth and immediately weighed (wet weight) to the nearest value 0.001 g. The percentage increase in weight during water immersion was calculated using the following equation.

$$\text{Water absorption}(\%) = \frac{\text{Wt. of the wet composite} - \text{Wt. of the dry composite}}{\text{Wt. of the dry composite}} \times 100$$

Mechanical Properties. Tensile and flexural strengths were measured using standard computerized Instron 3369 Universal testing machine. The tensile strength was measured as per ASTMD 6389 standards [165 mm× 13mm (Narrow width) × 3 mm specimens] with a cross-head speed of 5 mm/min. The load was 10 kN. The flexural strength of the samples was measured according to ASTM D790-03 with a cross-head speed of 2 mm/min using three-point bending mode (specimen dimensions of 80 × 24.2 × 3.2 mm³) tests. Impact test was performed using an Izod impact testing machine, supplied by International equipments, Mumbai, India. Rectangular strips of 75 × 12.7 ×

3 mm³ were used as per ASTM 256-88 specifications. The impact test was carried out at room temperature and impact energy was reported in J/m. For each test, five replicate test specimens were taken and the average value was recorded.

Morphology. Scanning electron microscope (SEM; JEOL JSM Model 6360) was used to study the morphology of the composites. The tensile fractured surface of the samples was sputter coated with gold using an Auto fine Coater (JEOL JFC-1600) prior to the fractographic examination.

RESULTS AND DISCUSSION

The prime work relating to the extraction of the BFF from fruit, study of the chemical composition, and the influence of the alkali treatment on the properties of the fibers were reported in the literature.[13] In this study, the SEM analysis of alkali treated fibers showed the roughness of the fibers after alkali treatment, suggested the removal of impurities; facilitate good interaction between fibers and matrices. The unique elastic nature, high modulus is one of the prime reasons for the choice of these fibers.

In this study, composites were prepared with untreated BFF/PP without compatibilizer (UPP), treated BFF/PP without compatibilizer (TPP), untreated BFF/PP/MAPP (UPPMAPP), and treated BFF/PP/MAPP (TPPMAPP) while maintaining fiber and MAPP of 5 wt %.

Table I. Thermal, Physical, and Mechanical Properties of Composites with Alkali Treated and Untreated BFF with MAPP

| Name of the sample	Weight loss 5% (°C)	T_{max} (°C)	T_m (°C)	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)	Water absorption test (%)
PP	347	445	170	22.451	1250.65	35.09	1083.24	22.82	0.21
UPP	374	448	172	22.318	1460.76	39.40	1077.37	23.89	0.71
TPP	357	452	172	22.262	1411.34	40.47	1086.27	21.81	0.63
UPPMAPP	344	455	173	22.986	1486.345	41.16	1113.39	24.93	0.42
TPPMAPP	358	457	173	23.487	1508.14	42.40	1189.96	25.36	0.35
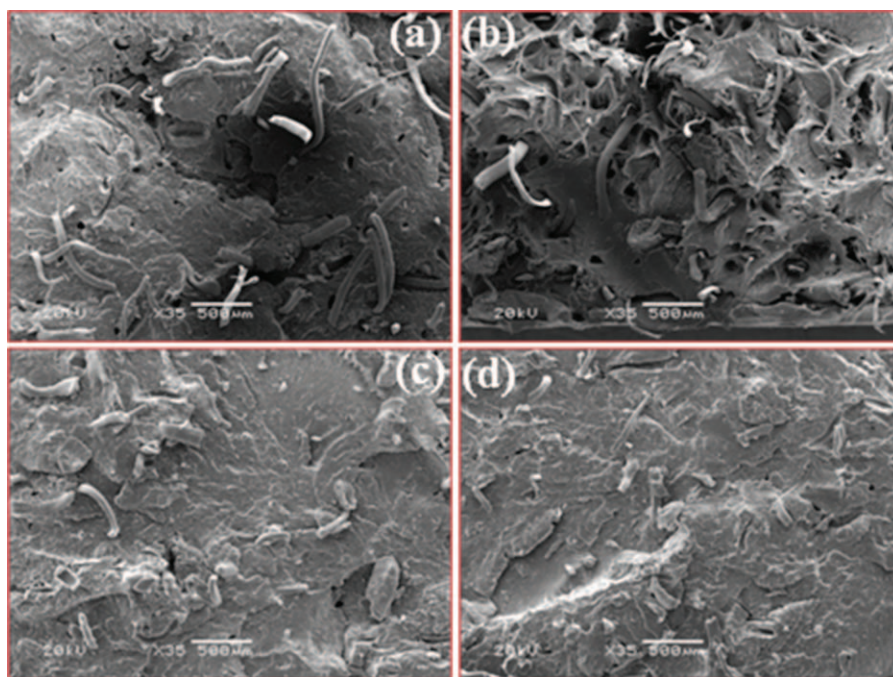
Figure 11. SEM micrograph of the tensile fractured surfaces: (a) untreated, (b) alkali treated, (c) untreated-MAPP, and (d) alkali treated-MAPP composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Properties

To study the thermal stability of the untreated, alkali treated BFF/PP/MAPP composites, thermogravimetric experiments were performed and the results are given in Table I and graphically shown in Figures 1 and 2. Temperature corresponding to 5% weight loss in TGA, and T_{max} in DTG was viewed as a rough index of thermal stability. Single-step degradation was observed in the case of virgin PP as well as in its corresponding composites. Except UPPMAPP (344°C), all the remaining samples showed higher thermal stability (357–374°C) than that of virgin PP(347°C).When compared the treated and untreated fiber composites, the treated one (TPP) demonstrated higher T_{max} (452°C) in DTG peak than untreated one (448°C). This may be due to the slow and continuous loss of hydroxyl and polar components of the untreated fiber.[1] Similarly, the treated fibers with compatibilizer (TPPMAPP) showed higher T_{max} (457°C) compared to the untreated fiber composites (455°C) with compatibilizer (UPPMAPP). The molecular chain extension of the matrix and the increase in molecular weight due to ester bond formation might be the possible reason for this marginal increase in T_{max} for TPPMAPP.[27] The DSC thermograms of virgin PP and its corresponding composites are depicted in Figure 3 and the melting temperature (T_m) was summarized in Table I. The T_m of virgin PP was observed around 170°C, which increased marginally to 172–173°C with the incorporation of natural fiber and MAPP confirming the effect of the reinforcement and compatibilizer.

Water Absorption Test

Moisture absorption of natural fiber/plastic composites is one major concern in their outdoor applications. They have an undesirable property, namely, hygroscopicity of their chemical constituents, thus affecting their long-term performance. For example, increased moisture decreases their mechanical properties[28,29] provides the necessary condition for biodegradation, and changes their dimensions.[30,31] Figure 4 and Table I show the trend of the water absorption property of the PP and its corresponding composites. From the data, we can see that the water absorption is comparatively less in the composites with treated fibers (TPP) than the untreated fiber composites (UPP). This is because of the fact that the action of alkali treatment, removes a substantial portion of uronicacid, a constituent of hemicellulose and other polar groups which are important factors for the water absorption.[1] On the other hand, the incorporation of MAPP also provides hydrophobicity to the fibers because of the esterification of the anhydride groups of MAPP with the hydroxyl groups of the natural fibers and the establishment of hydrogen bond between the hydroxyl groups of the fiber and the remaining carboxylic group of the MAPP. The expected mechanism is shown in Figure 5.[15]

Mechanical Properties

Figures 6–10 and Table I show the mechanical properties such as tensile strength, tensile modulus, flexural strength, flexural modulus, and impact strength of virgin PP and its corresponding untreated, alkali treated fiber composites with and without MAPP. The results indicated that the mechanical properties are influenced by the alkali treatment and presence of MAPP. Mechanical properties of untreated and alkali treated fiber composites without compatibilizer were inferior to those with compatibilizer. In general, cellulose is not compatible with nonpolar PP matrix causes poor adhesion between fiber and matrix results in lowering the mechanical properties. However, for UPPMAPP, the mechanical properties were increased with MAPP. It is reported that the incorporation of compatibilizer
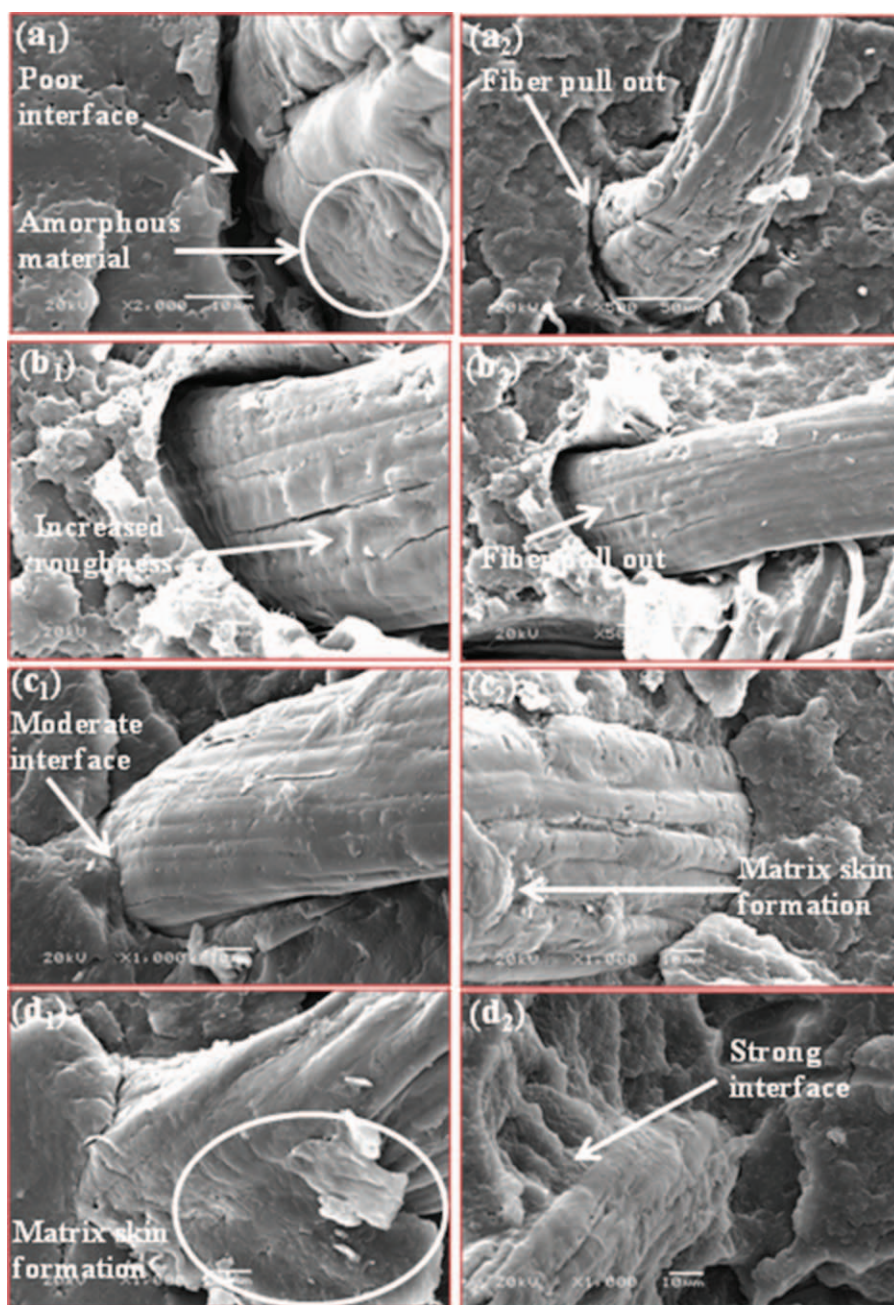
Figure 12. Interfaces of the tensile fractured: (a) untreated, (b) alkali treated, (c) untreated-MAPP, and (d) alkali treated-MAPP composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reduces the surface hydrophilicity of the fibers, leads to enhance fiber wetting and dispersion within the matrix [Figures 11(c) and 12(c)], decreases the water absorption and increases the mechanical properties.[1,32] The tensile and impact strength of treated fiber composites (TPP) is lower than that of PP composites; this may be due to crystalline nature; this may be due to crystalline nature of the fibers after removal of the amorphous impurities [(Figure 12 (b)] and similar observations were found in the literature [1]. In case of flexural properties, an increasing trend was observed for UPP, TPP, UPPMAPP, and TPPMAPP. The tensile strength and modulus, flexural strength and modulus, and impact strength were increased for TPPMAPP by 4.5%,

17%, 17.2 %, 9%, and 10%, respectively. This indicates clearly the reinforcing effect imparted by the fibers within the matrix. The results of BFF/PP composites indicates that these composites can also be an alternative materials for composites application similar to other important natural fiber reinforced (jute, banana, hemp, etc.) composites.[1,3,15,27,33]

Morphology

Figures 11 and 12 show the SEM photographs of tensile fractured surfaces and interfaces of fiber reinforced composites recorded at different magnifications. As evidenced from Figures 11(a) and 12(a) of UPP composites, fiber pull out from the

matrix during fracture process indicating poor interfacial interaction between fiber and PP matrix causes poor mechanical properties. We can also see the presence of amorphous hemicellulose [Figure 12(a)] on the surface of untreated fibers. Treated fiber composites [Figures 11(b) and 12(b)] also exhibits fiber pull-out on tensile stress; however, the fibrils are well trapped within the matrix attributed the removal of amorphous hemicellulose,[34] increases the roughness of the fiber surface as shown. On the other hand, the treated fiber composites with compatibilizer (TPPMAPP) exhibits improved adhesion with matrix skin formation [Figures 11(d) and 12(d)]. Hence, fibers have been broken during the tensile test, which indicates the strong interactions between fiber and matrix. In the case of UPPMAPP, the similar trend was noticed as shown in Figures 11(c) and 12(c), but the fiber-matrix interface is moderate compared with TPPMAPP. This is due to the synergetic effect of alkali treatment and compatibilizer in TPPMAPP. The interactions between fiber and compatibilizer are shown in Figure 5.[15]

CONCLUSIONS

The prime objective of this study is to explore the potential use of BFF as a green composite reinforcement. BFF/PP composites were prepared by melt mixing the short fiber and PP in twin screw extruder and injection molding technique for the first time. In addition to the alkali treatment of fiber, MAPP was also added for further enhancement of interfacial bonding between fiber and matrix. Thermal, water absorption, and mechanical properties were evaluated. Thermal stability of alkali treated composites in the presence of MAPP showed somewhat higher thermal stability compared with other samples. The addition of MAPP greatly reduced the water absorption property of UPPMAPP and TPPMAPP composites by 41% and 50%, respectively, than that of the untreated fiber composites (UPP). The tensile strength and modulus, flexural strength and modulus, and impact strength were increased for TPPMAPP by 4.5%, 17%, 17.2%, 9%, and 10%, respectively. SEM analysis revealed that the addition of MAPP to the treated fiber composites (TPPMAPP) greatly enhances the adhesion between the fiber and matrix and hence mechanical properties are improved.

ACKNOWLEDGMENTS

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