

Hybrid Natural Fibers/Isotactic Polypropylene Composites with Degraded Polypropylene as Compatibilizer

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Abstract

Interest on the field of natural fiber-thermoplastic composite has been considerably increased because of the new environmental legislation to use biodegradable fibers instead of pollution causing synthetic fibers like carbon, glass etc. In this investigation, an attempt was taken to use of inexpensive areka palm leaf fibers (APLF) as reinforcement of polypropylene (PP) composites. Degraded polypropylene (DgPP) was added in composites as a compatibilizer of hydrophilic natural fiber and hydrophobic PP matrix. The mechanical properties (tensile and flexural) of composites were more pronounced with the addition of 5 wt% DgPP. The weight percentage of APLF and PP were varied to get better mechanical strengths of composites. The (tensile and flexural) strengths were increased upto 10 wt% fiber loadings and thereafter decreased whereas the (tensile and flexural) modulus were increased with the increases of fiber loading upto maximum (20 wt%). Hybrid fibers composites were also fabricated with different combinations of APLF, pineapple leaf fiber (PALF), DgPP and PP (5+5+5+85 wt% and 5+10+5+80 wt%). The hybrid fiber composite with (5+5+5+85) wt% combination was exhibited superior mechanical properties than unreinforced PP and other composites. The water absorption properties of the composites were also studied.

Keywords

Areka Palm Leaf Fiber, Polypropylene, Hybrid Natural Fiber Composites, Mechanical Properties, Water Absorption

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1. Introduction

To protect the earth from 'white pollution', there is no alternative to use bio-based materials rather than synthetics. Natural fibers are the major contributors of daily needed bio-based materials. They have wide range of applications in textile, construction, paper, cosmetics, pharmaceutical, medical, automobile etc. Newly discovered composite technology is extended their use in different industrial applications. The conventional natural fibers such as jute, coir, sisal, hemp, wood flour etc. has been used for the manufacture of composite materials from last three decades

[1-4]. Recently, some non-conventional agro-residual fibers e.g. okra, banana, pineapple leaf, corn husk, areka palm leaf etc. have attracted much attention as a filler of polymer based composite materials for their low cost, high modulus and renewability [5-9]. The reinforcement of those natural fibers is considerably improved the mechanical properties of polymer composites. However, such mechanical properties of natural fiber composites are much lower than glass or other high performance fibers composites. The coarseness, void content, cluster formation and low interface properties are the barriers of the proper distribution of fiber in composites and hence showing ruthless performance. However, the combination of two or more natural fibers can improve the

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mechanical properties of composites. The hybrid fibers, having different shapes and dimension, are rarely make cluster which may gives better mechanical properties as compared to mono fiber reinforced composites [6, 10].

Polyolefines are commonly used as matrix materials for natural fiber reinforced composites. Among the polyolefins, polypropylene (PP) provides most advantages with regard to economic (price), ecological (recycling behavior) and technical requirements. PP in terms of stereoregular is divided into isotactic PP, syndiotactic PP and atactic PP. Isotactic PP is conventionally used in natural fiber composites, medical goods, fibers, raping films etc. [11-12]. Whenever, PP is used as matrix of natural fibers, a compatibilizer is compulsory for composite performance. The compatibilizers may play an important role in converting the hydrophilic fibrous cellulose surface to a hydrophobic one by the reaction. Maleic anhydride grafted PP has been used as models of PP polymer-type compatibilizers. MAPP enhanced the interfacial adhesion between non-polar PP and polar natural fibers through the interaction between the hydroxyl groups of fibers and the carboxyl groups of MAPP. PP chains of MAPP also diffused into PP matrix leading to the physical entanglement of PP molecules [13-15]. Therefore, the compatibilizer acts as like bridge of polar and non-polar terminal. However, due to toxic nature, maleated compounds are not preferably used in medical field. The degraded polypropylene might be used as alternative compatibilizer of PP based composites. Because the partially degraded PP contains vinylidene [16] groups, which may be able to form chemical bond with natural fiber. In addition, degraded PP is nontoxic and can easily obtain from an oxidative degradation reaction of PP at an elevated temperature and in sunlight.

Araka palm leaf fiber (APLF) is composed by 75% α -cellulose, 12% hemicelluloses, 10% lignin, and 3% others matter, viscosity average molecular weight 132,000 and degree of crystallinity 70% [7]. In previous study, APLF reinforced PP composites were shown brilliant mechanical, thermal and water absorption properties [7]. With that continuity, hybrid fibers i.e. combination of APLF and pineapple leaf fiber (PALF) reinforced composites have been prepared at the present investigation. The performance of degraded PP, the effect of fiber loading and hybrid fiber ratio on the mechanical and water absorption properties of composites have also been investigated.

2. Experimental

2.1. Materials

The aceka palm (*Areca catechu*) leaf and pineapple (*Ananas comosus* L.) leaf were collected from local agricultural farm

of Rajbari, Bangladesh. The fibers were extracted by water retting (Figure 1). Degraded PP (DgPP) was prepared according to the previous study [16]. The densities (in g/cm³) of fibers were measured by the Davenport density gradient column [17]. The isotactic polypropylene was obtained from Japan Polypropylene (Yokkaichi, Japan), Japan. The properties of filler and matrix are given in Table 1.

Table 1. Properties of fillers and matrix [7].

	PP	PALF	APLF
Diameter (μm)	--	18-20	30-50
Density (g/cm^3)	0.905	1.2	1.5
Tenacity (MPa)	31	290	100
Moisture content (%)		12	13
α -cellulose (%)	-	70-74	70-75
Hemicellulose (%)	-	10-14	12-15
Lignin (%)	-	8-12	5-10



Figure 1. Image of (a) areca palm leaf, (b) pineapple leaf, (c) areca palm leaf fibers, (d) pineapple leaf fibers and (e) short hybrid fiber/PP composite.

2.2. Methods

2.2.1. Scoring of Fibers

Scouring was carried out by the use of surface active agents, such as Na_2CO_3 and soap. APLF and PALF were scoured in a solution containing 6.5 g of soap solution and 3.5 g of Na_2CO_3 per liter at 70-75^oC for 30 minute in large beaker. The fiber to liquor ratio was maintained at 1: 50. The fiber was thoroughly washed with distilled water and dried in open air and finally stored in desiccators.

2.2.2. Preparation of Composites

Composites were fabricated by hot pressed compression molding. The proportions of fibers, DgPP and PP in composites are shown in table 2. The fibers were cut into 2-3 mm length and kept in oven at 80 ^oC for 24 h to remove moisture. Then the fibers, DgPP and PP were mixed homogeneously with a mechanical blender for 3 min at 450 rpm. Composites were fabricated on a stainless steel mold

which was sprayed by silicon mold releasing agents for easy opening the composite samples. The mixture of filler and matrix was poured into the mold. The mold was then placed in between the hot plates of compression molding machine. Pressure and temperature were fixed to 50 kN and 180 °C respectively. The heating was gradually increased upto maximum 180 °C. After 30 min, heating was stopped and mold was cooled by tap water through the outer area of the heating plates. Finally, composite was taken out from mold and cut for the mechanical testing.

Table 2. Weight fraction of filler, compatibilizer and matrix of composites.

Composite Samples	APLF, %	PALF, %	DgPP, %	PP, %
C1	0	0	0	100
C2	5	0	0	95
C3	5	0	5	90
C4	10	0	5	85
C5	20	0	5	75
C6	5	5	5	85
C7	5	10	5	80

2.2.3. Tensile Test

Tensile tests were carried out using Universal Testing Machine (Hounsfield UTM 10KN) according to ASTM methods D638 at a crosshead speed of 50 mm/min and gage length of 50 mm [18]. All obtained results are the average of 10 measurements. The tensile strength (σ_t), Young’s modulus (E_t) and elongation at break (% ϵ) was calculated according to the following equations:

$$\text{Tensile strength } \sigma_t = P/A \tag{1}$$

$$\text{Young’s modulus } E_t = \Delta(\text{stress})/ \Delta(\text{strain}) \tag{2}$$

$$\text{Elongation at break, } \% \epsilon = [(L-L_0)/L_0] \times 100 \tag{3}$$

Where, P is the test load, A is cross-sectional area, L_0 and L are original measured length and length of the specimen at breaking point respectively.

2.2.4. Flexural Test

The three-point bend flexural tests were measured by Universal Testing Machine (Hounsfield 10KN) in accordance

with ASTM D790M [19]. A span of 60 mm was employed maintaining cross-head speed of 5 mm/min. Flexural strength and flexural modulus were measured using the following equations [20]:

$$\text{Flexural strength, } \sigma_f = 3PL/2bd^2 \tag{4}$$

$$\text{Flexural modulus, } E_f = mL^3/4bd^2 \tag{5}$$

Where P is the maximum applied load, L is the length of support span, m is the slope of the tangent, b and d are the width and thickness of the specimen, respectively.

2.2.5. Water Absorption Test

The water absorption test of was performed in accordance with ASTM D570 [21]. The specimens were dried in an oven at 80 °C for 24h prior to testing. Then those samples were soaked into water at room temperature. The composites were taken out from water after every 24 h and all surface moisture was removed with tissue paper. The increase of weight during the immersion was calculated by following equation:

$$\text{Water absorption \%} = [(W-W_0)/W_0] \times 100 \tag{6}$$

Where W_0 and W is the initial weight and weight after water absorption, respectively. The data reported are average value obtained from ten separate samples of each bio-composite.

2.2.6. Scanning Electron Microscopy

Scanning electron microscope FEI QUANTA 200 3Dwas used to analyze the surface morphology of composite samples with accelerating voltage of 10kv. The surface was coated 3 nm thick gold before analysis.

3. Results and Discussion

The aim of this work was to study the mechanical and water absorption properties of the APLF-PALF hybrid fiber PP composites. The partially degraded polypropylene was introduced as a compatibilizer of composite and explored its impact on mechanical properties.

Table 3. Mechanical properties of virgin PP and composites.

Samples	ρ (g/cm ³)	σ_t (MPa)	E_t (GPa)	ϵ (%)	σ_f (MPa)	E_f (MPa)
C1	0.990	22.0±2.3	0.99±0.12	4.13±2.31	24.2±3.1	322±33
C2	1.003	20.8±4.9	1.52±0.38	1.18±0.56	23.6±5.7	312±68
C3	1.050	22.2±3.1	1.91±0.18	1.27±0.50	25.3±3.9	349±45
C4	1.104	23.2±3.2	2.02±0.23	2.05±0.72	29.6±4.0	434±72
C5	1.095	19.0±4.2	2.03±0.28	1.72±0.63	25.5±4.8	445±68
C6	1.050	24.2±2.9	2.33±0.20	2.24±0.73	30.1±4.2	446±53
C7	1.100	21.1±3.6	2.40±0.22	2.37±0.70	26.7±4.4	396±46

Density (ρ), tensile strength (σ_t), tensile modulus (E_t), elongation at break (ϵ), flexural strength (σ_f) and flexural modulus (E_f)

3.1. Tensile Properties

The tensile properties of virgin PP, short APLF and APLF-

PALF hybrid fibers reinforced polymer composites were compared terms on the effect of fiber loading, effect of DgPP compatibilizer and effect of hybrid fiber ratio.

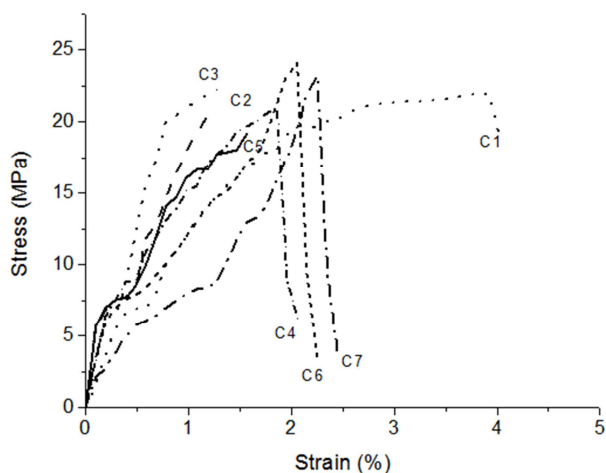


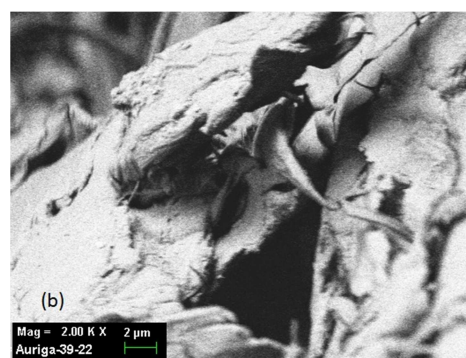
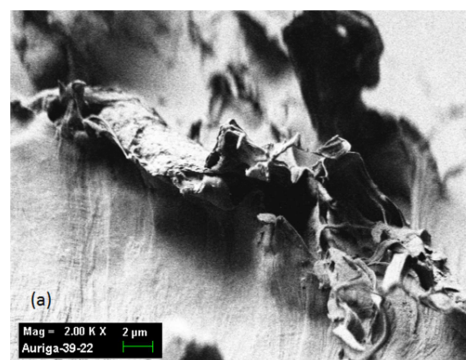
Figure 2. Tensile stress-strain curves of virgin PP and composites.

The tensile data of stress-strain curves (Figure 2) are put into Table 3. From the results, it is evident that the tensile strength (σ_t) of C2 is lower than C1. This may be due weak interfacial properties of fiber and polymer without presence of compatibilizer [2]. This behavior of the composites to be expected due to the destructive deformations of fiber, by which the formation of void in the PP matrix is simultaneously caused. Incorporation of DgPP compatibilizer, APLF/PP composites were exhibited superior tensile strength compare to composite C2. The DgPP may be enhanced the interfacial adhesion between non-polar PP and polar APLF through the interaction between the hydroxyl groups of fibers and the vinylidene groups of DgPP [22]. In addition, PP chains of DgPP perhaps diffuse into PP matrix leading to the physical entanglement of PP molecules. The increments of tensile strength (σ_t), tensile modulus (E_t) and elongation at break ($\% \epsilon$) of C3 are 6.7, 19.1 and 7.6% respectively from C2. On the other hand, the values of σ_t and E_t of C3 are higher than C1. The enhancements of the tensile strength and modulus of composites are probably due to their chemical structures, crystallinity as well as bond formation with couplings agent DgPP. However, the elongation behavior of C3 is lower than C1. This may due to the short length fibers cannot extent more under tensile loads and therefore crack propagation of composite is higher [6].

The effect of different fiber loadings (5, 10 and 20 wt%) on the tensile properties of composites are also represented by table 3. Composites C3, C4 and C5 are composed by 5, 10 and 20 wt% loaded APLF, respectively. It is evident that the value of σ_t was increased with the increases of fiber addition upto 10wt% and thereafter it decreased. Upto 10 wt% fiber loading, the composite bear the greater load and make resistance to slip as in the case of age hardening. It may be due to, 10wt% loaded short fibers were finely distributed in the composites and above that loading, the fibers were coagulated as like bundle. That bundle of fibers were

fractured during load to slips and does not make resistance to slips [23]. Consequently, tensile strength of 20wt% fiber loaded composite was decreased. It has been also seen that, the value of E_t was increased upto maximum at highest fiber loading (20 wt%) whereas elongation at break ($\% \epsilon$) was decreased continuously with the increases of fiber loading. By the increases of fiber loadings, the crystalline portion of composites increases which may gives more stiffness of composites and consequently decreases elongation [7].

The reinforcement of two or more fibers in a single matrix leads to hybrid composites with a great diversity of material properties. It appears that the behavior of hybrid composites is simply a weighted sum of the individual components so that there is more favorable balance of properties in the resulting composite material. In this study, hybrid composites were prepared with the combination of APLF and PALF with two different blend percentage in PP matrix and their tensile properties were also tabulated in Table 3. It has been realized that the tensile strength of composite C6 was greater compared to the other composites whereas tensile modulus was found higher for composite C7. The tensile properties of composites are related to surface area of fibers, fiber density as well as their homogeneous distribution into matrix. Generally, fibers are functioned to neutralize the stress when composites are placed under tensile loads. Due the increase fibers surface area in hybrid composites, the physical interaction and stress transfer in unit area might be received higher than mono APLF composites. Previous studies were also showed the improvement of stress transfer in hybrid fibers composite compared to the mono fiber composite [24].



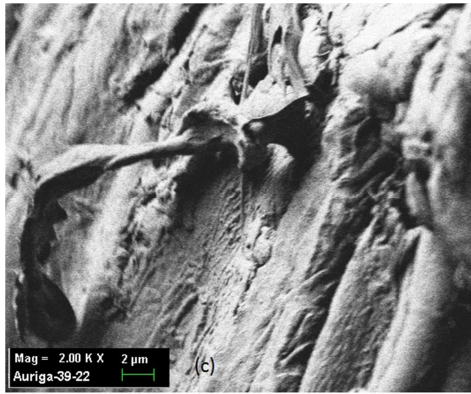


Figure 3. SEM images of tensile fractured surface of (a) unreinforced PP C1, (b) composite C5 and (c) composite C6.

The scanning electron micrographs (SEM) of tensile fracture surface were studied to predict the adhesion between the matrix and its reinforcing fibers. From the SEM images of Figure 3, it is clearly observed that the fractured composite of C5 contain hole due to pull-out of fiber. On the other hand, C1 and C6 composites are ruined rather than fiber pull-out. It was reported earlier that the criterion for optimum adhesion between the matrix and its reinforcing fiber is based on maximization of the wetting tension [25, 26].

3.2. Flexural Properties

Table 3 represents the effect of DgPP and fiber loadings on the flexural properties of composites made with mono and hybrid fibers. DgPP functionalization were seemed to leading to strength improvement of composites. Polypropylene chains of the DgPP smooth the different surface energy values of matrix and reinforcement fiber, helping to achieve a better wetting of fibers in the melted polymer, and as a result it improves the interfacial adhesion. It is also seen that the values of flexural strengths of composites C3, C4 and C5 are varied for different fiber loadings. As like tensile strength, the higher flexural strength was found for 10 wt% fiber loading. Flexural modulus of both mono and hybrid fibers composites are better than that for unreinforced polypropylene because fibers had higher stiffness than polymer. Again, flexural strength of the hybrid fiber composite C6 was found higher than the any other composites. As mentioned earlier, a higher compatibility and dispersion in the hybrid composites was achieved; this led to better stress-transfer ability in the composites. Hence, better flexural properties were found for the hybrid composites [20].

3.3. Water Absorption

The relationship between water absorption and immersion time of unreinforced PP, mono and hybrid fibers composites at various fiber contents is shown in Table 4. For all the composites, the water absorption was increased with increases of immersion time. The water absorption of the

mono and hybrid fibers composites were greater than unreinforced PP. Because of the hydrophilic character of the natural fibers, water absorption percentages of composites were increased. Moreover, water absorption of the composites were increased with increases of fiber content. However, DgPP was slightly reduced water absorption of the composites. The compatibilizer DgPP forms the strong interfacial bonding between fibers and polymer matrix which was caused the limited water absorption of the composites. Among the composites, C6 composite showed the lowest water absorption.

Table 4. Water absorption properties of composites at room temperature.

Samples	Water absorption(%)			
	0h	24h	48h	72h
C1	0	0.05	0.20	0.40
C2	0	1.62	2.46	2.72
C3	0	1.11	1.53	1.52
C4	0	2.08	3.18	3.12
C5	0	4.73	7.05	7.06
C6	0	0.95	1.35	1.36
C7	0	1.97	2.85	2.86

4. Conclusions

Two different nonconventional agro-residual fibers were fruitfully introduced for making composites with PP matrix. The compatibilizer degraded polypropylene was played a great role to improve the mechanical properties of the composites. 10 wt% fiber loaded composite was showed greater tensile and flexural strengths, 20 wt% fiber loaded composite was showed greater tensile and flexural modulus while elongation at break was decreased with the increases of fiber loadings. The hybrid fiber composites were showed better properties than those of mono fiber composites.

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