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Compression Molding of Flax Fiber-Polypropylene Composites: Factors Affecting Selected Properties

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ABSTRACT

Natural fibers have the potential to be used as reinforcement in thermoplastics, but they may have some undesirable effects on the mechanical and physical properties of the product. In this study, oilseed flax fiber was used as reinforcement for fiber-polypropylene composite manufactured by compression molding. For this purpose, retted flax fiber was used in different forms: untreated, sodium hydroxide treated and bleached (sodium hypochlorite treated), added at 15 and 30% of the total product mass. To investigate the effect of compatibilizer on product properties, maleic anhydride grafted polypropylene(MAPP) was added at 5% by mass in the formulations. After preparation of different formulations (12 formulations containing PP and flax fiber with or without MAPP), they were extruded in a single-screw extruder and the extrudates were pelletized to be formed further using compression molding. Typical mechanical and physical tests including: tensile strength, bending strength, water absorption and density were performed to evaluate the effect of different parameters on product quality. Results from the measurements indicated that fiber loading without compatibilizer caused inferior properties of composite especially tensile strength (even compared to virgin polypropylene), however (alkaline treated or bleached) fiber loading besides compatibilizer resulted in composites with favorable properties, especially improved mechanical properties.
Keywords: flax, fiber, polypropylene, composite, compression molding, tensile strength, bending strength, water absorption, density

INTRODUCTION

Natural fibers depending upon the source are classified into three types, namely: seed hair (cotton), bast fibers (ramie, jute and flax) and leaf fibers (sisal and abaca). Jute, ramie, flax, and sisal are the most commonly fibers which are used for polymer composites (Nabi Saheb and Jog 1999)**.** Natural fibers as fillers or reinforcements in biocomposites have some advantages including: low density, low cost, availability, biodegradability, no health hazard, non abrasion and high filling potential and high stiffness as well. Also, they can be produced with low investment at low cost, recyclable, and good thermal and acoustic insulations (Brouwer 2000; Nabi Saheb and Jog 1999)

The primary limitation of agro-fibers is the lower processing temperature permissible due to the degradation of lignocellulosic materials at high temperatures such that processing temperatures are limited to about 200°C. This limits diversity of the polymers that can be used with agro-fibers to commodity thermoplastics such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). There are also some other limitations including high moisture absorption and consequently swelling and dimension instability of the product, poor dispersion in polymer matrix, lower impact strength, variable quality, low durability without treatments and poor fire resistance (Rowell et al. 1986; Brouwer 2000).The inherent incompatibility of hydrophilic cellulose fibers with hydrophobic thermoplastic polyolefin usually yields poor interfacial adhesion, which results in impaired properties to the final products. For efficient transfer of stress from the matrix to the fibers, many works have been done to improve the interfacial adhesion, including physical methods (such as corona or plasma discharges) and chemical methods (pretreatment of fiber surfaces by coupling agents, such as silanes and isocyanates, and/or modification of the matrix by grafting with reactive moieties, such as acrylic acid, acrylic esters, maleic anhydride, etc.). Of all these attempts, maleic anhydride grafted polyolefines were found to be most efficient for composites made of fibers and polyolefin matrixes (Nabi Saheb and Jog 1999; Bledzki and Gassan 1999).

Despite positive influence of coupling agents in the enhancement of interaction between fiber and the matrix, the use of such additives reduces flow properties of the composite considerably because of the improvement of interactions and consequently, the reduction of viscosity of molten high density polyethylene-based composite. This can be compensated by contribution of lubricants in the formulation (Panthapulakkal 2005).

The objective of this study is to investigate the effects of fiber loading, fiber treatment and application of compatibilizer on some important physical and mechanical properties of flax fiber-polypropylene composite.

MATERIALS AND METHODS

Materials

Flax fiber (short and retted fiber) with a density of 1.52 g cm^{-3} was purchased from Biofiber Ltd., Canora, SK. Compression-grade polypropylene (PRO-FAX) with low melt flow index (MFI) (MFI = 0.65 g/10 min at 230°C and density of 0.904 g cm^{-3}) was obtained from Ashland Specialty Chemical Company (Vancouver, BC, Canada) and maleic anhydride polypropylene (MFI = 115 g/10 min at 190°C; maleic acid content of around 0.6%) was obtained from Aldrich Chemical Company (Toronto, ON, Canada).

Fiber treatment

For alkalization of flax fiber, it was first washed with a 2% detergent solution and thereafter was washed with distilled water to eliminate extractives, especially some waxy materials. It was dried at 60°C in 24 h. After drying, it was immersed in a 5% sodium hydroxide (NaOH) solution for 3 h and was thoroughly washed with distilled water and dried at 60°C in 24 h. Moderate bleaching of fiber was performed by immersion of alkaline treated fibers in a 0.25% sodium hypochlorite (NaOCl) for one hour and was thoroughly washed and dried in an oven (Despatch oven company, Minneapolis, MN, USA) at 60°C in 24 h.

Preparation of composites

After alkalization, bleaching and drying, flax fibers were ground in grinding mill (Retsch GmbH 5657 HAAN, West Germany) with 2 mm opening sieve and were used in composite formulations. Polypropylene was dried in an oven at 60°C for 15 h and MAPP was pretreated at 120°C for 15 h before being used. Extrusion of the materials was carried out in a single screw extruder (Akron Inc., Batavia, OH, USA) at temperature up to 190°C with a screw speed of 45 rpm. After extrusion, the extrudates were pelletized to be used for compression molding and making special specimens for physical and mechanical tests. Different formulations were prepared in this study (Table 1).

Table 1. Composites components based on polypropylene and flax fiber

Fiber	Formulation(%) PP/MAPP/Fiber
-	100/0/0
Untreated fiber	85/0/15
	80/5/15
	70/0/30
	65/5/30
Bleached fiber	85/0/15
	80/5/15
	70/0/30
	65/5/30
Alkaline treated fiber	85/0/15
	80/5/15
	70/0/30
	65/5/30

Extruded materials were formed by compression molding (J.B. Miller Machinery & Supply Co., Toronto, ON, Canada) under a pressure of 3.5 MPa at 190°C for 7 min to prepare plates with a thickness of about 3.2 mm. Finally, the plates were machined to prepare standard specimens.

Melt flow behavior

MFI for the extrudates was measured using a thermodyne shell (plastometer) development of the Tinius Olsen Testing Machine company (Richmond, California) at 190°C based on ASTM D 1238 (ASTM 2003a).

Water absorption

Water absorption characteristics of composites are affected by fiber loading and addition of additives. Water uptake of samples was measured according to ASTM test method D 570 (ASTM 2003b). Rectangular specimens from each sample were cut to dimensions of 25.4 mm x 76.2 mm. The samples were dried in an oven at 50°C for 24 h, cooled in a desiccator, and immediately weighed to the nearest 0.001 g. After immersing specimens in water for 24 h at room temperature, excess water on the surface of the samples was removed and specimens were weighed. The mass increase related to water absorption was obtained as follows:

$$W\% = \frac{M - M_0}{M_0} \times 100 \quad (1)$$

where M_0 is the initial dry mass (g) and M is the mass of the specimen after water absorption (g).

Density

Composites density is defined as the mass per unit volume (g cm^{-3}). The mass of the samples was measured using a Galaxy 160D weighing scale (OHAUS Scale Corporation, Florham Park, NJ, USA) and the volume of the samples was measured using a gas (Nitrogen)-operated pycnometer (Quantachrome Corporation, Boynton Beach, FL, USA). Density was calculated by dividing the mass by the volume.

Tensile strength of composites

Tensile tests were done to determine some important properties of the product including tensile strength, Young's (elastic) modulus and elongation at break. The familiar dog-bone shape of the molded sample, described in ASTM procedure D 638 (ASTM 2003c), was utilized in the testing procedure. An Instron Universal testing machine (SATEC Systems, Inc., Grove City, PA) was used to perform the tensile test at a crosshead speed of 5 mm/min; each test was performed until tensile failure occurred. The tensile strength at yield (σ_t) (MPa) was obtained as follows:

$$\sigma_t = \frac{F_{max}}{A} \quad (2)$$

Where F_{max} is the maximum load measured by the instrument (N) and A is the cross sectional area of the specimen before being tested (m^2). Also, the Young's modulus E_t (GPa) was obtained using the following equation :

$$E_t = \frac{\Delta\sigma_t}{\Delta\varepsilon} \quad (3)$$

where $\Delta\sigma_t$ (GPa) and $\Delta\varepsilon$ are changes in tensile strength and resulted strain in the elastic region, respectively.

Flexural test

Flexural test was performed by three-point bending method in standard atmosphere (20 ± 2°C and 65 ± 2% RH) using Instron (model 1011) (Instron Corp., Canton, MA) according to ASTM D 790M (ASTM 2003d). Crosshead speed of 5 mm min^{-1} was used in the experiments.

Data analyses and statistical methods

Data were analyzed using Statistical Analysis System (SAS, Cary, NC) software on the basis of a completely randomized design (CRD). Means obtained by analysis of variance (ANOVA) were employed for comparison by Duncan's multiple range test at 5% level of significance.

RESULTS AND DISCUSSION

Melt flow behavior

Results from the experiments performed using the plastometer are tabulated in Table 2. Analysis of variance (P = 0.05) indicated that components (formulation) of the product affected its melt flow index (MFI). According to the obtained data, any increase in fiber content of the composite resulted in a decrease of MFI. The maximum MFI value is that of the virgin polypropylene and the lowest values were those of formulations with 30% fiber content. Also, the use of maleic anhydride grafted polypropylene (MAPP) as compatibilizer, has a negative effect (in almost all cases) on flow behavior of the extrudate which is statistically significant (P = 0.05). This result agrees with that reported by Panthapulakkal et al. (2005). It can be concluded that the addition of MAPP has a substantial synergistic effect on melt flow reduction of the compounded material and this negative effect should be compensated by a flow enhancer.

According to the results (in most of the cases measured in this study), the use of treated fiber especially bleached fiber, increased extrudate MFI compared to untreated fiber at the same levels of fiber content and coupling agent. This could be due to the better dispersion of treated fiber in the matrix, thus, flow was smoother and MFI higher than untreated fiber where the fiber and polymer may not be well-mixed, thus flow was slower. However, because of more roughness of treated fiber resulting from elimination of waxy and some polymeric materials by pretreatment (Joseph et al. 2000) it was expected to have inferior flow behavior.

Density

The effect of variables on density of the molded material is shown in Table 2. Increase of fiber loading in the composite for all three types of fibers increased the density of the product because of the higher density of fiber compared to the polypropylene. However, fiber treatment has no significant effect on density at the same levels of fiber loading and

MAPP content (P = 0.05). Although the effect of fiber treatment is statistically not significant, the application of treated fibers in composites containing MAPP increased its density. For example, density of the material increased from 1.013 to 1.021 gcm^{-3} by replacement of untreated fiber with bleached or alkaline treated fibers, at 30% fiber loading. Comparison of the means reveals that addition of MAPP to formulations has no significant effect on product density.

Table 2. Effect of formulation on extrudate melt flow index and molded composite density.

Formulation	PP/MAPP/Fiber	Extrudate MFI (g/10 min-190°C)	Molded composite density ($g\ cm^{-1}$)
	100/0/0	0.224^{a}	0.901^{d}
Untreated fiber	85/0/15	0.115^{c}	0.956^{c}
	80/5/15	0.090^{d}	0.957^{c}
	70/0/30	0.056^{e}	1.006^{b}
	65/5/30	0.036^{g}	1.013^{ab}
Bleached fiber	85/0/15	0.136^{b}	0.953^{c}
	80/5/15	0.111^{c}	0.961^{c}
	70/0/30	0.045^{f}	1.019^{a}
	65/5/30	0.043^{f}	1.021^{a}
Alkaline treated fiber	85/0/15	0.112^{c}	0.964^{c}
	80/5/15	0.096^{d}	0.963^{c}
	70/0/30	0.057^{e}	1.021^{a}
	65/5/30	$0.043f^{g}$	1.022^{a}

a, b, c, d, e, f, g: means of the same letter designation within a column are not statistically different (P = 0.05) by Duncan's multiple range test.

Water absorption

ANOVA of composites' water uptake after 24 h indicated that product components could significantly affect this physical property (P = 0.05); the comparison of means is shown in Figure 1.

The lowest value (0.006%) of water uptake is associate with molded pure polypropylene and fiber loading increased water absorption such that the maximum value is with composites containing 30% (bleached, alkaline treated or untreated) fiber without compatibilizer. This corresponds to the results reported by Tajvidi and Ebrahimi (2002) and Hargitai and Racz (2005) which attributes this to the hydrophilic characteristic of natural fibers.

Using MAPP in formulations, especially those with treated fiber, improved product quality by reducing water absorption. The positive effect of compatibilizer on reduced water absorption is more obvious for products with higher percentage (30%) of fiber.

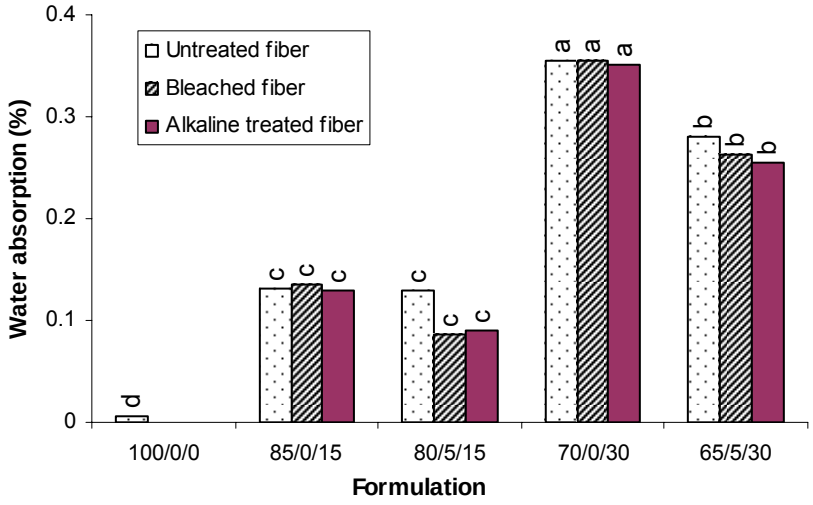

Figure 1. Comparison of water absorption of composites and virgin polypropylene; a, b, c: means of the same letter designation are not statistically different (P = 0.05) by Duncan's multiple range test.

Tensile properties

Figure 2 shows the effects of different components and pretreatments on tensile strength of the composite. The use of fiber without compatibilizer in formulations decreased product strength, but only the difference between composites containing 30% (treated or untreated) fiber and molded virgin polypropylene is statistically significant (P = 0.05). In other words, the increase of fiber loading in products causes inferior tensile strength for those formulations without MAPP which indicates the lack of stress transfer from the matrix to fiber. For example, addition of 30% bleached fiber to polypropylene reduced the tensile strength of the molded product from 25.32 to 20.47 MPa. Qiu and co-workers (2005) reported a similar trend in changes of tensile strength of compression-molded composite using fibrous cellulose in the product when no coupling agent was used. However, the application of MAPP in the products, especially those containing treated fiber, caused significant improvement of tensile strength at the same levels of fiber loading, such that the best results were achieved for bleached and alkaline treated-polypropylene composites containing 30% fiber and 5% MAPP. This result agreed with that reported by Arbelaiz and co-workers (2005) for flax fiber-polypropylene composites.

Tensile (Young's) modulus was also significantly affected by different formulations involved in this study based on ANOVA (P = 0.05). In contrast to tensile strength, almost all composites containing treated or untreated fiber, in the absence of MAPP, showed higher tensile moduli than molded 100% polypropylene (Figure 3) which is due to the higher tensile modulus of flax fiber (Arbelaiz et al. 2005). Fiber treatment was effective in tensile modulus improvement, especially at 30% fiber loading in the presence of MAPP. The best results were obtained for composites containing 5% MAPP and 30% bleached or alkaline treated fibers with values of 1.25 GPa and 1.21 GPa, respectively. Similar results were achieved in previously reported studies of Arbelaiz and co-workers (2005) and Qiu and co-workers (2005).

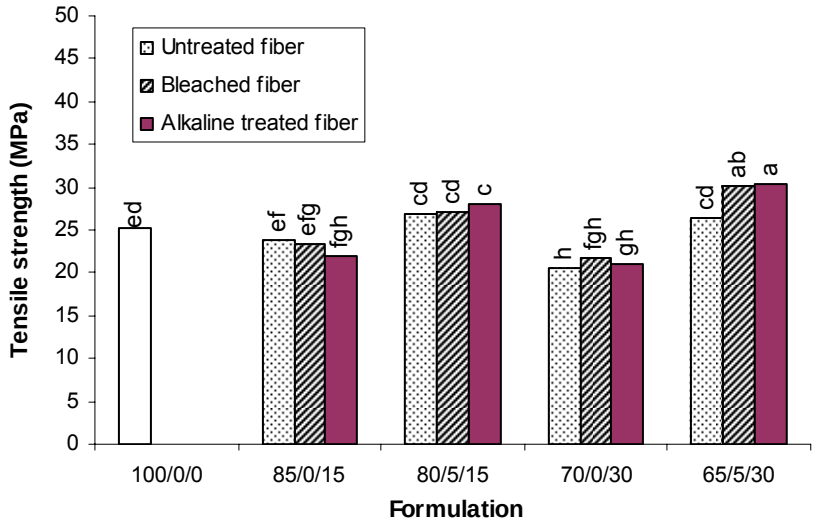

Figure 2. Effect of fiber pretreatment and components on tensile strength of composites; a, b, c, d, e, f, g, h: means of the same letter designation are not statistically different (P = 0.05) by Duncan's multiple range test..

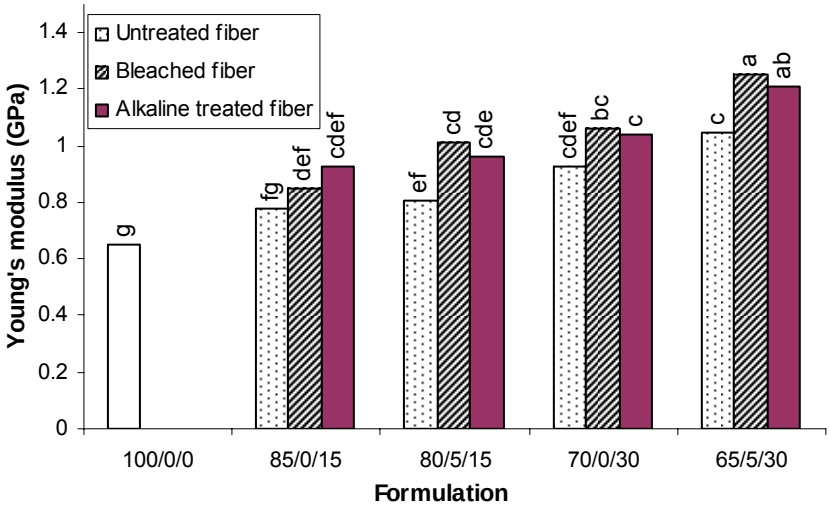

Figure 3. Effect of fiber pretreatment and components on tensile modulus of composites; a, b, c, d, e, f, g: means of the same letter designation are not statistically different (P = 0.05) by Duncan's multiple range test.

Elongation at break (another tensile property) was significantly influenced by fiber pretreatment and product components. Table 3 indicates that fiber pretreatment and composite components reduced the elongation at break of the composites. The increase in (treated or untreated) fiber percentage and the addition of MAPP decreased the elongation of the molded product. The lowest values of elongation at break were obtained for composites containing 5% MAPP and 30% of bleached or alkaline treated fibers with magnitudes of 6.57% and 7.04%, respectively. The use of pretreated fiber in most of the cases could have little effect on reduction of composites (with the same fiber and MAPP content) elongation at break.

Table 3. Comparison of means for tensile elongation at break of different formulations

Formulation	PP/MAPP/Fiber	Elongation at break (%)
	100/0/0	>200[a]
Untreated fiber	85/0/15	34.6[b]
	80/5/15	22.25[d]
	70/0/30	17.81[e]
	65/5/30	7.77[g]
Bleached fiber	85/0/15	27.71[c]
	80/5/15	15.9[ef]
	70/0/30	13.45[f]
	65/5/30	6.57[g]
Alkaline treated fiber	85/0/15	28.3[c]
	80/5/15	15.41[ef]
	70/0/30	15.5[ef]
	65/5/30	7.040[g]

a, b, c, d, e, f, g: means of the same letter designation within a column are not statistically different (P = 0.05) by Duncan's multiple range test.

Flexural properties

Comparison of the means based on ANOVA (P = 0.05) for flexural properties of molded virgin and composites are shown in Table 4. Flexural strength of polypropylene composites was not affected by fiber loading in the absence of MAPP. Also, fiber pretreatment did not have a significant effect on flexural strength when no MAPP is used in the composites. For instance, the flexural strength of polypropylene (44.20 MPa) had a slight increase to 45.30 MPa and 44.48 MPa in composites (without MAAP) containing 30% of bleached and alkaline treated fiber, respectively. However, addition of MAPP to the composites increased flexural strength of the product significantly. Arbelaiz and co-workers (2005) and Karmaker and Youngquist (1996) reported that after adding jute or flax fiber to polypropylene, flexural strength increased compared to virgin polymer; fiber pretreatment to some extent, increased the flexural strength of the composites compared to that of the untreated fiber-based composites. Rana et al. (2003) reported improvement of flexural strength of jute fiber-polypropylene composite by increasing the concentration of MAPP.

The results for flexural modulus are different from those for flexural strength in that the increase of (untreated or treated) fiber percentage in composites (without MAPP) improved the flexural modulus significantly (P = 0.05). The lowest flexural modulus value was obtained for virgin polypropylene. Also, it was found that the influence of treated fibers on flexural modulus enhancement is higher than untreated fiber in the absence of MAPP, but in some cases it was not significant.

Flexural moduli of the composites were enhanced by application of MAPP and the best result was found for bleached and alkaline-treated fiber-based composites (containing MAPP) with values of 1817 MPa and 1757 MPa, respectively. Duncan's multiple range test indicated that values of flexural yield strain for all composites were lower than pure polypropylene, especially those with higher fiber loading.

Table 4. Comparison of means for flexural properties of different formulations of composites

Formula tion PP/MAPP/Fiber		Flexural strength (MPa)	Flexural modulus (MPa)	Yield strain (%)
	100/0/0	44.20^{c}	969^{g}	7.061^{a}
Untreated fiber	85/0/15	44.75^{c}	1245^{f}	5.772^{bcd}
	80/5/15	50.107^{b}	1305^{ef}	5.499^{cdef}
	70/0/30	43.90^{c}	1436^{d}	5.001^{efg}
	65/5/30	50.06^{b}	1683^{bc}	4.625^{g}
Bleached fiber	85/0/15	44.89^{c}	1295^{ef}	6.203^{b}
	80/5/15	51.62^{b}	1439^{d}	5.593^{bcde}
	70/0/30	45.30^{c}	1623^{c}	4.943^{fg}
	65/5/30	53.16^{a}	1817^{a}	4.928^{fg}
Alkaline treated fiber	85/0/15	44.07^{c}	1342^{def}	5.416^{cdef}
	80/5/15	50.47^{b}	1406de	5.872^{bc}
	70/0/30	44.48^{c}	1660^{bc}	5.194^{defg}
	65/5/30	53.40^{a}	1757^{ab}	5.198^{defg}

a, b, c, d, e, f, g: means of the same letter designation within a column are not statistically different (P = 0.05) by Duncan's multiple range test.

SUMMARY AND CONCLUSION

The results presented in this study indicate that enhancement of physical and mechanical properties (especially tensile and flexural properties) of flax fiber-polypropylene composite is possible by fiber surface modification using an alkaline pretreatment or combination of alkaline treatment and moderate bleaching followed by addition of an appropriate compatibilizer (MAPP) to improve adhesion between the reinforcing fiber and the matrix. However, addition of MAPP to the composite, increased the negative effect of fiber loading on flow behavior by raising viscosity or reducing MFI. Therefore, MFI must be compensated by using a lubricant (flow enhancer) to achieve successful extrusion and compounding and consequently, better distribution of fibers in the matrix.

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