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Investigations on biocomposites from oat hull and biodegradable polymers

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ABSTRACT Oat hull is abundantly available biomass in Canada, which is mostly used as low-value feed material. However, oat hulls with high fibre content can be used in the production of industrial products by providing opportunity in the replacement of petroleum-based products. The objectives of this investigation are to develop biocomposites from cellulose and lignin which are post-hydrolysis products of oat hull using biodegradable polymers (polylactic acid and polycaprolactone) and to compare the physical and mechanical properties of formulated biocomposites with polypropylene (PP) biocomposites so that a low cost and eco-friendly biomaterials can be made. Inclusion rates of AHB (acid-catalyzed hydrolysis byproduct) and CRB (cellulose-rich biofibre) fibres at 15% and 30% of the total mass of biocomposites were formulated. The composites with different formulations were extruded through the twin-screw extruder for compounding and thereafter were compression molded. The physical and mechanical properties such as color measurement, water absorption, tensile strength and flexural strength of formulated biocomposites were determined. The results indicated that strength of bicomposites generally varied to that of virgin polymers, while Young's modulus increased with corresponding increase in fibre content from 15% to 30%.

Keywords: Industrial products, oat, biofibre, polylactic acid, polycaprolactone, eco-friendly.

INTRODUCTION With increased economic development and energy consumption, alternative methods and materials have been developed to replace petroleum-based products by bio-based materials (Abril and Abril 2009; Huda et al. 2008). Bio-based materials could include industrial products made up of renewable resources such as agricultural residues. Therefore, innovative eco-

friendly bicomposites can play important role in daily life applications such as in construction, automobiles, furniture, plastic and packaging industries and also in biomedical applications (Li et al. 2009; Soleimani et al. 2008). Lignocellulosic biomass is the main source of natural fibres which can be collected from agricultural residues such as stem, leaf and hull aside from purpose-grown fibre crops. Natural fibres can be used as fillers or reinforcements into the polymeric matrix phase for making biocomposites, because of their biodegradabilty, large-scale availability, non-abrasion, low cost, low density, high stiffness and high filling potential (Soleimani et al. 2008).

Oat is a major grain crop grown in Canada with 36.4 million hectares of land used for oat production. Most of the oat is produced in the Canadian prairies (Alberta, Manitoba and Saskatchewan), and Saskatchewan produced the highest amount of oat (Sokhansanj et al. 2006). Oat hulls are abundantly present as a byproduct in oat processing plants because the hull constitutes approximately 19-25% of the grain (SaskSeed Guide 2014). In terms of chemical composition, oat hull principally consists of cellulose, hemicellulose, and lignin, with almost equal quantities of cellulose and hemicellulose of approximately 30-35%, and lignin and ash contents of 2-10% and 3.5-9%, respectively (Welch et al. 1983). Oat hull biomass produced by oat processors is usually ground and sold as low-value feed material. However, oat hull can be used as feedstock in the production of high-value products. Oat hull biomass has been investigated for the production of xylitol by integrated processes of acid-catalyzed hydrolysis and bioconversion (Soleimani and Tabil 2012). The hemicellulose portion from the hydrolysis has been used for the conversion of xylose to xylitol and analytical techniques were optimized to maximize the production of xylitol (Soleimani 2013). The by-product from the hydrolysis (other than hemicellulose) is rich in cellulose and lignin, could be a great source of fibre to be used as filler in the production of biocomposites. The biocomposites developed from the matrix of polypropylene (non-biodegradable polymer) and byproduct of oat hulls has shown approximately the same strength as that of virgin polypropylene (Soleimani and Tabil 2012). However, natural fibre-reinforced biocomposites using biodegradable polymers have been reported as the most environmental friendly bioproducts (dos Santos Rosa and Lenz 2013).

Many of the biodegradable polymers which belong to the polyester family such as polylactic acid (PLA) and poly-caprolactone (PCL) are widely used in biomedical applications. PLA is produced by the polymerization of lactic acid and found in the form of two optical isomers: L- and D- lactide. PLA has high biocompatibility and hydrophobicity, low degradation rate and better thermal processibility than other biodegradable polymers. However, it is very brittle in nature (low flexibility) and has poor resistance to humidity. On the other hand, PCL is produced by ring opening polymerization of the cyclic monomer ε-caprolactone and is relatively hydrophobic and biodegradable polymer with very low degradation rates. It has poor miscibility with other polymers which can be improved by physical and chemical modifications of the matrix (Gunatillake and Adhikari 2003; dos Santos Rosa and Lenz 2013). Apart from some limitations, these biodegradable polymers can be used in biocomposites manufacturing because of better thermal processibility with the natural fibres than other polymers. On the other hand, polypropylene (PP), a widely used polymer which is thermoplastic in nature and extensive research has been conducted on polypropylene composites reinforced with natural fibres (Gunatillake and Adhikari 2003; Li et al. 2007; Reddy et al. 2013).

In a study, conducted by Soleimani and co-workers (2008), the effect of fibre pretreatment on physical and mechanical properties of flax fibre-PP composites were investigated. The results indicated that the pretreatment of fibres with alkali treatment had increased the water absorption, impact and tensile properties. Oat hull reinforced PP-PLA composites were fabricated by Reddy and co-workers (2013) and results of PP-PLA composites had shown moderate rise in tensile and flexural properties than PP composites only. Also, thermo-gravimetric analysis of oat hull fibre had confirmed the processing temperature to be 190°C.

Few studies have been conducted on the manufacture of biocomposites with the use of biodegradable polymers and oat hull fibres. The main objective of this project is to develop biocomposites from cellulose and lignin derived from post-hydrolysis of oat hull. Biocomposites using PLA and PCL were formulated by reinforcement or filling with oat hull biofibres and then compared the engineering properties of these biocomposites with polypropylene (PP) biocomposites to afford low-cost and eco-friendly biomaterials.

EXPERIMENTAL

Materials

Oat hull biomass with an average density of 1.29 g cm^{-3} was supplied by Richardson Milling Ltd., Martensville, SK, Canada. Polylactic acid (PLA) powder (Ingeo Biopolymer 2003D) was obtained from NatureWorks LLC (Minnetonka, MN) and poly-caprolactone (PCL) with trade name CAPA 6506 was purchased from Perstorp Polyols Inc. (Toledo, OH) in powder form.

Cleaning of biomass

The original raw material (oat hulls) was cleaned using a sieving machine and then passed through an aspirator for maximum cleaning of the hulls where other materials such as whole grains and fines were separated. The cleaned hulls were then ground through a 2.7 mm opening sieve using a grinder mill (Retsch GmbH 5657 HAAN, West Germany).

Fibre preparation

The ground hulls were pretreated by dilute acid hydrolysis under atmospheric conditions, with 1.2N H_2SO_4 (sulfuric acid). Then, it was washed with distilled water to neutralize the pH. The solid fraction obtained after filtration is the acid-catalyzed hydrolysis byproduct (AHB) and, it was then dried in an oven at 60°C for 48 h. Thereafter, alkali treatment was conducted for the removal of lignin from AHB to convert it to cellulose-rich biofibre (CRB). AHB fibres were treated with 5% NaOH solution at 30°C and 65°C in a container with reflux and continuous stirring for 2 h. After thorough washing and drying, the solid fractions obtained at two different temperatures (30°C and 65°C) are called as cellulose-rich biofibres, namely CRB-30 and CRB-65.

Composites preparation

The three different fibres obtained in the first step of fibre preparation, namely acid-catalyzed byproduct (AHB), cellulose-rich biofibres (CRB-30 and CRB-65) were mixed with PLA and PCL in ratios shown in Table 1. A twin-screw extruder (SHJ-35, Nanjing Yougteng Chemical Equipment Co. Ltd., Jiangsu, China) was used to extrude the formulations. After cooling the extrudates, they were pelletized to prepare the material for molding process. Then slabs were prepared for each formulation by compression molding machine (Miller Machine Tools, J.B. Miller Machinery & Supply Co. Ltd., Toronto, ON) and specimens were cut off for physical and mechanical tests according to the ASTM standards.

Color measurement

The effect on the appearance of molded composites, developed with addition of acid treated and alkaline treated fibres was analyzed by HunterLab ColorFlex EZ spectrophotometer (Hunter Associates Laboratory, Inc., Reston, VA). The Hunter L*, a* and b* color coordinates were used for color measurement, where L* is the whiteness component and a* and b* are both chromatic components. Equations 1, 2 and 3 are used to illustrate the meaning of L*, a* and b* respectively. The difference between the L*, a* and b* color coordinates of the sample composites and virgin polymer (PLA or PCL) was used to calculate color index, ΔE, as shown in the equation 4 (Soleimani et al 2008).

$$L^* = 0(black) \ \ to \ \ 100(white) \tag{1}$$

$$a^* = -a^*(green) \ to \ + a^*(red) \tag{2}$$

$$b^* = -b^*(blue) \ to \ + b^*(yellow) \tag{3}$$

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{4}$$

where: $\Delta L^* = L^*_{sample} - L^*_{virgin}$, $\Delta a^* = a^*_{sample} - a^*_{virgin}$, $\Delta b^* = b^*_{sample} - b^*_{virgin}$.

Table 1. Formulation of composites based on polymer matrix and fibres.

Polymer	Fibre	Formulation (%)
		Polymer/fibre
PLA	-	100/0
	AHB	85/15
		70/30
	CRB-30	85/15
		70/30
	CRB-65	85/15
		70/30
PCL	-	100/0
	AHB	85/15
		70/30
	CRB-30	85/15
		70/30
	CRB-65	85/15
		70/30

Water absorption test

ASTM test method D570 (Standard test method for water absorption of plastics) was followed for the water absorption of biocomposites (ASTM 2010). The test specimens were cut into rectangular shapes with dimensions of 76.2 mm in length and 25.4 mm in width. The specimens were then dried in an oven at 50°C for 24 h, cooled in a desiccator, and weighed immediately to the nearest 0.001 g (dried weight = W_{dried}). The dried specimens were immersed in water for the next 24 h at room temperature of 23°C, and weighed again after removing excess water from the surface (wet weight = W_{wet}). The percent increase in weight was measured by the following equation:

$$Water \ absorption \ (\%) = \frac{W_{wet} - W_{dried}}{W_{dried}} \times 100 \tag{5}$$

Tensile test

The tensile test of biocomposites was carried out by using Instron Universal testing machine (INSTRON 3366, Instron Corp., Norwood, MA). Specimens in a dog-bone shape were prepared from the biocomposite samples according to the ASTM standard test method D638 (ASTM 2014). The tensile test was performed at crosshead speed of 5 mm/min and two important properties, tensile strength (σ_t) and Young's modulus (E) were calculated using equations 6 and 7, respectively.

$$\sigma_t = \frac{F_{max}}{A} \tag{6}$$

$$E = \frac{\sigma}{\varepsilon} \qquad (7)$$

Where F_{max} is the maximum load; A, cross-sectional area; σ, tensile stress; and ε, extensional strain.

Flexural test

The flexural properties of acid treated and alkaline treated composites were determined as described in ASTM D790-10 (Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials) (ASTM 2010). Specimens were cut into dimensions of 12.7mm width and 127mm length. The test specimens were conditioned in an environment chamber at 23 ± 2°C and 50 ± 5 % relative humidity for more than 40 h before testing (BRYANT Manufacturing Associates, Ayer, MA). Three-point bending test was performed to all the specimens by using Instron Universal testing machine (INSTRON 3366) with crosshead speed of 5 mm/min and, flexural strength (σ_f) and flexural modulus (E_f) were calculated using equations 8 and 9, respectively.

$$\sigma_f = \frac{3PL}{2bd^2} \qquad (8)$$

$$E_f = \frac{mL^3}{4bd^3} \qquad (9)$$

Where P is the maximum load; L, length between support span; b, width of the specimen; d, thickness of the specimen; and m, slope of the load-displacement curve.

Data analysis

The data was analyzed by using SPSS statistical analysis software (IBM SPSS Statistics) on the basis of completely randomized design. Analysis of variance (ANOVA) was used to measure the means, which were compared by using Duncan's multiple range test at 5% significance level.

RESULTS AND DISCUSSION

Color measurement

The color index (ΔE) values measured for PLA- and PCL-based biocomposites are shown in Table 2. For molded virgin PLA, the L* value is the highest and a* and b* values are lowest than molded composites, indicating that the molded PLA composites appeared darker with addition of fibre. However, composites loaded with CRB-30 fibres have higher L* values than composites with AHB and CRB-65 fibres. The highest ΔE values for PLA were associated with acid treated composites, whereas the least ΔE values were seen in alkaline treated composites. PCL color measurements, also showed the lowest L* values and the highest a* and b* values for almost all the acid and alkaline treated molded composites than molded virgin PCL. The low L* values could be due to inclusion of fibres; but there was no degradation of fibres as per lower processing temperature conditions for PCL. However, no significant effect was observed by fibre loading in both formulations with PLA and PCL.

Water absorption

The water absorption characteristics of PLA and PCL formulations are shown in Figure 1 and Figure 2, respectively. For molded PLA and PCL-based biocomposites, approximately 0% to 2% increase in weight was observed and ANOVA of composites showed that weight increase was significantly dependent on fibre loading (p = 0.05). The lowest values of water uptake were

Table 2. Values of color coordinates and color index with standard deviation (SD) and comparison of means by Duncan's multiple range test (p = 0.05) designated with [a,b,c,d] for PLA and [A,B,C,D,E] for PCL formulation type.

Polymer	Fibre	Formulation (%) Polymer/fibre	L*	SD$_{L*}$	a*	SD$_{a*}$	b*	SD$_{b*}$	ΔE	SD$_{ΔE}$
PLA	-	100/0	35.41	±0.36	-0.41	±0.07	10.96	±0.29	0[d]	±0.00
	AHB	85/15	28.15	±0.22	10.33	±0.31	15.92	±0.27	13.88[a]	±0.36
		70/30	28.89	±0.08	10.38	±0.25	16.23	±0.24	13.67[a]	±0.25
	CRB-30	85/15	30.30	±0.41	8.94	±0.13	15.47	±0.15	11.57[c]	±0.23
		70/30	31.05	±0.29	9.58	±0.39	16.89	±0.34	12.42[b]	±0.41
	CRB-65	85/15	27.39	±0.19	8.69	±0.23	14.04	±0.26	12.52[b]	±0.30
		70/30	28.12	±0.28	8.83	±0.17	14.41	±0.24	12.27[b]	±0.10
PCL	-	100/0	59.33	±0.59	-0.69	±0.02	-1.09	±0.07	0[E]	±0.00
	AHB	85/15	36.72	±0.14	10.14	±0.17	19.19	±0.14	32.25[C]	±0.18
		70/30	33.90	±0.33	10.96	±0.11	19.37	±0.38	34.66[A]	±0.43
	CRB-30	85/15	33.97	±0.57	8.67	±0.39	16.40	±0.42	32.21[C]	±0.23
		70/30	34.17	±0.73	8.39	±0.31	16.18	±0.44	31.85[C]	±0.35
	CRB-65	85/15	34.48	±0.26	8.31	±0.25	16.19	±0.24	31.58[D]	±0.16
		70/30	33.12	±0.37	8.64	±0.22	17.05	±0.37	33.22[B]	±0.30

SD$_{L*}$, standard deviation of L*; SD$_{a*}$, standard deviation of a*; SD$_{b*}$, standard deviation of b*; SD$_{ΔE}$, standard deviation of ΔE

associated with virgin polymers and it started rising with incorporation of fibre content from 15% to 30% in each formulation. For PLA, acid-treated composites (AHB) showed least absorption of water followed by CRB-30 composites and highest with CRB-65 composites. On the other hand, water uptake in PCL composites followed the same trend as PLA but with almost same absorption in alkaline treated (CRB-30and CRB-65) composites. These results are in accordance with the studies which reported that natural fibres have high affinity for water absorption (Soleimani et al. 2008; Li et al. 2009).
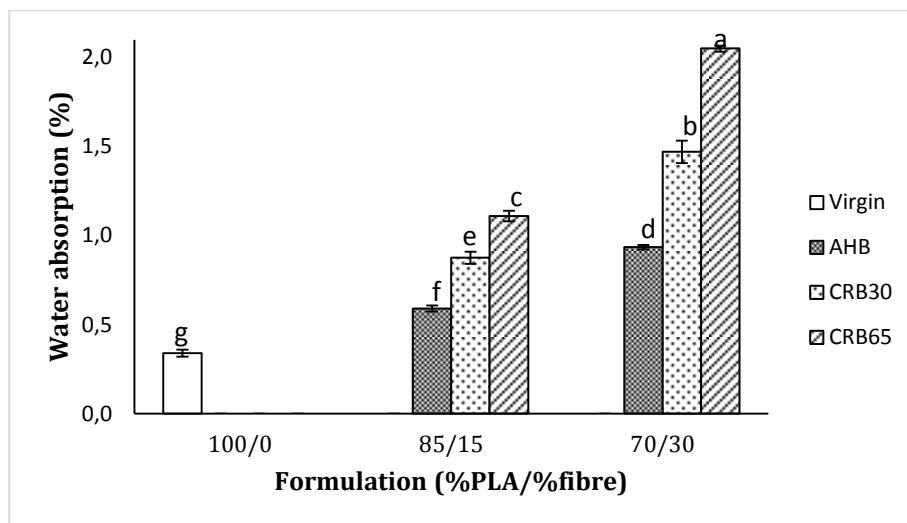

Figure 1. Water absorption of PLA-based bicomposites and comparison of means by Duncan's multiple range test (p = 0.05) designated with [a,b,c,d,e,f] .

Tensile properties

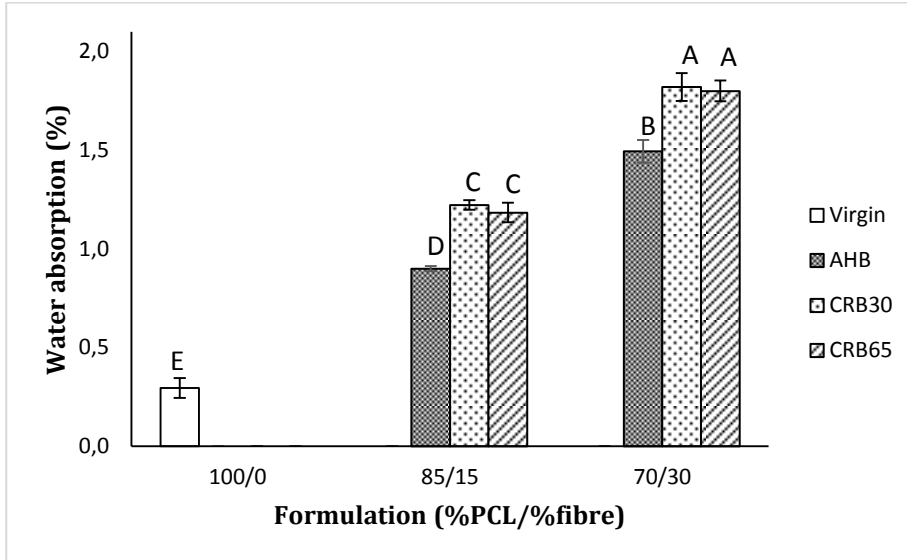The results for tensile strength and Young's modulus are tabulated in Table 3 for PLA and PCL

Figure 2. Water absorption of PCL-based bicomposites and comparison of means by Duncan's multiple range test (p = 0.05) designated with ^{A,B,C,D,E}.

composites and statistically shown by ANOVA that these properties are dependent on different formulations (p = 0.05). These results are in agreement as reported by Soleimani and co-workers (2008) for effect of pretreatment on the strength of PP-flax fibre composites. The tensile strength of the composites was decreased with increase in the fibre content in PLA and PCL formulations. For PLA, the strength of composites with 30% fibre loading almost decreased to half of the strength of virgin PLA; however, alkaline formulations with 15% fibres had higher strength than acid-treated. On the other hand, the tensile strength of PCL composites was slightly lower than virgin PCL which varied from 12 MPa to 16 MPa (approximately).

Table 3. Mechanical properties of PLA- and PCL-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated with ^{a,b,c,d,e,f} for PLA and ^{A,B,C,D,E,F,G} for PCL formulation type.

Polymer	Fibre	Formulation (%)	Tensile		Flexural	
		Polymer/fibre	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
PLA	-	100/0	47.32[a]	2.19[e]	86.65[a]	4.38[d]
	AHB	85/15	33.03[d]	2.36[d]	74.68[b]	4.84[a,b]
		70/30	28.22[e]	2.52[b,c]	55.50[d]	4.98[a]
	CRB-30	85/15	36.57[c]	2.42[c,d]	66.18[c]	4.37[d]
		70/30	26.07[f]	2.61[b]	64.85[c]	5.00[a]
	CRB-65	85/15	38.79[b]	2.41[d]	58.93[d]	4.56[c,d]
		70/30	19.01[g]	2.81[a]	48.40[e]	4.67[b,c]
PCL	-	100/0	16.06[A]	0.33[E]	20.03[D]	0.45[G]
	AHB	85/15	15.64[B]	0.60[D]	19.70[D]	0.66[F]
		70/30	13.01[E]	0.91[A]	23.21[C]	0.99[C]
	CRB-30	85/15	15.01[C]	0.68[C]	20.76[D]	0.77[E]
		70/30	12.23[E,F]	0.84[B]	27.84[A]	1.33[A]
	CRB-65	85/15	13.35[D]	0.60[D]	23.71[C]	0.90[D]
		70/30	12.47[E,F]	0.84[B]	25.25[B]	1.19[B]

In contrast to tensile strength, Young's modulus of PLA and PCL composites showed opposite trend, as it increased with increase in fibre loading. The modulus of PCL composites with 15% and 30% formulations increased from 0.33 GPa (virgin) to 0.68 GPa and 0.91 GPa, respectively.

Flexural properties

Flexural properties for PLA and PCL biocomposites are shown in Table 3. ANOVA of composites showed that flexural properties were affected with increase in fibre content ($p = 0.05$). For PLA, the strength of virgin polymer was the highest and it started decreasing with increase in fibre content from 15% to 30%. While, in PCL composites, the bending strength of virgin PCL was 20 MPa and it began to increase slightly from 15 % to 30% with 23.71 MPa to 27.84 MPa.

Flexural modulus of PLA composites increased slightly with fibre loading, but in some cases the modulus of virgin polymer was almost same. Moreover, flexural modulus for PCL composites was found almost doubled with increase in fibre content with values from 0.45 GPa (for virgin PCL) to 1.3 MPa.

CONCLUSION Oat hulls were used to produce three different types of fibres using dilute acid hydrolysis and alkaline treatment, which were then incorporated to the biodegradable polymers. The physical and mechanical properties of the produced biocomposites were investigated. The water absorption of composites has shown the hydrophilic behavior of natural fibres; composites based on acid-treated fibres showed less water uptake than composites based on alkaline-treated fibres which means modification of fibres with alkaline treatment has not affected the water absorption characteristics. The mechanical properties of PLA composites were close to virgin polymer (but not more than that); on the other hand, PCL showed the promising results. Furthermore, future work will include the improvement in mechanical properties of PLA using chemical modifications within different concentrations. Moreover, this research has provided different ways to utilize high volume oat hull biomass by manufacturing environmentally friendly bioproducts.

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