

The Canadian Society for Bioengineering
*The Canadian society for engineering in agricultural, food,
environmental, and biological systems.*



**La Société Canadienne de Génie
Agroalimentaire et de Bioingénierie**
*La société canadienne de génie agroalimentaire, de
la bioingénierie et de l'environnement*

Paper No. CSBE16-041

Study of alkaline treated oat hull fibres and PLA- biocomposites with impact modifier

Ramanpreet Kaur Grewal

Department of Chemical and Biological Engineering, University of Saskatchewan,
rkg785@mail.usask.ca

Lope G. Tabil

Department of Chemical and Biological Engineering, University of Saskatchewan,
lope.tabil@usask.ca

Lee Wilson

Department of Chemistry, University of Saskatchewan,
lee.wilson@usask.ca

**Written for presentation at the
CSBE/SCGAB 2016 Annual Conference
Halifax World Trade and Convention Centre
3-6 July 2016**

ABSTRACT Bio-based plastics/ biodegradable polymers like polylactic acid (PLA) are gaining popularity, as matrices reinforced or filled with natural fibres to produce biodegradable composites. However, the major drawback associated with PLA is its brittleness (low flexibility). The objective of this study was to investigate the effect of adding impact modifier on the physical and mechanical properties of PLA-biocomposites made of cellulose-rich biofibres (CRB). The oat hull biomass was delignified at different temperatures of 30°C and 65°C to produce two types of fibres, i.e. CRB-30 and CRB-65, respectively. Formulations with 15% and 30% CRB fibres of the total mass of biocomposites were tested. The effect of impact modifier at 15% inclusion rate was also investigated with PLA-based composites. A twin screw extruder and a compression molding machine were respectively used for compounding the formulations and product molding. The performance of the composites in all formulations was assessed by measuring their physical and mechanical properties. The combination of impact modifier with alkaline-treated fibres has shown promising results i.e. the tensile-impact strength of biocomposites increased.

Keywords: biodegradable polymers, biocomposites, oat hull fibres, impact modifier.

Papers presented before CSBE/SCGAB meetings are considered the property of the Society. In general, the Society reserves the right of first publication of such papers, in complete form; however, CSBE/SCGAB has no objections to publication, in condensed form, with credit to the Society and the author, in other publications prior to use in Society publications. Permission to publish a paper in full may be requested from the CSBE/SCGAB Secretary, 2028 Calico Crescent, Orleans, ON, K4A 4L7 or contact secretary@bioeng.ca. The Society is not responsible for statements or opinions advanced in papers or discussions at its meetings.

INTRODUCTION Degradation of petroleum-based plastics caused the release of toxic compounds into the atmosphere, which brought a whole new paradigm shift towards developing innovative biodegradable polymers. Moreover, biodegradable polymers should have advantages over synthetic and non-biodegradable plastics for sustainable and reliable product life, including renewability, recyclability, and comparable properties to that of non-biodegradable polymers (Duhovic et al. 2008; Staiger and Tucker 2008). Polylactic acid (PLA) is a thermoplastic biodegradable polymer which belongs to an aliphatic polyester family (Gunatillake and Adhikari 2003; Tokiwa et al. 2009; dos Santos Rosa and Lenz 2013). It can be derived from numerous renewable resources such as corn starch, sugarcane, sugar beet, or tapioca (Islam 2008; Talimi 2011; Hassan et al. 2013; Salit 2014).

PLA has already been used over decades as a replacement to petroleum-based polymers (Nagarajan et al. 2016). The mechanical properties of PLA are almost similar to that of petrochemical polymer polypropylene (PP) and the comparable properties of PLA with PP are shown in the Table 1.

Table 1. Properties of polylactic acid (PLA) and polypropylene (PP) based on the literature review (Faisant et al. 1998; Gunatillake and Adhikari 2003; Karnani et al. 1997; Maier and Calafut 2008; Murphy 2011; Reddy et al. 2013; Soleimani et al. 2008).

Polymer	Tensile Modulus (GPa)	Melting Point (°C)	Melt Flow Index (g/10min)	Glass Transition Temperature (°C)
Poly (<i>l</i> -lactic acid)	2.7	173 – 178	10 - 25 (@210°C/2.16 kg)	60 to 65
Polypropylene	0.69-1.2	130 - 170	18.6 – 21 (@230°C/2.16 kg)	-35 to 26

Despite of advantages, brittleness is the inferior property associated with PLA limiting its applications for durable industrial products (dos Santos Rosa and Lenz 2013; Nagarajan et al. 2016). In order to overcome brittleness, certain additives or impact modifiers have been developed to improve impact properties of composites. Several studies have been carried out using impact modifiers with successful outcomes (Afrifah and Matuana 2010; Balakrishnan et al. 2012; Notta-Cuvier 2014).

Biocomposites from abundantly available oat hulls have already been developed with PLA and their physical and mechanical properties have been investigated by our research group (Grewal et al. 2015). The present work has extended the study conducted by these researchers by using an impact modifier to enhance the toughness of biocomposites and comparison has been made with the previous results.

MATERIALS AND METHODS

Materials The raw material/ oat hull was provided by Richardson Milling Ltd., Martensville, SK, Canada and its average density was measured to be 1.290 g/cm³. Polylactic acid (PLA) (Ingeo Biopolymer 2003D) was acquired from NatureWorks LLC (Minnetonka, MN) and the impact modifier, Biomax Strong 120 (BS), an ethylene copolymer was purchased from DuPont Company (Wilmington, DE).

Isolation of cellulosic fibres from oat hulls The raw material was cleaned and ground through a mesh size of 2.7mm in a grinder mill (Retsch GmbH 5657 HAAN, West Germany). The ground hulls were then subjected to the prior treatment with 1.2N H₂SO₄ (sulfuric acid) under atmospheric conditions, for 80 min with continuous stirring at temperature of 99°C. The washed and neutralized acid-treated fraction was called acid-catalyzed hydrolysis byproduct (AHB) which was delignified with 5% (w/w) NaOH solution at 30°C and 65°C, in a glass container with reflux and continuous stirring for 2 h. The resulted products were called cellulose-rich biofibres, namely CRB-30 and CRB-65 which were washed and pH neutralized.

Formulation and composite preparation The formulations for composites were prepared in two manners (shown in Table 2):

- 1) without impact modifier / Un-modified
- 2) with impact modifier (BS) / Modified

Two types of cellulosic fibres (CRB-30 and CRB-65) obtained were used in both formulations at levels of 15% and 30% (w/w). The inclusion rate of impact modifier, Biomax Strong 120 (BS) in modified biocomposites was taken 15% (w/w). Virgin PLA sample was made as a reference material with 0% fibre content All formulations were mixed by a blender to achieve homogenous mixture of fibres and polymers and then extruded through twin screw extruder (SHJ-35, Nanjing Yougteng Chemical Equipment Co. Ltd., Jiangsu, China). The pelletized material from extruder was dried and then molded using compression molding machine (Miller Machine Tools, J.B. Miller Machinery & Supply Co. Ltd., Toronto, ON) for the preparation of composites.

Table 2. Formulations based on polymer matrix, cellulose-rich biofibres (CRB), and impact modifier (BS) for unmodified and modified composites.

Type	Fibre	Formulation (%)
		PLA/BS/Fibre
Virgin PLA	-	100/0/0
Unmodified	CRB-30	85/0/15
		70/0/30
	CRB-65	85/0/15
		70/0/30
Modified	CRB-30	70/15/15
		55/15/30
	CRB-65	70/15/15
		55/15/30

Characterization of composites:

Compositional Analysis The raw material (ground hulls) and recovered fibres (AHB, CRB-30, and CRB-65) were analyzed to determine the proportions of cellulose, hemi-cellulose and lignin. Association of Official Analytical Chemists (AOAC) standards No. 2002.04 (AOAC 2005) and No. 973.18 (AOAC 1997) were used for NDF and ADF measurements to determine the contents of

hemi-cellulose and cellulose, respectively. The percentage of lignin was measured by National Renewable Energy Laboratory (NREL) standard No. 03 (Sluiter 2008).

Density test Density is defined as mass per unit volume and is expressed in grams per cubic centimeter. The mass of the samples was measured in grams using a weighing scale (OHAUS Scale Corporation, Florham Park, NJ). The volume of the samples was measured by using a pycnometer, which was operated by nitrogen gas (Quantachrome Corporation, Boynton Beach, FL) and density of the samples was calculated.

Water absorption Water uptake in biocomposites was measured by following ASTM test method D570 (Standard test method for water absorption of plastics) (ASTM 2010). The test specimens were dried first over a period of 24h at 50°C and then immersed in water for the next 24 h at room temperature of 23°C. The water uptake/ absorption was measured in percentage by the following equation (1):

$$\text{Water absorption (\%)} = \frac{W_{\text{wet}} - W_{\text{dried}}}{W_{\text{dried}}} \times 100 \quad (1)$$

Where W_{wet} is the wet weight and W_{dried} , dried weight.

Mechanical tests Biocomposites were tensile tested in a dog-bone shape as shown in Figure 1, for the measurement of tensile strength and Young's modulus according to the ASTM standard test method D638 (ASTM 2014) by using Instron universal testing machine (INSTRON 3366, Instron Corp., Norwood, MA).

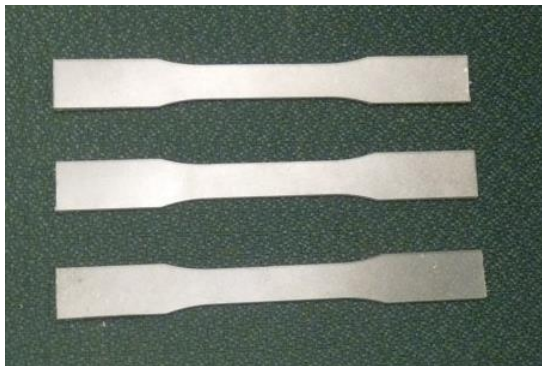


Figure 1. Dog-bone shaped specimens for tensile test (from virgin PLA compression molded sheet).

Flexural properties such as flexural strength and flexural modulus were determined by three-point bending test done on aforesaid Instron universal testing machine as stated in ASTM D790-10 (Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials) (ASTM 2010).

The tensile-impact test was done to measure the impact properties of modified and unmodified biocomposites according to ISO 8256 standard (ISO 2004). The test was conducted using a tensile-impact testing machine (Tinius Olsen Testing Machines Co., Willow Grove, PA). The test specimen was broken by a single impact at the bottom of the swing of the pendulum and tensile-impact energy (kJ/m^2) was calculated as using equation (2).

$$a_{tu} = \frac{E_i}{x \times h} \quad (2)$$

Where a_{tu} is the tensile-impact strength in kJ/m^2 ; E_i , impact energy in J; x , width of the sample in mm; and h , thickness of the sample in mm.

RESULTS AND DISCUSSION

Compositional analysis The chemical compositions of raw oat hulls and its fibres namely, AHB, CRB-30, and CRB-65 are presented in Table 3. The data obtained after chemical treatments has resulted in the reduction of hemi-cellulose and lignin contents, with increased cellulose composition. In the delignification process of AHB fibres, followed by increase in reaction temperature from 30 to 65 °C, has resulted in increase of cellulose content from 56.90% to 83.23%, with decrease in the percentage of lignin from 30.24% to 13.55% from AHB to CRB-65, respectively.

Table 3. Percentage of cellulose, lignin, and hemicellulose in raw oat hulls and chemically treated fibres.

Material	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Lignin/Cellulose
RM	24.70	17.70	39.33	0.72
AHB	56.90	30.24	0	0.53
CRB-30	71.00	23.81	0	0.33
CRB-65	83.23	13.55	0	0.16

RM, raw material (oat hulls); AHB, acid-catalyzed hydrolysis byproduct; CRB, cellulose-rich biofibre

Density analysis The unit density of unmodified and modified biocomposites with PLA and fibres is tabulated in Table 4. In unmodified PLA composites, the fibre loading from 15% to 30% with CRB-30 and CRB-65 fibres resulted in an increased density of the molded material. The results are in accordance with the literature review, as PP-flax fibre composites density has also been increased with addition of fibres (Soleimani et al. 2008). Moreover, the density of unmodified biocomposites varied from 1.272 to 1.302 g/cm^3 depending upon CRB-30 and CRB-65 fibre types, while the density of virgin PLA was found to be 1.250 g/cm^3 . On the other hand, in modified PLA composites, formulations containing 30% fibre loading have high density values in comparison to biocomposites with 15% fibre loading. Apart from this, composites with 15% fibre loading had lower densities to that of virgin molded material; the reason could be because of lower density of impact modifier which was 0.940 g/cm^3 and lower fibre content with less percentage of polymer.

Table 4. Density of virgin PLA and molded composites with and without impact modifier (BS).

Type	Fibre	Formulation (%)		
		PLA/BS/Fibre	Density of molded composites (g/cm ³)	SD
Virgin PLA		100/0/0	1.250	±0.0040
Unmodified	CRB-30	85/0/15	1.272	±0.0071
		70/0/30	1.283	±0.0015
	CRB-65	85/0/15	1.276	±0.0021
		70/0/30	1.302	±0.0020
Modified	CRB-30	70/15/15	1.214	±0.0016
		55/15/30	1.254	±0.0031
	CRB-65	70/15/15	1.236	±0.0309
		55/15/30	1.243	±0.0007

SD, standard deviation

Water absorption The results of water absorption in composites are shown in Figure 2 (the error bar represents 1 standard deviation above and below the average). The literature review is effectively connected with the results of water absorption, which shows the hydrophilic nature of fibres are evident according to an increase in water absorption characteristics with fibre loading (Soleimani et al. 2008; Soleimani and Tabil 2012). Additionally, the water absorption capacity of composites in both formulations increased as the fibre loading varied from 15% to 30%.

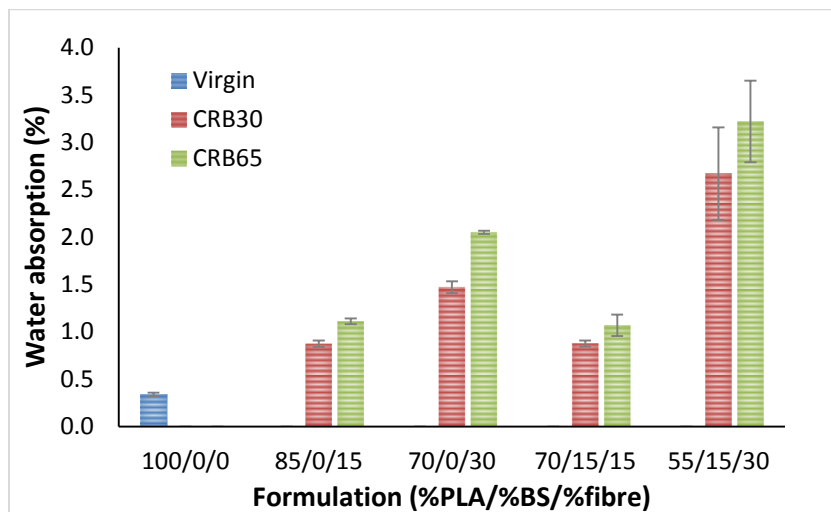


Figure 2. Water absorption in unmodified and modified alkaline PLA-composites.

Mechanical properties The results of tensile properties are presented in Table 5 for unmodified and modified composites of PLA. In both formulations, the tensile strength of composites decreased as the fibre loading increased from 15% to 30%. In comparison to unmodified composites, the tensile strength of modified composites decreased rapidly and the values are approximately halved. On the other hand, Young's modulus of unmodified composites was higher than molded virgin PLA and it increased with fibre content, upto 2.77 GPa in CRB-65 with 30% fibre

loading. However, for modified PLA-composites, the Young's modulus was close to the virgin molded polymer; still lower than unmodified composites.

Table 5. Tensile properties of virgin PLA and molded composites with and without impact modifier (BS).

Type	Fibre	Formulation (%)		Tensile Strength		Young's Modulus	
		PLA/BS/Fibre	(MPa)	SD	(GPa)	SD	
Virgin PLA		100/0/0	46.216	±1.544	2.144	±0.074	
Unmodified	CRB-30	85/0/15	36.627	±0.993	2.400	±0.052	
		70/0/30	25.474	±0.880	2.575	±0.088	
	CRB-65	85/0/15	38.105	±1.305	2.385	±0.035	
		70/0/30	18.768	±0.370	2.775	±0.055	
Modified	CRB-30	70/15/15	20.731	±0.264	2.010	±0.062	
		55/15/30	12.212	±0.413	2.179	±0.049	
	CRB-65	70/15/15	15.378	±0.252	2.130	±0.090	
		55/15/30	15.745	±0.524	2.148	±0.065	

SD, standard deviation

Flexural strength and flexural modulus are tabulated in Table 6. Using impact modifier on PLA-based biocomposites, a resulting sharp drop in the flexural strength was observed when compared to virgin PLA and PLA-based biocomposites without impact modifier. The flexural strength of virgin PLA was around 86 MPa, which reduced to the lowest (approximately 13 MPa) on the application of impact modifier with 30% CRB-30 fibre content. Furthermore, modified composites exhibited lower flexural modulus than virgin PLA and unmodified composites.

Table 6. Flexural properties of virgin PLA and molded composites with and without impact modifier (BS).

Type	Fibre	Formulation (%)		Flexural Strength		Flexural Modulus	
		PLA/BS/Fibre	(MPa)	SD	(GPa)	SD	
Virgin PLA		100/0/0	86.864	±2.546	4.302	±0.126	
Unmodified	CRB-30	85/0/15	64.460	±2.458	4.300	±0.133	
		70/0/30	62.113	±5.052	4.884	±0.195	
	CRB-65	85/0/15	56.692	±3.472	4.440	±0.234	
		70/0/30	47.441	±1.811	4.605	±0.136	
Modified	CRB-30	70/15/15	33.623	±2.074	3.596	±0.090	
		55/15/30	13.282	±1.517	3.102	±0.551	
	CRB-65	70/15/15	46.184	±2.891	3.764	±0.286	
		55/15/30	25.233	±1.950	3.935	±0.085	

SD, standard deviation

Impact modifier, Biomax Strong 120 (BS), is an ethylene acrylate copolymer which is known to be compatible with PLA and mostly used to improve the impact properties of PLA (Talimi 2011). The influence of impact modifier in PLA composites is displayed in Figure 3 (where error bar represents 1 standard deviation above and below the average). The combination of impact modifier with alkaline-treated fibres revealed promising results as evidenced by the tensile-impact strength of modified PLA-composites according to the increase relative to biocomposites without impact modifier.

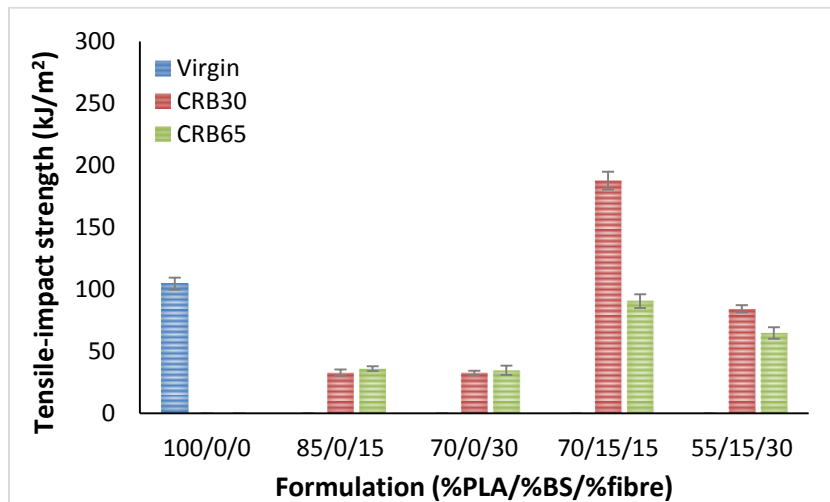


Figure 3. Tensile-impact strength in unmodified and modified alkaline PLA-composites.

CONCLUSION This research has demonstrated several different ways to utilize high volume oat hull biomass by manufacturing low cost bioproducts. The beneficial effects of impact modifier on the tensile-impact properties of PLA-composites could bring durable products. However, other mechanical properties like tensile and flexural strength were negated with the use of impact modifier.

Acknowledgements. The authors thank Natural Sciences and Engineering Research Council of Canada (NSERC) for the support.

REFERENCES

- Afrifah, K. A. and L. M. Matuana. 2013. Fracture toughness of poly (lactic acid)/ethylene acrylate copolymer/wood-flour composite ternary blends. *Polymer International* 62(7): 1053-1058.
- AOAC. 1997. AOAC Method 973.18-Fiber (acid detergent) and lignin in animal feeds. In. *Official Method of Analysis of the Association of Official Analytical Chemists*, ed. P. Cunniff. Gaithersburg, MD: AOAC International.
- AOAC. 2005. AOAC Method 2002.04-Amylase-treated neutral detergent fiber in feeds. In *Official Method of Analysis of the Association of Official Analytical Chemists*, ed. W. Horwitz. Gaithersburg, MD: AOAC International.
- ASTM D570-98. 2010. Standard test method for water absorption of plastics. West Conshohocken, PA: ASTM International.
- ASTM D638-14. 2014. Standard test method for tensile properties of plastics. West Conshohocken, PA: ASTM International.
- ASTM D790-10. 2010. Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials. West Conshohocken, PA: ASTM International.

Balakrishnan, H., I. Masoumi, A. A. Yussuf, M. Imran, A. Hassan and M. U. Wahit. 2012. Ethylene copolymer toughened polylactic acid nanocomposites. *Polymer-Plastics Technology and Engineering* 51(1): 19-27.

dos Santos Rosa, D. and D. M. Lenz. 2013. Biocomposites: influence of matrix nature and additives on the properties and biodegradation behaviour. In *Biodegradation – Engineering and Technology*, eds. S. K. Sharma, A. Mudhoo and J. H. Clark, 433- 475. Cambridge, UK: Royal Society of Chemistry.

Duhovic, M., S. Peterson and K. Jayaraman. 2008. Natural-fibre-biodegradable polymer composites for packaging. In *Properties and Performance of Natural-Fibre Composites*, ed. K. Pickering, 301-329. Cambridge, UK: Woodhead Publishing Limited.

Faisant, J. B., A. Ait-Kadi, M. Bousmina and L. Deschenes. 1998. Morphology, thermomechanical and barrier properties of polypropylene-ethylene vinyl alcohol blends. *Polymer* 39(3): 533-545.

Grewal, R.K., M. Soleimani and L.G. Tabil. 2015. Investigations on biocomposites from oat hull and biodegradable polymers. CSBE15-019. Winnipeg, MB: CSBE.

Gunatillake, P. A. and R. Adhikari. 2003. Biodegradable synthetic polymers for tissue engineering. *European Cells and Materials* 5(1): 1-16.

Hassan, A., H. Balakrishnan and A. Akbari. 2013. Polylactic acid based blends, composites and nanocomposites. In *Advances in Natural Polymers*, ed. S. Thomas, P. Visakh and A. P. Mathew, 361-396. Johor Bahru, Malaysia: Springer.

Islam, M. S. 2008. The influence of fibre processing and treatments on hemp fibre/epoxy and hemp fibre/PLA composites. Unpublished Ph.D. thesis. Hamilton, New Zealand: Materials and Process Engineering, University of Waikato.

ISO 8256:2004(E). 2004. Plastics- Determination of tensile-impact strength. Geneva, Switzerland: *ISO- International Organization for Standardization*.

Karnani, R., M. Krishnan and R. Narayan. 1997. Biofiber-reinforced polypropylene composites. *Polymer Engineering & Science* 37(2): 476-483.

Maier, C. and T. Calafut. 1998. *Polypropylene: The Definitive User's Guide and Databook*. New York, NY, US: Plastics Design Library, William Andrew, Inc.

Murphy, S. 2011. Melting point depression in biodegradable polyesters. Unpublished M.Sc. thesis. Birmingham, England: Department of Metallurgy and Materials in School of Engineering, University of Birmingham.

Nagarajan, V., A.K. Mohanty and M. Misra. 2016. Perspective on polylactic acid (PLA) based sustainable materials for durable applications: focus on toughness and heat resistance. *ACS Sustainable Chemistry & Engineering* 4: 2899-2916.

Notta-Cuvier, D., J. Odent, R. Delille, M. Murariu, F. Lauro, J. M. Raquez, B. Bennani and P. Dubois. 2014. Tailoring polylactide (PLA) properties for automotive applications: Effect of addition of designed additives on main mechanical properties. *Polymer Testing* 36:1-9.

Reddy, J. P., M. Misra and A. Mohanty. 2013. Injection moulded biocomposites from oat hull and polypropylene/polylactide blend: Fabrication and Performance Evaluation. *Advances in Mechanical Engineering* 5(2013): 1-8.

Salit, M. S. 2014. *Tropical Natural Fibre Composites: Properties, Manufacture and Applications*. Singapore: Springer.

- Sluiter, A., B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker. 2008. Determination of Structural Carbohydrates and Lignin in Biomass Laboratory Analytical Procedure. Golden, CO: National Renewable Energy Laboratory.
- Soleimani, M., L. Tabil, S. Panigrahi and A. Opoku. 2008. The effect of fiber pretreatment and compatibilizer on mechanical and physical properties of flax fiber-polypropylene composites. *Journal of Polymers and the Environment* 16(1): 74-82.
- Soleimani, M and L.G. Tabil. 2012. An integrated process for production of xylitol and biocomposites from lignocellulosic biomass. Report 20070013 for the Agriculture Development Fund. Saskatoon, Saskatchewan: Department of Chemical and Biological Engineering, University of Saskatchewan.
- Staiger, M. P. and N. Tucker. 2008. Natural-fibre composites in structural applications. In *Properties and Performance of Natural-Fibre Composites*, ed. K. Pickering, 269-300. Cambridge, UK: Woodhead Publishing Limited.
- Talimi, M. 2011. Characterization of natural fibre reinforced biodegradable composites. Unpublished M.Sc. thesis. Oshawa, ON: Department of Mechanical Engineering, University of Ontario Institute of Technology.
- Tokiwa, Y., B. P. Calabia, C. U. Ugwu and S. Aiba. 2009. Biodegradability of plastics. *International Journal of Molecular Sciences* 10(9): 3722-3742.