MULTI-DIE, VACUUM ASSISTED PULTRUSION OF FLAX/PLA THERMOPLASTIC BIOCOMPOSITE RODS

A. Oswald[1], F.L. Lapointe[1], L. Laberge Lebel[1]

[1]Advanced Composites and Fibre Structures Laboratory, Mechanical Engineering Department, Polytechnique Montréal, 2900 blvd. Édouard-Montpetit QC H3T1J4, Canada
Email: arnold.oswald@polymtl.ca, felix.lapointe@polymtl.ca, lll@polymtl.ca

Keywords: Pultrusion, Vacuum, Multi-die, Biocomposites, Flax

Abstract

Natural fibres have shown mechanical properties promising enough to replace conventional reinforcement materials in composites, and help tackle environmental issues. In addition, thermoplastic use in pultrusion can lead to potential gain in toughness, impact resistance, chemical resistance, post-pultrusion forming possiblities, and recyclability. Both natural fibres and thermoplastics uses in pultrusion face challenges respectively because of thermal degradation or high viscosity. This study reports the successful pultrusion of unidirectional fibre reinforced thermoplastic rod from biosourced materials. Polylactic-Acid (PLA) yarns were used as matrix, and flax yarns were used as reinforcement fibres. A modular pultrusion line was built to test different combinations of heating and geometry, as well as the use of a vacuum chamber. The effects of heating temperature, vacuum chamber and die configuration on the void content were investigated.

1. Introduction

Studies on pultrusion using natural fibres and/or biosourced matrix have demonstrated that biocomposite parts can be highly valuable for their mechanical properties, price and environmental benefits [1-3]. In pultrusion, yarns of reinforcement fibres are fed into the system from a creel. Thermosets are added using a resin bath. Thermoplastics are added as parallel yarns or injected as melted pellets. Fibres and resin pass through a heated die of a certain cross-section shape. For thermoplastics, tapered die entrance and resin overfilling are used to ensure pressure build-up for impregnation [4, 5]. A cooling system is added to prevent deconsolidation. The beam is pulled by a mechanism controlling the process speed. Pultrusion is a scalable and continuous process producing complex cross-section profiles. Therefore, its economic advantages for mass production adds up to those of biocomposites. Since impregnation of the fibres is difficult when using high viscosity thermoplastics, thermoset polymers are commonly used for pultrusion [5]. However, a shift toward thermoplastic matrices is promising because of their high toughness, chemical resistance, recyclability and their ability to be post formed [6]. While natural fibres and bio-sourced thermoplastics are attractive for pultrusion, their respective uses face difficulties. Above 200°C, natural fibres gradually starts to thermically degrade [1]. This prevents from using high process temperatures. Moreover, thermoplastics' viscosity is a major obstacle to good impregnation quality. In order to reduce the viscosity of a given thermoplastic, the process temperature is increased. This prevents from using low process temperatures. Thus, while it can be difficult to use natural fibres or thermoplastic matrices in pultrusion, it is even more difficult to use both. Several attempts to pultrude thermoplastic biocomposites have been made since the early 2000s [7-10]. The reviewed studies reported either high void contents (higher than 10%), presence of unimpregnated areas, or unmelted resin regions.

This study presents an attempt to enhance impregnation quality of thermoplastic biocomposites pultruded parts through several changes to the conventional pultrusion system setting. Firstly, the use of a vacuum chamber to remove residual air inside the strand was tested. Secondly, the use of a second pultrusion die to further impregnate fibres was investigated, regardless of vacuum chamber use. Parts were characterized using density measurements, in-plane shear tests and microscopic observations.

Excerpt from ISBN 978-3-00-053387-7

2. Experimental

2.1. Material

The properties of the materials used in this study are shown in Table 1. PLA yarns are trilobal 180 tex spun by Applied Polymer Innovations (from 4032D, NatureWorksLLC). Flax yarns (Roving400, Safilin) density was determined by gas pycnometry, after three hours of drying at 105 °C. Materials were wound on spools containing both PLA and flax. The number of yarns is determined by a nominal fibre volume content of 40%.

Table 1. Material properties

Material denomination	*Yarn count (tex)*	*Solid density (g/cm^3)*	*Melt density at 230 °C (g/cm^3)*	*Melting temperature (°C)*	*Number of yarns*
Roving400	*400*	*1.53*	-	-	*28*
PLA 4032D	*180*	*1.24* [11]	*1.08* [11]	*155-170* [11]	*87*

2.2. Pultrusion system

Figure 1 shows the schematic of the pultrusion system. Yarns are fed from a creel into the system. A ring ensures all yarns are aligned before entering the line. Pre-Heating module is a 300 mm long chamber opened at both ends, with two finned strip heater above the yarns. Heating and cooling dies have circular cross-sections. All dies are mounted on two rails and are horizontally stacked. Two configurations of the impregnation zone were used. The single-die impregnation zone configuration (Fig.1b) is a single pultrusion die. It is a 76 mm long, 5° tapered section, followed by a 20 mm long section with a 4.78 mm constant diameter. The multi-die configuration (Fig.1c) consists of two similar pultrusion die and an interspaced vacuum chamber. Pultrusion dies 1 and 2 posess the same geometry as described above. However pultrusion die 1 has a larger final diameter of 5 mm to let additional resin flow into pultrusion die 2, for overfilling purposes. The vacuum chamber is 100 mm long. In both configurations, the cooling die is a 140 mm long section with a constant diameter of 4.78 mm. Speed was measured by a rotary encoder. Temperature control was achieved using regularly space thermocouples. The vacuum chamber is sealed with pultrusion dies overfilling and sealant tape between the parts. The pulling force was acquired by load cells placed between the rails and the pulling mechanism.

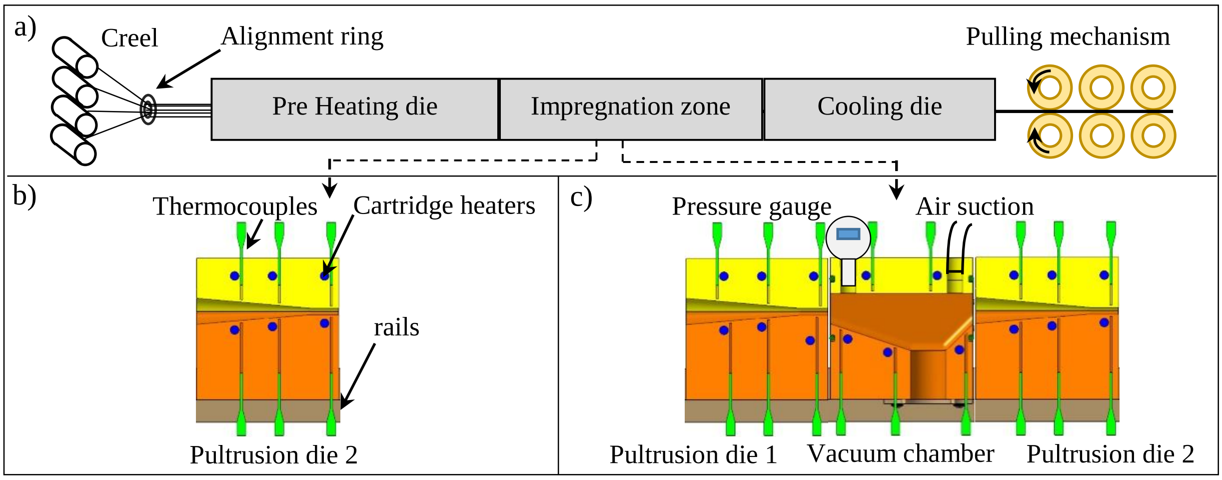

Figure 1 : (a) Schematic of the modular pultrusion line. (b) Details of single-die impregnation zone. (c) Details of multi-die impregnation zone composed of two pultrusion dies separated by a vacuum chamber

2.3. Experiments

Dies were coated with 5 layers of sealing agent (SEALER GP, Chem-Trend LP) and 5 layers of release agent (CHEMLEASE 70-90 EZ, Chem-Trend LP). Table 2 presents the different parameters sets for pultrusion. One experiment was conducted for each impregnation zone configuration described in Fig. 1. The different temperature and pressure parameters in the multi-die configuration were carried on during the same pultrusion experiment. Using an estimated PLA melt density of 1.1 g/cc for both 200 °C and 220 °C, resin overfilling is determined as a pourcentage of the cross-section area of pultrusion die 2. It is 19.3% under the single-die configuration. In the multi-die configuration, it is distributed as 9.8% in pultrusion die 1 and 9.5% in pultrusion die 2.

Table 2. Pultrusion Parameters

Specimen type	*Pulling Speed* (mm/min)	*Pre-Heating Temperature* (°C)	*Heating Temperature* (°C)	*Cooling Temperature* (°C)	*Vacuum command*	*Heating zone configuration*
P1	50	170	200	130	0	Single-die
P2A	50	170	200	130	0	
P2B	50	170	200	130	1	
P2C	50	170	220	130	1	Multi-die
P2D	50	170	220	130	0	
P2E	220	170	220	130	0	

2.4. Sample characterization

20 mm long cylindrical samples were cut on the pultruded rod using a band saw. For specimen P1 and P2D, three samples were prepared for each type. For specimen P2B, P2C and P2D, four samples were prepared for each type. Void content was determined by comparing the experimental and theoretical biocomposite density (see equation 2). The theoretical density ρ_{theo} was calculated using equation 1, where N is the number of flax yarns, λ_{flax} is the flax yarns count, ρ_{flax} is the flax density and ρ_{PLA} is the solid density of PLA. The cylinder sample diameter was measured to obtain its cross-section area S.

$$\rho_{theo} = \frac{N * \lambda_{flax}}{S} + \left(1 - \frac{N * \frac{\lambda_{flax}}{\rho_{flax}}}{S} \right) * \rho_{PLA} \qquad (1)$$

Sample length was measured to obtain its volume. The sample mass was measured. This gave the experimental density of the sample ρ_{exp}. Finally, the void content V_C was calculated using equation 2 :

$$V_C = 1 - \frac{\rho_{exp}}{\rho_{theo}} \qquad (2)$$

The in-plane shear test method was adopted from the standard test method ASTM D3914-02 [12]. Samples for this test were also previously used for density measurements. Those samples were further prepared with a dedicated notching jig and a precision saw to cut two grooves (Fig. 2a). Groove depth equalled rod radius. Compression tests were then conducted on samples with a MTS Insight at a crosshead speed of 1mm/min to achieve shear failure between the notches (Fig. 2b). Load and crosshead position were acquired. Shear modulus was calculated as the maximum slope of the stress-strain curve. Shear strength was calculated according to the standard test method.

Excerpt from ISBN 978-3-00-053387-7

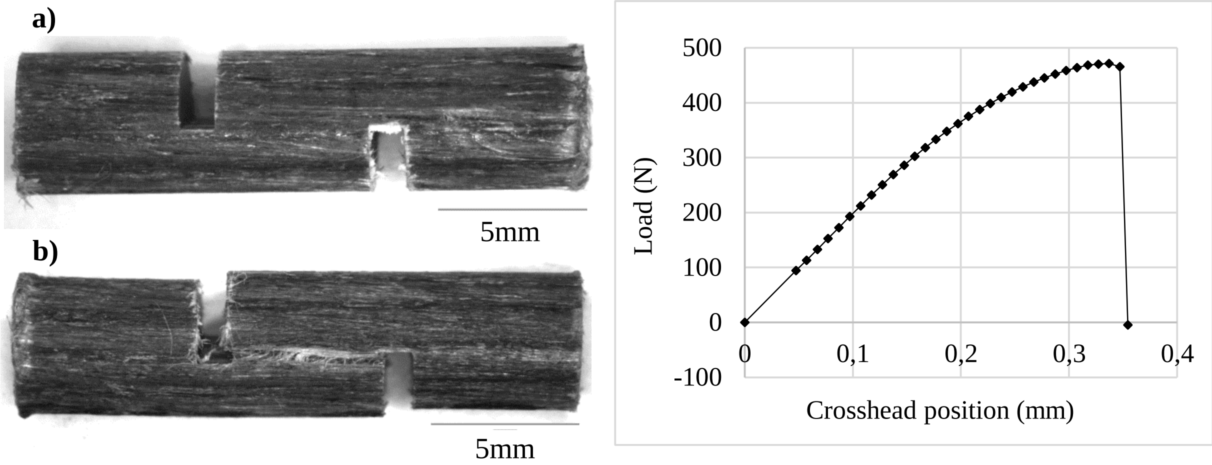

Figure 2: Pictures of Flax/PLA pultruded specimens before (a) and after (b) shear test. Failure occurs between the notches, parallel to flax fibres. (c) Load-deformation curve obtained during this test, toe compensated according to ASTM D790-15 [13]. Data shown are the test results from a P2A specimen.

For microscopic observation purposes, new samples were cut on the pultruded rods. They were dipped in epoxy and polished with diamond pastes. Observations were conducted on an optical microscope (Metallovert, Leitz).

3. Results and discussion

3.1. Observations

Table 3 shows the pultrusion process parameters measured during the experiments. One must note that the pre-heating temperature was measured in the air 1cm above the yarns. Therefore, even though the measured temperature corresponded to the set point, temperatures experienced by fibres on the bottom of the strand could be lower. A constant pulling force of 150±10 N was measured for all specimen except P2E. Fibre breakage and a pulling force of 350±15 N were observed during P2E pultrusion because of high viscous forces in pultrusion dies at 220 mm/min. When setting vacuum on, the vacuum pressure achieved in the vacuum chamber equalled the maximum vacuum pressure provided by the air pump. This indicates that resin overfilling was effective at sealing the vacuum chamber in both pultrusion dies.

Table 3. pultrusion experiments parameters

Specimen type	*Pulling Speed* (mm/min)	*Pre-Heating Temperature* (°C)	*Heating Temperature* (°C)	*Cooling Temperature* (°C)	*Relative Vacuum Pressure* (kPa)	*Heating zone configuration*
P1	50±1	170±3	200±1	130±1	0	One heating die
P2A	50±1	170±3	200±1	130±2	0	Two heating dies & vacuum chamber
P2B	50±1	170±3	200±1	130±2	91,4±0.5	
P2C	50±1	170±3	220±1	130±2	91,4±0.5	
P2D	50±1	170±3	220±1	130±2	0	
P2E	220±5	170±3	220±1	130±2	0	

Excerpt from ISBN 978-3-00-053387-7

3.2. Void Content

Fig. 3 shows the void contents measured on the specimens extracted from the five experimental conditions. P1 specimens (single die) have a high void content compared to all P2 samples (multi-die). This suggests that the use of several pressure build-up in separated tapered sections enhances impregnation quality. Although void content of all P2 samples are quite similar, data of P2A type (without vacuum) and P2B type (with vacuum) suggests that the vacuum has a relatively low, but negative effect on the impregnation quality at 200 °C. Further experiments will be conducted to confirm this observation. Comparisons of P2A vs. P2D (both without vacuum) and P2B vs. P2C (both with vacuum) suggest that temperature has no influence on void content in the 200-220 °C range. Contrasting with previously published thermoplastic biocomposite pultrusion experiments [7-10], low void contents were achieved for P2 samples (see Fig. 3).

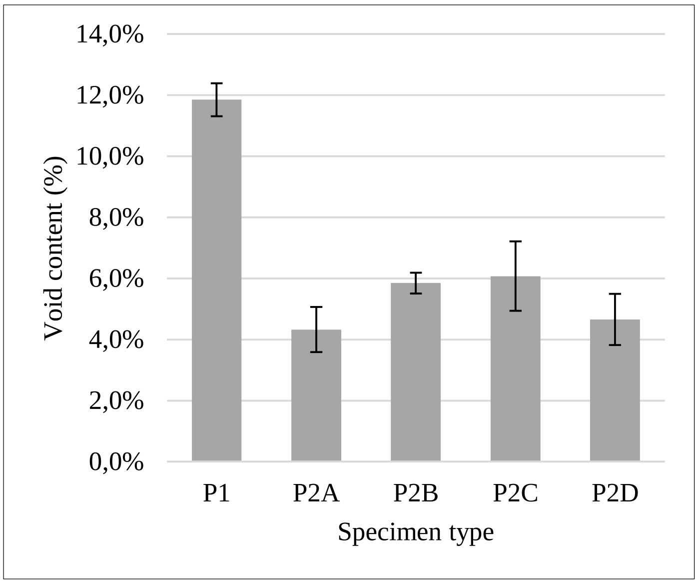

Figure 3: Void content of 5 pultruded specimen types. P1 data suggests that multi-die pultrusion system reduces the void content.

3.2. In-Plane shear test

Fig. 4 shows the results of in-plane shear test for 4 specimen types. Results include the tangent shear modulus (Fig.4a), and the the shear strength (Fig.4b). P1 samples have lower shear modulus and lower shear strength than P2 specimens. Lower shear strength and modulus (Fig. 4) correlates with higher void content (Fig.3). The presence of voids lowers the quality of fibre/matrix interface quality and thus the ability to transfer shear stress. No significant difference is observed between P2-type specimens. This can be explained by the close values of void contents (Fig. 3). This suggests that neither vacuum use (P2A vs P2B), nor temperature increase in the studied range (P2B vs P2C) have significant impact on the impregnation.

Excerpt from ISBN 978-3-00-053387-7

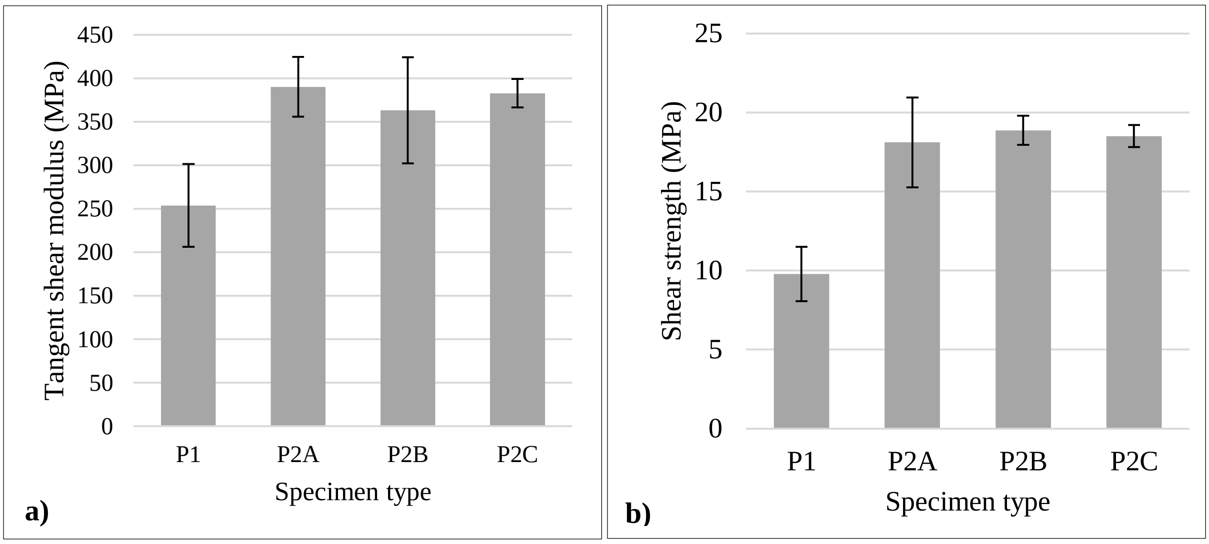

Figure 4 : Shear tests results for 4 pultruded specimen types with crosshead speed of 1mm/min.
(a) Tangent shear modulus determined as the maximal slope of the stress-strain curve.
(b) Shear strength, the maximal shear stress experienced by the sample during test.

3.3. Micrographs

Figure 5 shows representative micrographs of specimen types P1 (single-die) (a), P2A (multi-die withouth vacuum) (b) and P2B (multi-die with vacuum) (c). No unmelted resin fibres were observed. In all three samples, the majority of the fibres were observed to remain in clusters of three to ten individual fibres. P2A and P2B (multi-die) presents significantly less voids than P1 (single-die). P1 void areas are connected to one another. P2A and P2B present similar void types and sizes. Voids are mainly located in area of locally high fibre volume fraction. The spatial flax fibres distribution in P2A is more homogeneous than in P2B and P1. P2B and P1 specimen present fibre bundles, roughly corresponding in size and number to flax yarns fed into the pultrusion system. However, more experiments and micrographs are needed to conclude on any potential influence of the vacuum on fibre spatial distribution.

Micrographs observations correlates well with void content measurements and shear test results in regards. It supports the fact that the use of a second pultrusion die enhances the impregnation quality. Observations do not indicate void content differencies when the vacuum is used.

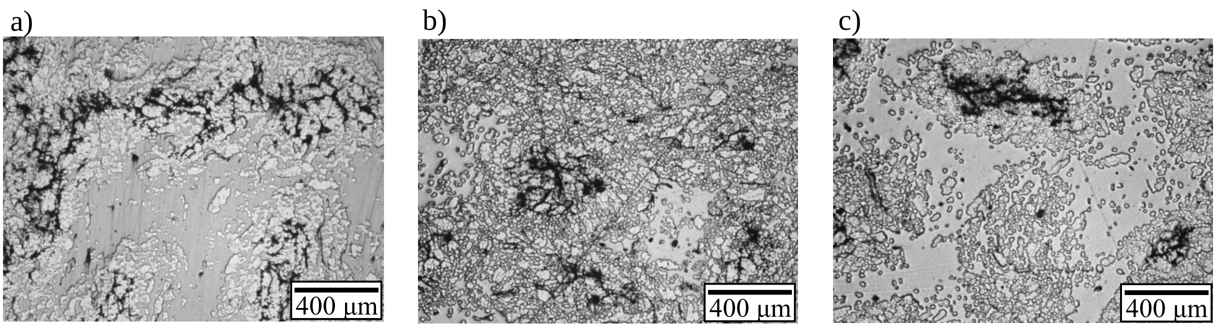

Figure 5 : Micrographs of pultruded specimen : (a) P1 (single-die), (b) P2A (multi-die without vacuum), (c) P2B (multi-die with vacuum).

Excerpt from ISBN 978-3-00-053387-7

4. Conclusions

In this study, flax/PLA pultrusion experiments in different die configurations were conducted on a modular pultrusion system. The ability to seal the vacuum chamber by overfilling the pultrusion die was demonstrated. Flax/PLA rod with fibre volume content of 40% were successfully pultruded. In light of density measurements, in-plane shear tests and microscopic observations, we can conclude on the effect of the proposed pultrusion system design. The presence of a second pultrusion die led to significant reduction of the void content in unidirectionally reinforced flax/PLA rod. This was associated to improved shear performance of the pultruded parts. In the performed experiments, the use of a vacuum chamber did not yield significant improvements on impregnation quality of flax/PLA pultruded parts. Further experiments are to be conducted to understand whether the vacuum has an influence on the fibre/resin impregnation.

The proposed design enabled pultrusion of fully biosourced thermoplastic biocomposite rod with lower void contents than previous attempts found in the literature. It is a step towards replacing glass-fibre reinforced thermoset profiles by environmentally friendly composite beams. In addition, such parts could be used as preforms for further transformation.

Excerpt from ISBN 978-3-00-053387-7

References

[1] F. Ahmad et al., "A Review: Natural Fiber Composites Selection in View of Mechanical, Light Weight, and Economic Properties," *Macromolecular Materials and Engineering*, vol. 300, nº. 1, p. 10-24, Jan 2015.

[2] O. Faruk et al., "Biocomposites reinforced with natural fibers: 2000–2010," *Progress in Polymer Science*, vol. 37, nº. 11, p. 1552-1596, 2012.

[3] K. Van de Velde et al., "Biopolymers: overview of several properties and consequences on their applications," *Polymer Testing*, vol. 21, nº. 4, p. 433-442, 2002.

[4] W. Michaeli et al., "Thermoplastic pull-braiding: Pultrusion of profiles with braided fibre lay-up and thermoplastic matrix system (PP)," *Composites Part A: Applied Science and Manufacturing*, vol. 27, nº. 1, p. 3-7, 1996.

[5] S. Wiedmer, "An Experimental Study of the Pultrusion of Carbon Fiber-Polyamide 12 Yarn," *Journal of Thermoplastic Composite Materials*, vol. 19, nº. 1, p. 97-112, 2006.

[6] W. Tomlimson et al., "Advantages of pultruding thermoplastics," *Reinforced Plastics*, vol. 37, nº. 10, p. 46-49, 1993.

[7] K. Van de Velde et al., "Thermoplastic pultrusion of natural fibre reinforced composites," *Composite Structures*, vol. 54, nº. 2-3, p. 355-360, 2001.

[8] I. Angelov et al., "Pultrusion of a flax/polypropylene yarn," C*ompos. Pt. A-Appl. Sci. Manuf.*, vol. 38, nº. 5, p. 1431-1438, 2007.

[9] L. Z. Linganiso et al., "Pultrusion of flax/poly(lactic acid) commingled yarns and nonwoven fabrics," *Journal of Thermoplastic Composite Materials*, vol. 27, nº. 11, p. 1553-1572, 2013.

[10] A. Memon et al., "The Processing Design of Jute Spun Yarn/PLA Braided Composite by Pultrusion Molding," *Advances in Mechanical Engineering*, vol. 5, nº. 0, p. 816513-816513, 2013.

[11] NatureWorks. (2015). *Ingeo™ Biopolmer 4032D Technical Data Sheet*. [En ligne]. Disponible: http://www.natureworksllc.com/~/media/Technical_Resources/Technical_Data_Sheets/TechnicalDataSheet_4032D_general_pdf.pdf?la=en

[12] *Standard Test Method for In-Plane Shear Strength of Pultruded Glass-Reinforced Plastic Rod*, ASTM D3914-02(2016), 2008.

[13] *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials1*, ASTM D790-15, 2016.

Excerpt from ISBN 978-3-00-053387-7