WOVEN FLAX FABRIC FIBER REINFORCED IN-SITU POLYMERIZED POLY(BUTYLENE TEREPHTHALATE) COMPOSITES PRODUCED BY RTM

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Abstract

The work described in this paper refers to the mechanical characterization of woven flax fiber fabric reinforced in-situ polymerized poly(butylene terephthalate) thermoplastic composites, produced by the RTM technique. It is made a brief description of the developed RTM set-up, the composite manufacturing details and the processing parameters control. This study is accompanied by matrix thermal behavior investigations (DSC).

1 Introduction

Thermoplastic composites offer some interesting advantages over thermosets counterparts, such as higher toughness and impact resistance, design freedom, recyclability and faster production cycles. The use of vegetable fibers as reinforcement, in place of glass fibers, further increases the range of benefits because they are renewable, less expensive, not abrasive, have lower density, better specific stiffness and lower environmental impact, since they are biodegradable and easily recyclable. The thermoplastic selection needs to take into account the low thermal resistance of vegetal fibers and the processing technique that will be used. The cellulosic component of the fibers goes through degradation rapidly and irreversibly at temperatures of around 200 °C [1, 2]. The usual thermoplastic processing techniques do not allow the combination of engineering or high performance thermoplastics with vegetal fibers due to its high melting temperature. The reactive processing of thermoplastics composites is a recent technique, currently under development and optimization [3-9], which makes use of polymer precursors (monomers or oligomers) that, after mixing with an activator system, impregnate the reinforcement and polymerize in-situ to form the desired matrix. Due to its low molecular weight the polymer precursors have extremely low melt viscosity (in order of mPa.s), allowing a fast and appropriate impregnation of short and continuous reinforcement at lower processing pressure and moderate temperature (180 to 250 ºC for PA12 and PBT). The traditional liquid moulding technologies of thermoset composites can be used (RTM, VARTM, SRIM, RRIM, among others). It´s necessary, however, to make adjustments in the equipment as a result of the existing differences in the processing of these two types of polymeric materials. Due to the constraints posed by both the in situ polymerization and the liquid molding process, only a

limited amount of polymer systems are available for thermoplastic RTM, including the anionic ring-opening polymerization of polyamides and the entropically driven ring-opening polymerization of cyclic oligoesters [3].

This paper describes the mechanical properties of unreinforced and flax fiber reinforced in-situ polymerized poly(butylene terephthalate) produced by the isothermal RTM technique, starting from the prepolymer cyclic butylene terephthalate (CBT$^®$resin). It is made a brief description of the developed RTM set-up, the composite manufacturing details and the processing parameters control. This will be accompanied by CBT thermal behavior investigations (DSC).
Our objective was to investigate the possible compatibility between these two kinds of materials, both very sensitive to humidity. Reactive processing of vegetal fiber reinforced thermoplastics, as far as the authors know, was never tested.

2 Materials

The prepolymer used in this study is the cyclic butylene terephthalate oligomer (CBT$^®$160, $M_w = (220)_n$, n = 2-7) in granule form, supplied by *Cyclics Corporation Corporation* (Schwarzheide, Germany). It is a mixture of low molecular weight oligomers (around dimer 40 wt%, trimer 35 wt%, tetramer 15 wt%, and pentamer and higher 10 wt%) with two to seven butyl groups, resulting in a melting range from 130–160°C [3]. Already contains a premixed tin-based catalyst (*Fascat$^®$* 4101, butylchlorotin dihydroxide (C$_4$H$_9$Sn(OH)$_2$Cl, M_w = 245.29, 0.35 wt%) and was termed as one-component CBT. Before processing, the oligomers were dried for about 2 h at 80 ºC in order to remove residual moisture, which could interfere with the polymerization reaction.

The reinforcement used is a non-treated flax woven fabric, supplied by *Composites Evolution* (Chesterfield, UK), suitable for processing by traditional liquid molding techniques such as hand lay-up, vacuum infusion and RTM. The woven fabric type is 3H Satin (Figure 1), with a surface weight of 420 g/m^2. Before processing, the flax fabric was dried 24 h at 80 ºC in order to remove residual moisture.

Figure 1 Biotex Flax woven fabric 3H Satin

3 RTM set-up

It was created a new experimental RTM set-up for moderate temperatures (180 to 200 ºC) to produce pure thermoplastic and composite plates with the one-part CBT$^®$160 resin. It consists of a flat heated mold, a system for melting the resin under nitrogen atmosphere, a system to inject the resin into the fiber bed and three temperature controllers (Figure 2). The mold is in steel, tripartite, heated by cartridge heaters, with orifices for the placement of temperature sensors type Pt100. The heaters and the sensors are connected to a PID control temperature unit in order to achieve and maintain the set temperature. The mold cavity allows

the production of 100x100x4 mm^3 plates and it was treated with a PTFE coating, applied by the company *Flupol* (Portugal), in order to facilitate the demoulding of the plates. The fusion system consists of a sealed cylindrical vessel heated by resistances and closed with a lid, which contained 5 inlets/outlets. These are used for a temperature sensor type Pt100 (to measure the resin temperature), a resin delivery tube (to inject the resin from the fusion system to the mold), a nitrogen pressurizing tube and a mechanical stirrer. Within the fusion vessel the CBT is placed inside a glass cup, surrounded by thermal bath oil. The vessel heaters and the Pt100 sensor are connected to a control temperature unit in order to achieve the set temperature. The mechanical agitator provides the resin mixing to homogenize its temperatures before injection. The injection system consists of nitrogen bottle, two pressure regulators systems, valves and other accessories. The nitrogen is heated by means of a serpentine heat exchanger. All transfer tubes are heated by flexible silicon elastomer heaters which are connected to an ON/OFF temperature controller.
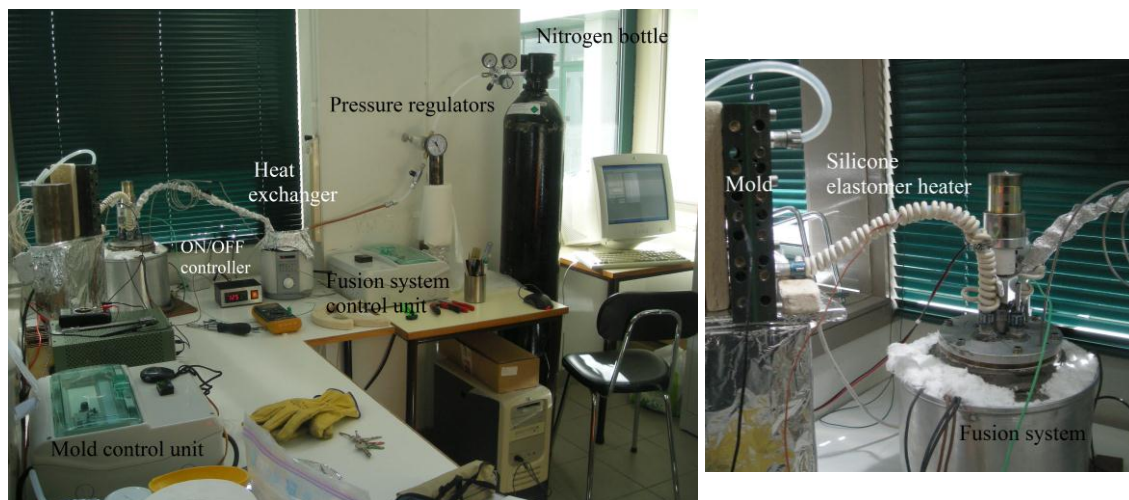

Figure 2 Developed RTM set-up

4 Processing

Since isothermal processing is a distinct advantage for closed mould processes and is possible for CBT$^®$ resin, the temperature of the molten oligomers and the mold are both 190 ºC, lower than the thermal degradation temperature of vegetal fibers. The CBT resin is heated under nitrogen atmosphere to about 170 ºC and then stirred for homogenization of its temperature (120 to 180 s). The resin and nitrogen delivery tubes are heated at 180 ºC. When the low viscous catalyzed oligomer mixture reaches the temperature of 190 °C is injected, under nitrogen pressure, into the closed mold containing the flax fibers reinforcement (in the case of composites plates production). This means that both polymerization and crystallization take place at the same temperature. Once the mold is completely filled, inlet and outlet ports are closed and the temperature maintained during 30 min, to complete the polymerization reaction and to allow for cold crystallization. In principle, the part could be demoulded at this temperature. However, since demolding at such high temperatures is rather troublesome with the current mold set-up, the part is allowed to cool before demolding.

Flat plates of unreinforced and reinforced polymerized CBT (pCBT) were successfully produced using the method described above (Figure 3). The pure pCBT plates exhibit a higher shrinkage in the mold during which fissuration have also occurred. The incorporation of the reinforcement reduced the matrix shrinkage, however it was observed the presence of

microcracks distributed randomly on the surface of the produced plates. The presence of microcracks are also reported by others researchers for glass fiber reinforcements [10].
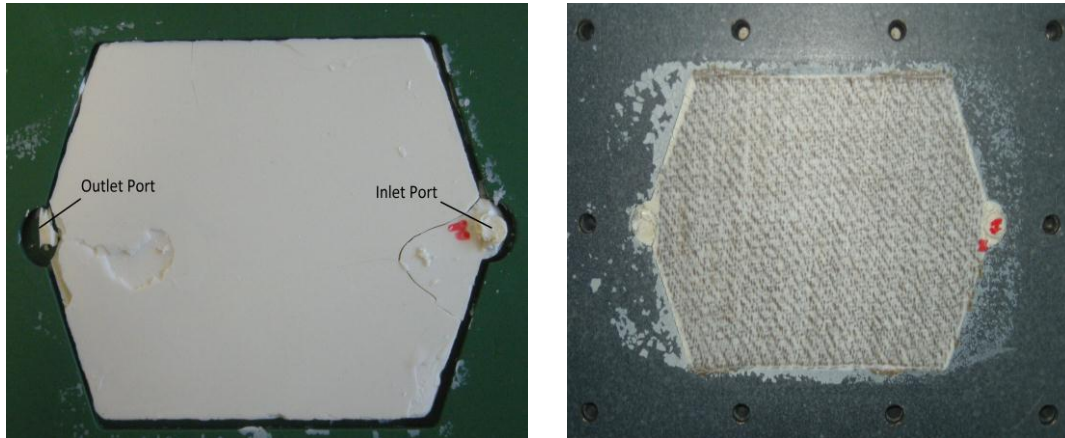

Figure 3 Pure and flax reinforced pCBT plates produced by RTM

5 DSC Analysis

Differential scanning calorimetry (DSC Q20 V24.2, TA Instruments) were used to investigate the thermal behavior of CBT. Experiment run with the sample under dry nitrogen to prevent moisture and oxidative degradation. The sample was subjected to the following thermal cycle: first heating to 190 ℃, isothermal at 190 ℃ for 30 min, cooling to room temperature, reheating to 250 ℃ and cooling to room temperature. For the heating steps a temperature ramp of 10℃/min was used (Figure 4).
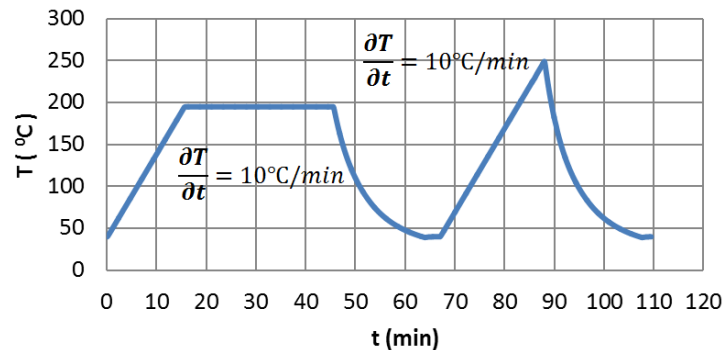

Figure 4 Thermal cycle defined for the DSC

The data were analyzed by the Universal Analysis software package of TA Instruments, version 4.5 A. The typical DSC thermograms of CBT$^{®}$ 160, submitted to the thermal cycle described above, are displayed in Figure 5. The first heating curve showed the characteristic behavior of the CBT used in this investigation, consisting of three small melting peaks at 113, 156 and 187 ℃ and a large at 141 ℃. These peaks of CBT are ascribed to different size oligomers and are in agreement with earlier observations reported by other researchers [3, 11-14]. When the temperature is maintained at 190 ℃ for 30 min the CBT resin polymerize into pCBT that, at the same time, crystallizes. Because isothermal polymerization of CBT is athermic, DSC cannot be used to investigate the reaction dynamics. The second heating/cooling curve showed a melting peak at 229 ℃ that is related to the polymerized pCBT. During the second cooling step, pCBT crystallized at 173 ℃.
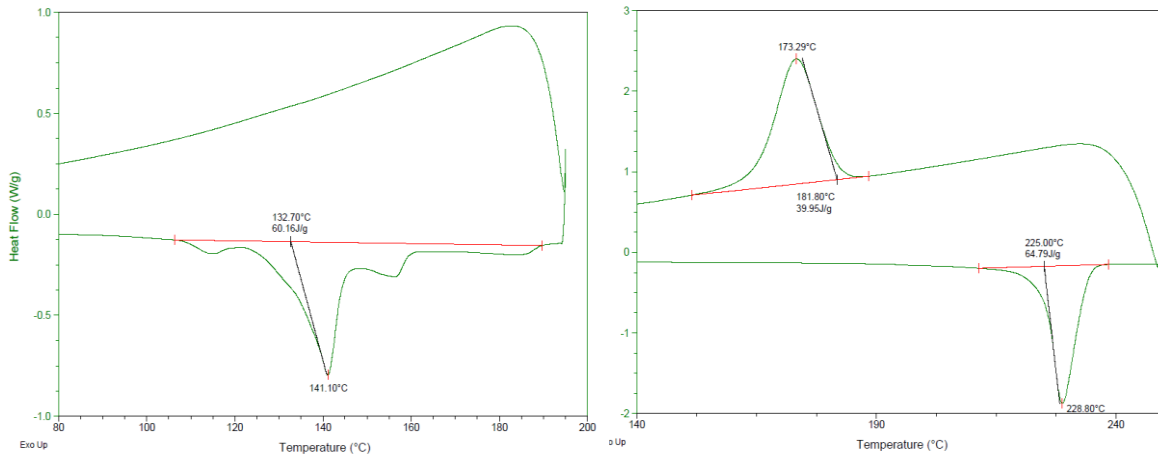
Figure 5 DSC thermograms analysis: first heating/cooling (left) and second heating/cooling (right)

The degree of crystallinity is defined as follows:

$$\chi_{c,DSC}\,(\text{wt\%}) = \left[\frac{\Delta H_f}{\Delta H_f^0}\right] \times 100$$

Where ΔH_f is the melting enthalpy of the polymer and ΔH_f^0 is the melting enthalpy of the fully perfect crystal of PBT, which is found in literature to be 142 J/g and 134 J/g for the α phase and β phase, respectively. Since the β phase is usually only obtained by drawing of PBT, the crystallinity of polymerized CBT (pCBT) is calculated by assuming it to consist of 100% α form [3]. Table 1 summarizes the melting temperatures and enthalpies associated with the first and second DSC heating, as well as the crystallization temperatures and crystallization enthalpies, deduced from the cooling regime. Melting temperature (T_m) was considered to be the maximum of the endothermic melting peak from the heating scans, whereas crystallization temperature (T_c) was taken as the maximum of the exothermic peak of crystallization from the cooling scans. The heat of fusion and the crystallization heat (ΔH_c) were determined from the areas under the melting and crystallization peaks, respectively.

Material	1st heating/cooling		2nd heating/cooling				
	T_m [°C]	ΔH_m [J/g]	T_m [°C]	ΔH_m [J/g]	χ_c [%]	T_c [°C]	ΔH_c [J/g]
CBT®160	141,10	60,16	-	-	-	-	-
Pure pCBT	-	-	228,80	64,79	45,63	173,29	39,95

Table 1 Results of DSC measurements

All the results are in agreement with earlier observations reported by other researchers [3,12, 13, 15-19]. The in-situ polymerized CBT showed to be more crystalline than the normal PBT (35%) [11, 3] and this has been assigned to isothermal processing. The higher degree of crystallinity can substantially reduce ductility. Hilde Parton [3], concluded that for temperatures below 200ºC, where polymerization is relatively slow, crystallization starts before polymerization is completed and this simultaneity can affect the crystal structure, the final degree of crystallinity and hence the mechanical properties.

6 Mechanical characterization

Pure and reinforced pCBT were tested in three point bending according, respectively, to ISO 178 [20] and ISO 14125 [21]. The tests were performed on a universal TIRA test 2705 machine equipped with a 500 N load cell. The span length was 64 mm and the test speed 2mm/min.

Tensile tests were performed according to ISO 527-4 [22], on a universal *INSTRON* 3367 machine equipped with a 30 KN load cell and an extensometer with a gauge length of 25 mm. The test speed was 2 mm/min.

Typical flexural stress–strain curves of pure and reinforced pCBT are shown in Figure 6 whereas Table 2 summarizes the tensile and flexural properties.
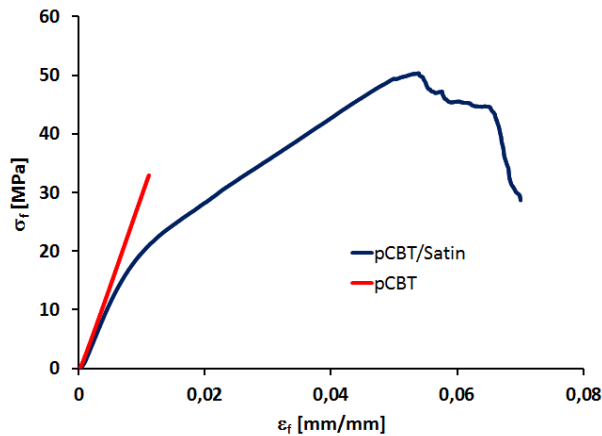

Figure 6 Typical three point bending stress–strain plots for pCBT woven flax fabric reinforced pCBT

Material	V^1_f [%]	$\overline{\sigma}^{max}_t$ [MPa]	$\overline{E}_t$ [GPa]	$\overline{\sigma}^{max}_f$ [MPa]	$\overline{E}_f$ [GPa]
pCBT	0	$15,0 \pm 1,0$	$2,48 \pm 0,26$	$32,5 \pm 2,1$	$3,00 \pm 0,08$
pCBT/Satin	34	$21,7 \pm 0,9$	$1,21 \pm 0,44$	$52,1 \pm 4,1$	$2,60 \pm 0,10$

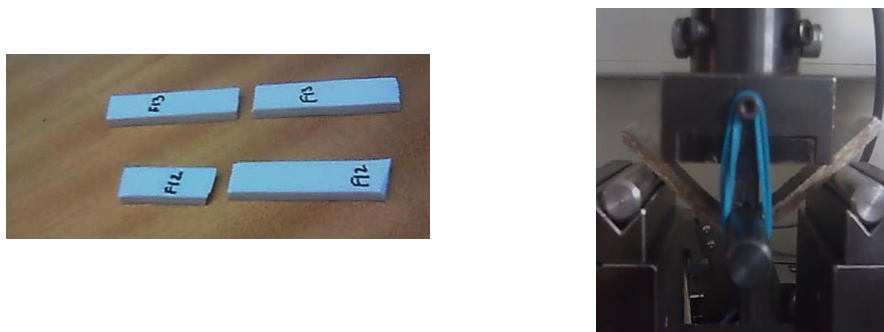**Table 2** Tensile and flexural properties of pure and woven flax fabric reinforced pCBT

Figure 7 Three point bending samples after testing (left) pCBT (right) flax reinforced pCBT

For the unreinforced pCBT a brittle behavior was observed (Figure **7**). As expected the incorporation of woven flax fabric reinforcement resulted in an enhancement of tensile and flexural strength, however there is a decrease in stiffness.

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[1] Percentage by volume of fiber in the composite

7 Conclusions

From the results presented above, it is clear that pCBT isothermally processed at 190ºC is brittle, breaking at very small strains. This brittleness is related to the high crystallinity of CBT resin, determined by DSC analysis. The incorporation of woven flax fabric reinforcement resulted in an enhancement of tensile and flexural strength, however with a stiffness decrease. This can be justified by a weak interfacial adhesion fiber/pCBT. These results can be significantly improved if the flax fibers are subjected to a surface treatment compatible with the CBT resin.

References

[1] Bailie C. *Green composites: Polymer composites and the environment*. WoodHead Publishing Limited, Canada (2004).

[2] Romão C. *Estudo do Comportamento Mecânico de Materiais Compósitos de Matriz Polimérica Reforçados com Fibras Naturais.* Universidade do Porto, Porto (2003).

[3] Parton H. *Characterisation of the in-situ polymerisation production process for continuous fibre reinforced termoplastics*. Katholieke Universiteit Leuven, Leuven (2006).

[4] Baets J., Dutoit D.M., Verpoest I. Toughening of glass fiber reinforced composites with a cyclic butylene terephthalate matrix by addition of polycaprolactone. *Composites: Part A,* **vol. 39**, pp. 13–18 (2008).

[5] Mallon P.J., Dweib M.A., Ziaee S., Chatterjee A., Gillespie J.W., Hieider D., Coll S.M., Greaney M., O´Bradaigh C.M. VARTM&RTM Processing of PBT&PA Thermoplastic Composites. University Of Limerick, Limerick (2002).

[6] Verrey J., Wakeman M., Michaud V., Manson J.-A.E. Manufacturing cost comparison of thermoplastic and thermoset RTM for an automotive floor pan. *Composites: Part A*, **vol. 37**, pp. 9–22 (2006).

[7] Zingraff L., Michaud V., Bourban P.-E., Manson J.-A.E. Resin transfer moulding of anionically polymerised polyamide 12. *Composites: Part A,* **vol. 37**, pp. 1675–1686 (2005).

[8] Baets J., Godara A., Devaux J., Verpoest I. Toughening of polymerized cyclic butylene terephthalate with carbon nanotubes for use in composites. *Composites: Part A,* **vol. 39**, pp. 1756–1761 (2008).

[9] Aurrekoetxea J., Zurbitu J., Mendibil I. O., Agirregomezkorta A., Sánchez-Soto M., Sarrionandia M. Effect of superelastic shape memory alloy wires on the impact behavior of carbon fiber reinforced in situ polymerized poly(butylene terephthalate) composites. *Materials Letters,* **vol. 65** , pp. 863–865 (2011).

[10] Prabhakaran R. T. D., Andersen T. L., Lystrup A. *Glass/CBT laminate processing and quality aspects* in " *The 10th International Conference on Flow Processes in Composite Materials (FPCM10)*, Ascona, Switzerland, (2010).

[11] Ishak Z.M., Leong Y., Steeg M., Karger-Kocsis J. Mechanical properties of woven glass fabric reinforced in situ polymerized poly(butylene terephthalate) composites. *Composites Science and Technology,* **vol. 67**, pp. 390–398 (2007).

[12] Chen H., Yu W., Zhou C. Entropically-driven ring-opening polymerization of cyclic butylene terephthalate: rheology and kinetics. *Polymer Engineering & Science,* **vol. 52,** pp. 91-101 (2011).

[13] Lanciano G., Greco A., Maffezzoli A., Mascia L. Effects of thermal history in the ring opening polymerization of CBT and its mixtures with montmorillonite on the crystallization of the resulting poly(butylene terephthalate). *Thermochimica Acta,* **vol. 493**, pp. 61-67 (2009).

[14] Brunelle D. Cyclic Oligomer Chemistry. *Journal of Polymer Science Part A: Polymer Chemistry,* **vol. 46**, pp. 1151–1164 (2008).

[15] Parton H., Baets J., Lipnik P., Goderis B., Devaux J., Verpoest I. Properties of poly(butylene terephthatlate) polymerized from cyclic oligomers and its composites. *Polymer,* **vol. 46**, pp. 9871–9880 (2005).

[16] Ishak Z.A.M., Shang P.P., Karger-Kocsis J. A modulated DSC study on the in situ polymerization of cyclic butylene terephthalate oligomers. *Journal of Thermal Analysis and Calorimetry,* **vol. 84**, pp. 637–641 (2006).

[17] Ishak Z.M., Gatos K., Karger-Kocsis J. On the In-Situ Polymerization of Cyclic Butylene Terephthalate Oligomers: DSC and Rheological Studies, *Polymer Engineering and Science,* **vol. 46**, pp. 743-750 (2006).

[18] Liu Y., Wang Y.F., Gerasimov T.G., Heffner K.H., Harmon J.P. Thermal Analysis of Novel Underfill Materials with Optimum Processing Characteristics. *Journal of Applied Polymer Science,* **vol. 98**, pp. 1300–1307 (2005).

[19] Bank D., Cate P., Shoemaker M. pCBT: A New Material for High Performance Composites in Automotive Applications in "*4th Annual SPE Automotive Composites Conference*. Michigan, USA (2004).

[20] ISO 178. Plastics - Determination of flexural properties (2010).

[21] ISO 14125. Fibre reinforced plastic composites - Determination of flexural properties (1998).

[22] ISO 527-4. Plastics - Determination of tensile properties - Part 4: Test conditions for isotropic and orthotropic fibre-reinforced plastic composites (1997).