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# Toughened carbon fibre fabric-reinforced pCBT composites

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**Abstract:** Toughened carbon fibre reinforced pCBT composites were obtained by chemical modification of CBT with small amounts of epoxy resin and isocyanates as chain extenders. Homogeneous CBT/epoxy and CBT/isocyanate blends were prepared by melt blending the components in a lab-scale batch mixer at low temperatures and high shear rate. Melt blending was stopped before the ring-opening polymerization of CBT could start. The modified CBT was the starting material for carbon fibre fabric-reinforced pCBT composites (fibre content at about 70 vol.%) which were prepared by ringopening polymerization during compression moulding using a simple powder prepreg method.

Interlaminar shear strength, flexural strength and failure strain of the chemically modified composites increased up to 60% with respect to unmodified pCBT composites. Nevertheless, the flexural moduli slightly decreased due to the toughening effect of the chain extender on the pCBT matrix. Falling weight impact tests revealed that the energy absorption of the

modified composites was relatively higher as compared to unmodified pCBT composites.

**Keywords:** Cyclic butylene terephthalate, **A.** carbon fibres, **E.** powder processing, **A.** textile composites, **B.** mechanical properties

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# Introduction

The interest in thermoplastic composites (TPCs) has increased in the past years because TPCs typically outperform thermosets in toughness and impact strength. Moreover, TPCs can be produced in a shorter time as compared to thermosets because no curing step is needed. Additionally, they can be welded and recycled due to their meltability. However, the main disadvantage of thermoplastics is the need for high processing temperatures and pressures due to the high melt viscosity of the matrix. In addition, proper impregnation of the fibre at a micro level might prove difficult and often results in products with a locally high void content [1].

These shortcomings can be overcome using ring-opening polymerization (ROP) of cyclic oligomers such as cyclic butylene terephthalate oligomers (CBT<sup>®</sup>) which exhibit a very low, water-like melt viscosity (0.02 Pa·s at 190 °C [2]). CBT oligomers undergo an entropically driven ROP in the presence of a tin-based catalyst at temperatures below as well as above the melting temperature of polymerized CBT (referred to as pCBT), *i.e.*  $T_m = 225$  °C [3]. This allows for

isothermal processing below  $T_m$  where crystallization and polymerisation occur simultaneously, hence demoulding can be done without further cooling [4-6]. Nevertheless, pCBT was shown to be considerably more brittle than conventional PBT [5, 7]. The pCBT brittleness is due to a relatively higher degree of crystallinity together with the formation of large perfect crystals and a lack of intercrystalline tie molecules [5, 8]. The inherent brittleness of pCBT is a critical problem and hinders a wide application of fibre reinforced pCBT composites as structural materials and at industrial scales. This problem has been addressed by various researchers, e.g. by decreasing the crystallinity and thus increasing the toughness, either by nonisothermal processing using fast cooling [9] or copolymerization of CBT with poly(ethylene-co-vinyl acetate) [10], poly(vinyl butyral) [11], *E*-caprolactone [12] and polycaprolactone [13]. However, these methods are little effective or lead to a decrease of other relevant mechanical properties such as stiffness and strength. Wu et al. [14-16] proposed a simultaneous binding and ex situ toughening concept for textile reinforced pCBT composites by applying an epoxy preforming binder among textile fabric layers. The pCBT matrix in the interply region was toughened. Nevertheless, the brittle nature inherent in the composite laminate based on pCBT matrix was not completely eliminated with the proposed concept. This was because the pCBT polymer matrix was toughened locally since the preforming binder was mainly located in the interply region of the composite laminate whereas bulk pCBT remained brittle.

Recently, we showed that reactive chain extension of pCBT with epoxy resin [17] as well as isocyanates [18] is a useful way to increase the molecular weight and to toughen pCBT without considerably affecting other properties.

In this work it is demonstrated that the developed toughening methods not only work for pCBT matrix but also for fibre reinforced pCBT composites.

## 1. Experimental Section

#### 1.1. Materials

Cyclic butylene terephthalate oligomers were termed as one-component CBT<sup>®</sup>160 and contained butyl tin chloride dihydroxide as a catalyst. The material was provided as granules by Cyclics Europe GmbH (Schwarzheide, Germany). A low-viscous, bifunctional epoxy resin (referred to as EP), Eporai 450/A was purchased from IQRaisa, S.L. (Valencia, Spain). The epoxy equivalent weight was 148–155 g/eg. Three different types of isocyanates were used as toughening agents; a bifunctional liquid aliphatic hexamethylene diisocyanate (referred to as HDI) with a molecular weight of 168.2 g/mol, a bifunctional solid aromatic 4,4"-methylenebis(phenyl isocyanate) (referred to as MDI) with a molecular weight of 250.3 g/mol and a solid polymeric methylene diphenyl diisocyanate (referred to as PMDI). The PMDI was based on 4,4"methylenebis(phenyl isocyanate) and contained oligomers with an average functionality of ~2.7 and a NCO content of 31.8%. HDI and MDI were obtained from Sigma-Aldrich (St. Louis, MO, USA) while PMDI was purchased from BASF Poliuretanos Iberia SA, Rubí, Spain. All toughening agents were used as received. The reinforcement used in the pCBT composites was a high strength carbon fibre fabric with balanced plain weave architecture, referred to as CF. It consisted of two sets of interlacing threads, commonly referred to as warp and weft, and was a bi-directional [0/90]. It was characterised by a surface weight of 193 g/m<sup>2</sup> and was supplied by Jordi Sagristà, SL, Barcelona, Spain with the reference TAFE 3K.

#### **1.2. Sample preparation**

The CBT was ground into a fine powder using mortar and pestle and vacuum dried at 80°C for 8 h prior to processing. EP- and NCO-modified CBT as starting materials for composite production were prepared by melt blending in a lab-scale batch mixer (Brabender Plasti-Corder W50EHT, Brabender GmbH & Co. KG, Duisburg, Germany). A mixing chamber temperature of 200 °C, protective N<sub>2</sub> blanket and a rotor speed of 180 min<sup>-1</sup> were used for all blends. Around 40 g of previously dried CBT and the corresponding amount of chain extender were melt blended for 2 min. Then the liquid materials were quickly collected from the mixing chamber, cooled to room temperature and ground into a fine powder using mortar and pestle. CBT blends containing 2, 3 and 4 wt.% of EP as well as blends containing 1 wt.% of PMDI, MDI and HDI, respectively, were prepared using these processing parameters.

A simple powder prepreg method was used to manufacture pCBT-CF composites *via* compression moulding. The composite lay-up was as follows. Previously dried CBT/chain extender powder (~1.1 g) was evenly spread on a CF fabric (size: 10x10 cm<sup>2</sup>; weight: ~2 g; vacuum dried for 8 h at 80 °C). In this manner, two types of powder prepregs consisting of 10 or 20 layers of CF fabric and 9 or 19 layers of CBT powder, respectively, were prepared. The related composites are designated as [0/90]<sub>10</sub> and [0/90]<sub>20</sub>, respectively. The powder prepregs were placed between two PTFE-covered steel plates and compression moulded at 230 °C in an IQAP LAP PL-15 hot plate press (IQAP SL, Barcelona, Spain). A pressure of 0.5 MPa was applied for 10 s in order to compact the powder prepreg and to facilitate melting. Then the pressure was released, *i.e.* the moving hot plate remained in its position without applying

pressure, and the powder prepreg was *in situ* polymerized. During the last two minutes of the polymerization step a pressure of 3 MPa was applied in order to compact the composite. Then the sample was cooled at *ca*. -50 °C/min to room temperature (*RT*) under the same pressure. The polymerization time was 20 min for pristine CBT samples as well as for samples containing EP. Isocyanate-modified samples were polymerized for 15 min because of the fast chain extension reaction of the CBT/isocyanate blend [18]. [0/90]<sub>10</sub> composites had a nominal thickness of 1.5 mm and were used for microscopy, dynamic mechanical thermal analysis (DMTA) and mechanical testing. [0/90]<sub>20</sub> composites had a nominal thickness of 3 mm and were used for puncture impact properties determination. All specimens were obtained by water jet cutting.

## 1.3. Characterization

Unmodified and modified pCBT-CF composites were characterized by DMTA using a Q800 TA device (TA Instruments, New Castle, DE, USA) in single cantilever mode at a frequency of 1 Hz and a strain of 0.01%. The temperature range was set from 30 °C to 210 °C at a heating rate of 2 °C/min. the composite sheets and had dimensions of *ca.* 20x15x1.5 mm<sup>3</sup>. The span length was set to 17 mm for all experiments. The density of the pCBT-CF composites was determined according to ISO 1183 method A. Fibre weight contents of the pCBT-CF composites were determined by direct calcination in a Q600 device (TA Instruments, New Castle, DE, USA) using dry nitrogen with a flow rate of 30 mL/min. Samples with a weight of 20–30 mg were heated in aluminium oxide pans from room temperature to 900 °C at a heating rate of 10 °C/min. The void content of pCBT-CF composites was calculated according to ISO 7822 method

A. The morphology was analysed by scanning electron microscopy (SEM) on fracture surfaces of cryo-fractured composite samples. The fracture surfaces were then sputter coated with a thin gold layer using a Bal-Tec SCD005 Sputter Coater (Bal-Tec, Liechtenstein). SEM analysis was performed on a Jeol JSM-5610 scanning electron microscope (Jeol, Tokyo, Japan) using an acceleration voltage of 10 kV. Optical microscopy (OM) was used to study the fibre distribution and impregnation on polished pCBT composites (Leica MEF4, Leica Microsystems GmbH, Wetzlar, Germany). The flexural properties of pCBT-CF composites were determined according to ISO 14125 method A at RT on a Galdabini Sun 2500 universal testing machine (Galdabini, Cardano al Campo, Italy) using a crosshead speed of 1 mm/min. The specimens had dimensions of *I*=30 mm, *b*=15 mm, *h*=1.5 mm and the span *L* was 24 mm. The short beam interlaminar shear strength (ILSS) was determined according to ISO 14130 at RT and a crosshead speed of 1 mm/min was used on the above mentioned universal testing machine. Specimens had dimensions of *I*=15 mm, *b*=7.5 mm and a thickness of *h*=1.5 mm. Drop weight impact properties were determined at RT according to ISO 6603-2. A Ceast Fractovis Plus (Ceast, Pianezza, Italy) instrumented falling weight impact testing machine was used. The hemispherical striker tip had a diameter of 20 mm and was lubricated prior to impact tests. [0/90]<sub>20</sub> composite specimens were placed simply supported on an annular ring with inner and outer diameter of 40 mm and 60 mm, respectively. The nominal impact energy  $(E_0)$  ranged from 0.5 to 20 J and the impact velocity  $(v_0)$  ranged from 0.5 to 3.3 m/s. Contact force-real time history was stored at a sampling rate of 333 kHz. Energy, velocity and deflection were numerically deduced from the force-time data.

## 2. Results and Discussion

## 2.1. Physical properties

The density, fibre- and void contents of the prepared composites are compiled in table 1. It can be seen that the chemical modifications did not significantly alter the densities of the polymers and composites. The void contents of the composites were in the range of 0.7–3.3%, which are in good agreement with published results. Mohd Ishak *et al.* [7] reported void contents of <1% and 4.7% for pressure-controlled and for displacement-controlled conditions, respectively. Using vacuum infusion, Agirregomezkorta *et al.* [19] obtained a void content of 3.3%.

Void content was lower in epoxy-modified samples but increased with the amount of EP, reaching the highest value of 3.3% when 4 wt.% of EP was used. This can be ascribed to a hampered fibre impregnation due to the increasing viscosity of the CBT/EP blends with EP caused by the relatively higher viscosity of EP resin as compared to molten CBT. The isocyanate modification led to a void content of 1–3%, depending on the type of isocyanate used. Isocyanates preferably react with pCBT carboxylic end groups, thereby releasing CO<sub>2</sub> during amidation [20]. Therefore, one might expect higher void contents for these samples. On the contrary, relatively smaller values were found as compared to pCBT-CF. This may be explained by the fact that during moulding the polymerization step was pressure-less, while pressure was applied after polymerization. Thus, the amount of entrapped gas in the composite is thought to be reduced to a similar level in all composites.

#### 2.2. Morphology

The morphologies as well as fibre distribution and impregnation of pCBT-CF, pCBT/EP 3%-CF and pCBT/PMDI 1%-CF were assessed by SEM analysis (*c.f.* figure 1 a–c) and OM analysis (figure 1 d–f).

Generally, no significant differences between the prepared composites were observed. SEM morphologies show that some matrix material was bonded to the carbon fibres, indicating a good interfacial adhesion between fibre and matrix in all cases. Regarding the OM micrographs, warp and weft rovings and a good macro-impregnation can be seen on a macroscopic scale. Taking a closer look, one can see a uniform inter-fibre distribution and a good micro-impregnation in all composites. Good fibre impregnation is observed because the low viscosity of the molten CBT facilitates the penetration of the resin through the fabric and the impregnation of intra-bundle fibres [7, 19, 21]. Nevertheless, some intra-bundle voids were detected which are in line with the calculated void contents of 0.7–3.3%.

## 2.4. DMTA analysis

The stiffness as a function of temperature of the prepared composites was studied using DMTA; results are shown in figure 2. The observed DMTA storage moduli at room temperature agree well with the flexural moduli as will be shown later. It can be seen that the highest stiffness at room temperature was found for the sample containing 3 wt.% of EP. Then it decreased with temperature and reached a storage modulus equal to the one of neat pCBT-CF at 119 °C. Storage moduli of isocyanate-modified composites were similar to the one of pristine pCBT-CF but all curves ran below the one of the unmodified sample. The lower stiffness is indicative that chain extension was successful.

This assumption receives further support from the relatively lower glass transition temperatures of the modified samples (*c.f.* fig. 2) [17-18]. An exception was the sample containing MDI which exhibited the lowest stiffness together with the highest  $T_g$  of all tested samples. As will be shown later, this sample also exhibited poor interlaminar shear strength as well as inferior flexural properties.

## 2.5. Short beam interlaminar shear strength

The apparent interlaminar shear strengths of unmodified and modified pCBT-CF composites were determined; results are listed in table 2. It can be seen that pCBT-CF exhibited a rather low interlaminar shear strength of 30 MPa due to its brittle behaviour, which is in good agreement with values published in the literature [7, 19, 22]. Apparent interlaminar shear strength remarkably increased by 35–53% when the pCBT composites were toughened with EP and NCO; the highest observed ILSS was 45 MPa and was found for the sample containing 2 wt.% of EP. Nevertheless, an exception was the sample containing MDI; its ILSS value decreased by 5% with respect to the unmodified sample. Recall from [18] that MDI showed only a minor toughening effect on pCBT as compared to PMDI, HDI and EP, respectively. This demonstrates that EP, PMDI and HDI are effective toughening agents for fibre reinforced pCBT composites.

## 2.6. Flexural properties

The flexural properties of unmodified and modified pCBT-CF composites were determined; results are shown in figure 3 as well as in table 2. The failure modes of unmodified and modified pCBT composites were tensile fracture at the outermost layer and compressive failure including inter-ply

fracture. The brittleness and pronounced notch sensitivity of pCBT-CF is well reflected in the low flexural strength and failure strain (linked with the maximum stress), whereas the relatively high flexural modulus may be ascribed by the somewhat higher degree of crystallinity [17-18]. Apparently, the maximum composite strength could not be reached because the matrix failed before the fibre reinforcement reached its maximum strength.

In contrast, all modified samples exhibited a much higher strength and failure strain but a slightly lower stiffness due to the toughening effect of the chain extenders. Flexural strength generally increased by *ca.* 50% and failure strain increased by up to 63% when the pCBT composites were toughened with EP and NCO. If failure strain is taken as a criterion for toughness, then the toughest sample was pCBT/EP 2%-CF whereas the stiffest and strongest sample was the one containing 3 wt.% of EP. Again, an exception was the sample containing MDI; this sample showed only minor improvement in strength and toughness. These results are in line with the earlier discussed mechanical performances of the EP- and NCO-modified pCBT matrices [17-18] and demonstrate that EP, PMDI and HDI also effectively toughen fibre reinforced pCBT composites.

## 2.6. Drop weight impact properties

The drop weight impact properties of unmodified and modified pCBT-CF composites were determined; contact force–real time curves are shown in figure 4 and impact data is presented in table 3. For the sake of clarity, only one [0/90]<sub>20</sub> composite for each group of chain extenders with the best mechanical performance was prepared and impact tested as described above, namely pCBT-CF, pCBT/EP 2.5%-CF and pCBT/PMDI 1%-CF.

Impact events can be divided into subcritical impacts with no damage and supercritical impacts with delamination. The impact energy at which the first damage occurs is referred to as the delamination threshold energy or also as the critical energy,  $E_{crit}$ . The corresponding delamination threshold force,  $F_d$ , is defined as the point at which a significant drop in contact force occurs (exemplarily marked by an ellipse in figure 4 b). It was shown that this delamination threshold force does not depend on the nominal impact energy,  $E_0$  [23]. The maximum contact force during impact is called the peak force,  $F_M$ . The difference between maximum energy,  $E_M$ , and absorbed energy,  $E_{abs}$ , is the rebound energy or elastic energy. Total contact time is referred to as  $t_c$  and deflection at the peak force is denoted as  $I_M$ .

As can be seen in fig. 4, modified composites exhibited higher peak forces together with shorter contact times for all tested energies, suggesting a lower loss of transversal stiffness of these samples [19]. Subcritical impacts occurred at impact energies up to 0.5 J; the force curves in fig. 4a are smooth and bell-shaped where no peaks are observed and no visible damage could be seen on the sample surfaces after impact. It is noteworthy that the absorbed energy of pristine pCBT-CF was relatively higher at subcritical impacts. Conversely at supercritical impacts, the absorbed energies of the modified samples were relatively higher, indicating a greater amount of plastic deformation. At an impact energy of 3 J, the first damages in form of small indentations on the impacted surfaces were found, as is apparent from the load oscillations below the peak maxima of the force curves in figure 4b. Nevertheless, no damage at the back sides of the specimens were found. At this low energy level, the damage mode was local plastic deformation of the matrix. The damage mode at impact energies higher than 3 J was essentially the same for

all samples, namely horizontal and vertical cracks oriented parallel to the (0°/90°) fibre orientations on the impacted surfaces and localized fibre breakage at the impact points on the back surfaces. Crack lengths increased with impact energy. Nevertheless, the modified samples exhibited a more prominent distortion at the back surface which had a hemispherical shape with a diameter similar to the inner diameter of the annular support. This suggests that EP- and PMDI-modified pCBT possessed a greater ability to undergo plastic deformation whereas neat pCBT-CF showed little plastic deformation due to its brittle behaviour, suggesting a greater overall damage.

Critical energy and delamination threshold force were fairly constant in the studied impact energy range (*c.f.* table 3) and therefore may be considered as independent of the nominal impact energy [23]. The delamination threshold forces and related critical energies were averaged for all impact energies and results are presented in table 4. The found delamination threshold force of pCBT-CF was 1562 ± 71 N, somewhat lower than the one reported by Agirregomezkorta and co-workers [19] (namely 1760 ± 35 N). The results suggest that the modified composites exhibited a relatively higher delamination threshold. *E*<sub>crit</sub> increased by 21% and 57% and *F*<sub>d</sub> increased by 13% and 45% for the EP- and PMDI-modified composites respectively.

The relation between impact energy and absorbed energy can be seen in the energy profile diagrams of the composites in figure 5. They show that the three composites behaved similarly for low impact energies up to 10 J. For higher impact energies, EP- and PMDI-modified composites absorbed more energy because they underwent a greater amount of matrix plastic deformation during impact, which was ascribed to the higher toughness of the matrix materials. Due

to this greater deformability, a higher penetration threshold was deduced for the modified composites.

## 3. Conclusions

CBT was chemically modified with small amounts of chain extenders, namely bifunctional epoxy resin and bi- or polyfunctional isocyanates. Homogeneous CBT/epoxy and CBT/isocyanate blends were obtained by melt blending the components in a lab-scale batch mixer at low temperatures and high shear rate without polymerizing the blends.

It was found that the chemical modifications did not significantly alter the physical and thermal properties or the morphology of the composites. On the other hand, interlaminar shear strength, flexural strength and failure strain of the chemically modified composites were considerably enhanced. Nevertheless, the flexural moduli slightly decreased due to the toughening effect of the chain extenders on the pCBT matrix. Low energy impact tests revealed that the modified composites absorbed relatively more energy as compared to unmodified pCBT composites. Moreover, critical energy and delamination threshold force were higher for modified composites. It can be concluded that toughening of pCBT with epoxy or isocyanates, namely PMDI and HDI, is very effective for improving the mechanical properties, most importantly the toughness of fibre reinforced pCBT composites.

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## 4. References

- van Rijswijk, K and Bersee, HEN. Reactive processing of textile fiberreinforced thermoplastic composites – An overview. Composites Part A: Applied Science and Manufacturing **38**(3), 666-681 (2007).
- Mohd Ishak, ZA, Gatos, KG, and Karger-Kocsis, J. On the in-situ polymerization of cyclic butylene terephthalate oligomers: DSC and rheological studies. Polymer Engineering & Science 46(6), 743-750 (2006).
- Brunelle, DJ, Bradt, JE, Serth-Guzzo, J, Takekoshi, T, Evans, TL,
  Pearce, EJ, and Wilson, PR. Semicrystalline Polymers via Ring-Opening
  Polymerization: Preparation and Polymerization of Alkylene Phthalate
  Cyclic Oligomers. Macromolecules **31**(15), 4782-4790 (1998).
- Karger-Kocsis, J, Shang, PP, Mohd Ishak, ZA, and Rösch, M. Melting and crystallization of in-situ polymerized cyclic butylene terephthalates with and without organoclay: A modulated DSC study. eXPRESS Polymer Letters 1(2), 60-68 (2007).
- Parton, H, Baets, J, Lipnik, P, Goderis, B, Devaux, J, and Verpoest, I.
  Properties of poly(butylene terephthatlate) polymerized from cyclic oligomers and its composites. Polymer 46(23), 9871-9880 (2005).
- Wunderlich, B. Crystallization during Polymerization. Angewandte Chemie International Edition in English 7(12), 912-919 (1968).
- Mohd Ishak, ZA, Leong, YW, Steeg, M, and Karger-Kocsis, J.
  Mechanical properties of woven glass fabric reinforced in situ polymerized poly(butylene terephthalate) composites. Composites Science and Technology 67(3–4), 390-398 (2007).

- Yu, T, Wu, CM, Chang, CY, Wang, CY, and Rwei, SP. Effects of crystalline morphologies on the mechanical properties of carbon fiber reinforcing polymerized cyclic butylene terephthalate composites.
   eXPRESS Polymer Letters 6(4), 318-328 (2012).
- Baets, J, Devaux, J, and Verpoest, I. Toughening of basalt fiberreinforced composites with a cyclic butylene terephthalate matrix by a nonisothermal production method. Advances in Polymer Technology 29(2), 70-79 (2010).
- Bahloul, W, Bounor-Legare, V, Fenouillot, F, and Cassagnau, P.
  EVA/PBT nanostructured blends synthesized by in situ polymerization of cyclic cBT (cyclic butylene terephthalate) in molten EVA. Polymer **50**(12), 2527-2534 (2009).
- Tripathy, AR, Chen, WJ, Kukureka, SN, and MacKnight, WJ. Novel poly(butylene terephthalate)/poly(vinyl butyral) blends prepared by in situ polymerization of cyclic poly(butylene terephthalate) oligomers. Polymer 44(6), 1835-1842 (2003).
- Tripathy, AR, MacKnight, WJ, and Kukureka, SN. In-Situ
  Copolymerization of Cyclic Poly(butylene terephthalate) Oligomers and ε Caprolactone. Macromolecules **37**(18), 6793-6800 (2004).
- Baets, J, Dutoit, M, Devaux, J, and Verpoest, I. Toughening of glass fiber reinforced composites with a cyclic butylene terephthalate matrix by addition of polycaprolactone. Composites Part A: Applied Science and Manufacturing **39**(1), 13-18 (2008).
- 14. Wu, W, Klunker, F, Xie, L, Jiang, B, and Ziegmann, G. Simultaneous binding and ex situ toughening concept for textile reinforced pCBT composites: Influence of preforming binders on interlaminar fracture

properties. Composites Part A: Applied Science and Manufacturing **53**(0), 190-203 (2013).

- Wu, W, Xie, L, Jiang, B, and Ziegmann, G. Simultaneous binding and toughening concept for textile reinforced pCBT composites: Manufacturing and flexural properties. Composite Structures **105**(0), 279-287 (2013).
- Wu, W, Xie, L, Jiang, B, and Ziegmann, G. Influence of textile preforming binder on the thermal and rheological properties of the catalyzed cyclic butylene terephthalate oligomers. Composites Part B: Engineering 55(0), 453-462 (2013).
- Abt, T, Sánchez-Soto, M, and Martínez de Ilarduya, A. Toughening of insitu polymerized cyclic butylene terephthalate by chain extension with a bifunctional epoxy resin. European Polymer Journal 48, 163-171 (2012).
- Abt, T, de Ilarduya, AM, Bou, JJ, and Sanchez-Soto, M. Isocyanate toughened pCBT: Reactive blending and tensile properties. eXPRESS Polymer Letters 7(2), 172-185 (2013).
- Agirregomezkorta, A, Martínez, AB, Sánchez-Soto, M, Aretxaga, G, Sarrionandia, M, and Aurrekoetxea, J. Impact behaviour of carbon fibre reinforced epoxy and non-isothermal cyclic butylene terephthalate composites manufactured by vacuum infusion. Composites Part B: Engineering 43(5), 2249-2256 (2012).
- Torres, N, Robin, JJ, and Boutevin, B. Chemical modification of virgin and recycled poly(ethylene terephthalate) by adding of chain extenders during processing. Journal of Applied Polymer Science **79**(10), 1816-1824 (2001).

- Parton, H and Verpoest, I. In situ polymerization of thermoplastic composites based on cyclic oligomers. Polymer Composites 26(1), 60-65 (2005).
- Balogh, G. Development of cyclic butylene terephthalate matrix composites. PhD thesis. Department of Polymer Engineering. Budapest University of Technology and Economics: Budapest, Hungary, 2012
- Cartié, DDR and Irving, PE. Effect of resin and fibre properties on impact and compression after impact performance of CFRP. Composites Part A: Applied Science and Manufacturing 33(4), 483-493 (2002).

# **Figure captions**

Fig. 1: Micrographs of pCBT-CF (a), pCBT/EP 3%-CF (b) and pCBT/PMDI 1%-CF (c). Left hand side: OM micrographs of polished surfaces; right hand side: SEM morphologies of fracture surfaces of cryo-fractured samples, pictures were taken parallel to fibre direction.

Fig. 2: DMTA storage modulus curves of pristine, epoxy-modified and isocyanate-modified pCBT composites.

Fig. 3: Typical 3-point-bending stress-strain curves for neat as well as (a) epoxy-modified and (b) isocyanate-modified pCBT-CF composites.

Fig. 4: Force and absorbed energy *versus* time plots of pCBT-CF, pCBT/EP-

CF and pCBT/PMDI 1%-CF composites; subcritical impact (a) and supercritical impacts (b–d).

Fig. 5: Energy profile diagrams of pCBT-CF, pCBT/EP-CF and pCBT/PMDI 1%-CF composites.







Fig 2 (single column size)









Fig 4 (single column size)



Fig 5 (single column size)

Table 1: Polymer and composite densities, fibre weight fractions and voidcontents of unmodified and modified pCBT-CF composites.

	Polymer	Composite	Fibre weight	Void
Sample	density	density	fraction	content
	[g/cm <sup>3</sup> ]	[g/cm <sup>3</sup> ]	[vol.%]	[%]
pCBT-CF	1.33	1.60	76.6	2.9
pCBT/EP 2%-CF	1.33	1.62	74.0	0.7
pCBT/EP 3%-CF	1.31	1.63	77.9	1.5
pCBT/EP 4%-CF	1.32	1.59	76.4	3.3
pCBT/PMDI 1%-CF	1.32	1.61	73.5	0.9
pCBT/MDI 1%-CF	1.33	1.63	79.2	1.6

	Flexural	Flexural	Failure	II SS
Sample	modulus	strength	strain	1200
	[GPa]	[MPa]	[%]	[MPa]
pCBT-CF	35.3 ± 7.0	453 ± 31	1.1 ± 0.1	29.6 ± 2.0
pCBT/EP 2%-CF	27.0 ± 3.8	692 ± 53	1.8 ± 0.2	45.2 ± 6.0
pCBT/EP 3%-CF	37.7 ± 5.5	736 ± 86	1.5 ± 0.2	40.8 ± 3.3
pCBT/EP 4%-CF	33.0 ± 5.5	703 ± 66	1.4 ± 0.2	40.1 ± 1.4
pCBT/PMDI 1%-CF	34.7 ± 6.8	668 ± 79	1.4 ± 0.2	42.2 ± 3.2
pCBT/MDI 1%-CF	34.3 ± 6.5	476 ± 29	1.2 ± 0.1	28.1 ± 3.6
pCBT/HDI 1%-CF	34.1 ± 5.9	680 ± 152	1.3 ± 0.3	42.5 ± 2.0

Table 2: Flexural properties and apparent interlaminar shear strengths of unmodified and modified pCBT-CF composites.

Table 3: Drop weight impact properties of unmodified and modified pCBT-CF composites

E <sub>0</sub>		Ecrit	$F_d$	$F_M$	tc	I <sub>M</sub>	E <sub>abs</sub>
[J]	Sample	[J]	[N]	[N]	[ms]	[mm]	[J]
	pCBT-CF	-	-	1264	3.6	0.8	0.4
0.5	pCBT/EP 2.5%-CF	-	-	1535	3.4	0.5	0.5
	pCBT/PMDI 1%-CF	-	-	1625	3.0	0.6	0.4
	pCBT-CF	0.3	1490	2501	4.7	1.4	2.0
3	pCBT/EP 2.5%-CF	0.4	1562	2926	4.1	1.5	2.6
	pCBT/PMDI 1%-CF	0.8	2528	3197	3.6	1.2	2.6
	pCBT-CF	0.3	1643	6998	4.0	3.1	9.2

10	pCBT/EP 2.5%-CF	0.3	1860	6384	4.0	3.0	9.4
	pCBT/PMDI 1%-CF	0.6	2294	6854	3.9	3.2	9.7
	pCBT-CF	0.4	1517	9066	3.9	3.8	13.3
20	pCBT/EP 2.5%-CF	0.6	1806	8533	4.4	4.2	16.9
	pCBT/PMDI 1%-CF	0.5	2176	10971	3.5	3.9	18.9
	pCBT-CF	0.3	1598	14177	3.3	4.8	26.5
30	pCBT/EP 2.5%-CF	0.3	1860	15839	3.0	4.6	28.6
	pCBT/PMDI 1%-CF	0.4	2068	17121	3.0	4.4	29.0

*m*<sub>*impact*</sub>: 3.62 kg; *h*<sub>*impact*</sub>: 13 - 563 mm; *v*<sub>*impact*</sub>: 0.5 - 3.3 m/s.

Table 4: Delamination threshold forces and critical energies of unmodified andmodified pCBT-CF composites.

Sample	E <sub>crit</sub>	F <sub>d</sub>
	[J]	[N]
pCBT-CF	0.33 ± 0.05	1562 ± 71
pCBT/EP 2.5%-CF	0.40 ± 0.14	1772 ± 142
pCBT/PMDI 1%-CF	0.58 ± 0.17	2267 ± 197