

TOUGHENED CARBON FIBRE FABRIC-REINFORCED THERMOPLASTIC COMPOSITES

T. Abt, M. Sánchez-Soto*, M. Ll. Maspoch, J.I. Velasco.

Centre Català del Plàstic, CCP, Universitat Politècnica de Catalunya, BarcelonaTech, C/ Colom n° 114, 08222 Terrassa, España.

** m.sanchez-soto@upc.edu*

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Abstract

Toughened carbon fibre fabric-reinforced composites were obtained by compression moulding of powder prepregs, using a modified cyclic butylene terephthalate (pCBT) matrix and a bi-directional [0°/90°] carbon fibre fabric. Modification of the pCBT matrix was done by adding small amounts of epoxy resin or isocyanates, acting as toughening agents. Homogeneous CBT/epoxy and CBT/isocyanate blends were obtained by melt blending in a lab-scale batch mixer by applying low temperatures and short processing times. Melt blending was stopped before the ring-opening polymerization of CBT could start. This was assured by monitoring the torque of the batch mixer. Modified CBT was then used as matrix for carbon fibre reinforced pCBT composites prepared by a simple powder prepreg method with subsequent in situ polymerization during compression moulding.

Physical properties such as composite density, fibre- and void content were not significantly altered by the presence of the toughening agents. Mechanical properties were assessed by short beam interlaminar shear strength and flexural tests. ILSS, flexural strength and failure strain of the chemically modified composites increased up to 50–60% 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. Moreover, it was found that thermal properties and stability were not affected by the presence of modifiers.

1. Introduction

Thermoplastic composites are well-known materials which are commonly used due their relatively higher toughness and impact strength as compared to thermoset-based composites. However, the high viscosity of the matrix in the molten state limits the use of typical thermoset processing techniques like resin transfer moulding and proper impregnation of the fibres is difficult, yielding products with a locally high void content [1]. These shortcomings can be overcome by using ring-opening polymerization (ROP) of cyclic butylene terephthalate oligomers (CBT[®]) which exhibit a very low melt viscosity (0.02 Pa·s at 190 °C). CBT oligomers undergo an entropically driven ROP in the presence of a catalyst at temperatures below as well as above the melting temperature of polymerized CBT (referred to as pCBT), *i.e.* $T_m = 225$ °C [2]. Nevertheless, pCBT was shown to be considerably more

brittle than conventional PBT [3-4]. 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. This is a critical problem for a wide application of fibre reinforced pCBT composites as structural materials and at industrial scales. Different approaches have been followed to address this situation *e.g.* by decreasing the crystallinity and thus increasing the toughness, either by nonisothermal processing using fast cooling or by copolymerization of CBT with different monomers [5-6]. However, these methods are little effective or lead to a decrease of other relevant mechanical properties such as stiffness and strength. Recently, we showed that reactive chain extension of pCBT with epoxy resin [7] as well as isocyanates [8] 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.

2. Experimental Section

2.1. Materials

Cyclic butylene terephthalate oligomers (CBT160) were 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/eq. 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 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, 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/m² and was supplied by Jordi Sagristà, SL, (Barcelona, Spain).

2.2. Sample preparation

The CBT granules were ground into a fine powder 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). A mixing chamber temperature of 200 °C, protective N₂ blanket and a rotor speed of 180 min⁻¹ 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. The output material was cooled to room temperature and ground into a fine powder. 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. The pCBT-CF composite lay-up was as follows. Previously dried CBT/chain extender powder (~1.1 g) was evenly spread on a CF fabric (size: 10x10 cm²; 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/chain extender powder, respectively, were prepared. The composites are designated as [0/90]₁₀ and [0/90]₂₀. The powder prepregs were placed between two PTFE-covered steel plates and compression moulded at 230 °C and 0.5 MPa in a hot plate press for 10 s. Then the pressure was released 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 under the same pressure. [0/90]₁₀ composites had a nominal thickness of 1.5 mm while [0/90]₂₀ composites had a nominal thickness of 3 mm. All specimens for testing were obtained by water jet cutting.

2.3. Characterization

The density of the pCBT-CF composites was determined according to ISO 1183 method A and the void content following ISO 7882 method A. Fibre weight contents were determined by thermogravimetric analysis (Q600 Mettler-Toledo) heating samples of about 20–30 mg from room temperature to 900 °C at a heating rate of 10 °C/min under dry nitrogen atmosphere. The morphology of pCBT-CF composites was analysed by scanning electron microscopy (Jeol JSM-5610) on cryo-fractured composite samples. Prior to observation fracture surfaces were sputter coated with a thin gold layer. Optical microscopy (OM) was used to study the fibre distribution and impregnation on polished pCBT composites (Leica MEF4). The short beam interlaminar shear strength (ILSS) was determined according to ISO 14130 at a crosshead speed of 1 mm/min. Composite specimens (20x15x1.5 mm³) were characterized by DMTA using a Q800 TA device (TA Instruments) in single cantilever mode operating with a span of 17 mm 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 flexural properties of pCBT-CF composites were determined according to ISO 14125 method A on a Galdabini Sun 2500 universal testing machine using a crosshead speed of 1 mm/min. All mechanical tests were performed at room temperature.

3. Results and Discussion

3.1. 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 composites. The void contents were in the range of 0.7–3.3%, which are in good agreement with published results. Mohd Ishak *et al.* [3] reported void contents of <1% and 4.7% for pressure-controlled and for displacement-controlled conditions, respectively. Using vacuum infusion, Agirregomezkorta *et al.* [9] 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 amount, 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 CO₂ during amidation [8]. 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.

Sample	Polymer density [g/cm ³]	Composite density [g/cm ³]	Fibre weight fraction [vol.%]	Void content [%]
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
pCBT/HDI 1%-CF	1.32	1.59	74.0	2.9

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

3.2. Morphology

The morphologies, 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 [3, 9-10]. Nevertheless, some intra-bundle voids were detected which are in line with the calculated void contents of 0.7–3.3%.

3.3. Short beam interlaminar shear strength

The apparent interlaminar shear strengths of the 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 [3, 9, 11]. 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 that MDI showed only a minor toughening effect on pCBT as compared to PMDI and HDI [8] as well as to EP [7], respectively. This demonstrates that EP, PMDI and HDI are effective toughening agents for fibre reinforced pCBT composites.

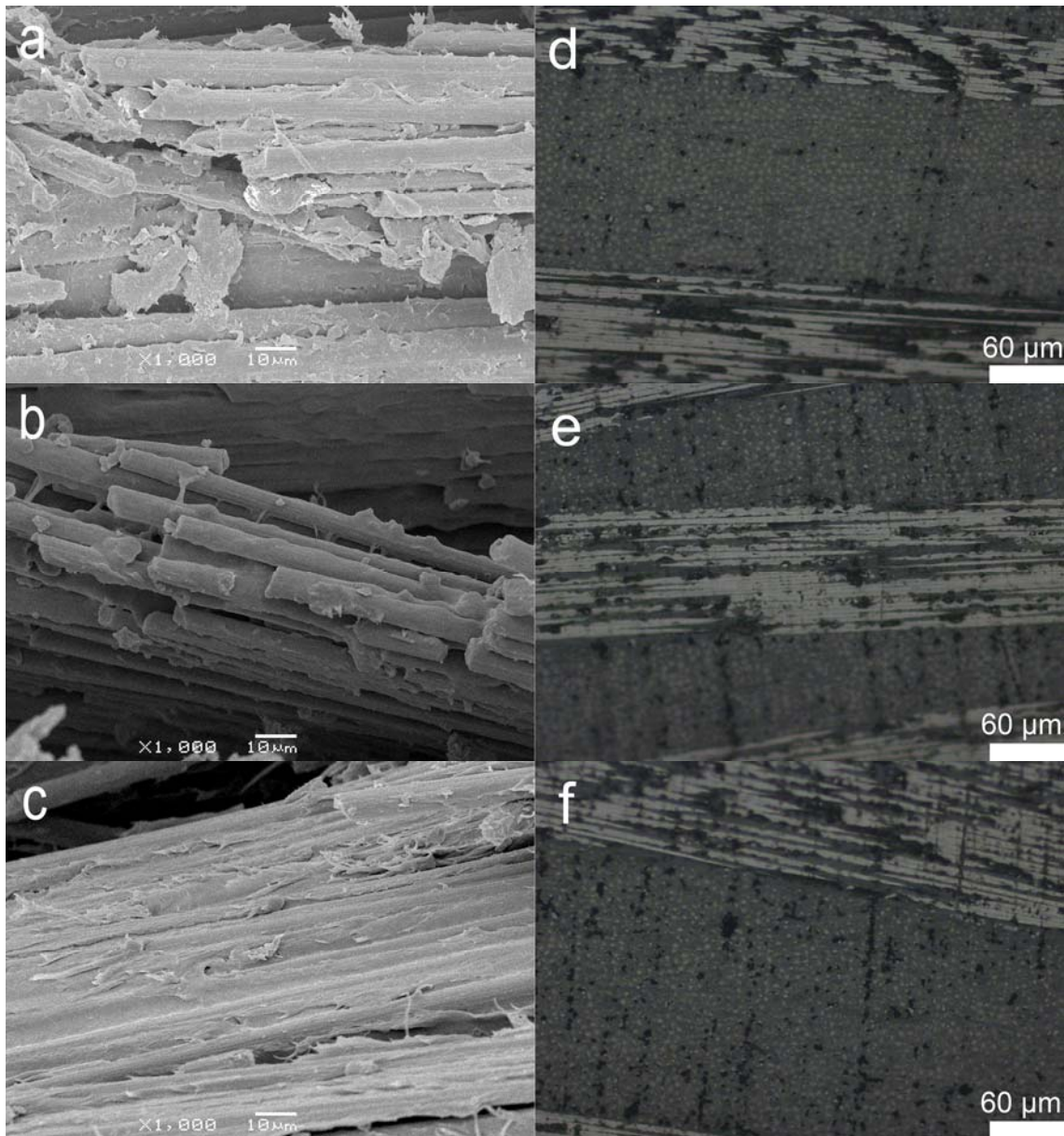


Figure 1. Micrographs of pCBT-CF (a and d), pCBT/EP 3%-CF (b and e) and pCBT/PMDI 1%-CF (c and f). Left hand side: SEM morphologies of fracture surfaces of cryo-fractured samples, pictures were taken parallel to fibre direction; right hand side: OM micrographs of polished surfaces.

3.4. DMTA analysis

The stiffness of the prepared composites was studied as a function of temperature using DMTA. The observed DMTA storage moduli at room temperature agree well with the flexural moduli as will be shown later. As it can be seen in figure 2, 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) [7-8]

ranging from 68.3 to 66.1 °C in comparison to the unmodified one 69.1 °C. An exception was the sample containing MDI which exhibited the lowest stiffness together with the highest T_g (70 °C) of all tested samples. As will be shown later, this sample also exhibited poor interlaminar shear strength as well as inferior flexural properties.

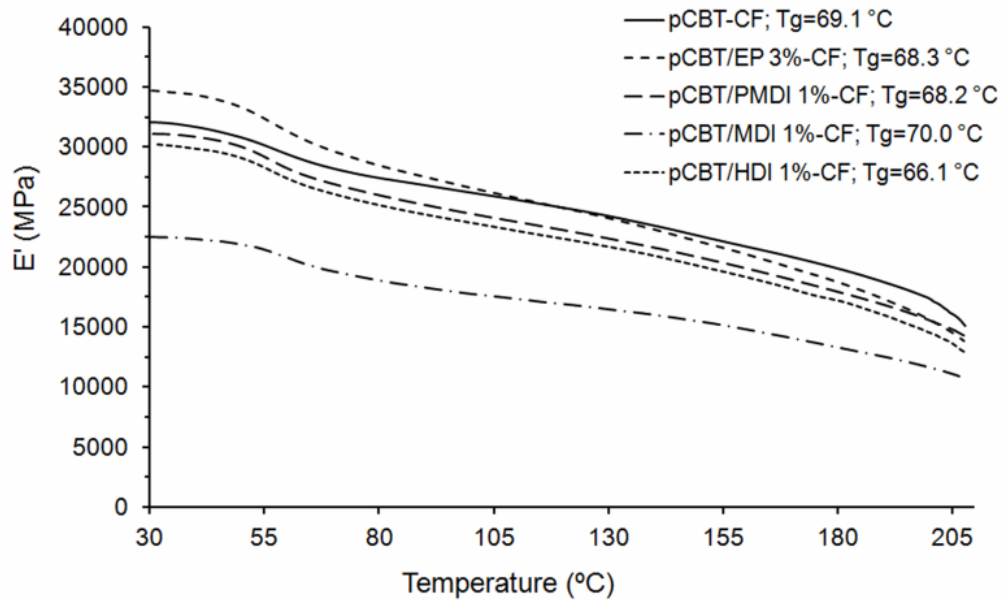


Figure 2. DMTA storage modulus curves of pristine, epoxy-modified and isocyanate-modified pCBT composites.

Sample	Flexural modulus [GPa]	Flexural strength [MPa]	Failure strain [%]	<i>ILSS</i> [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.

3.5. 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 to the maximum stress), whereas the relatively high flexural modulus may be ascribed by the somewhat higher degree of crystallinity.

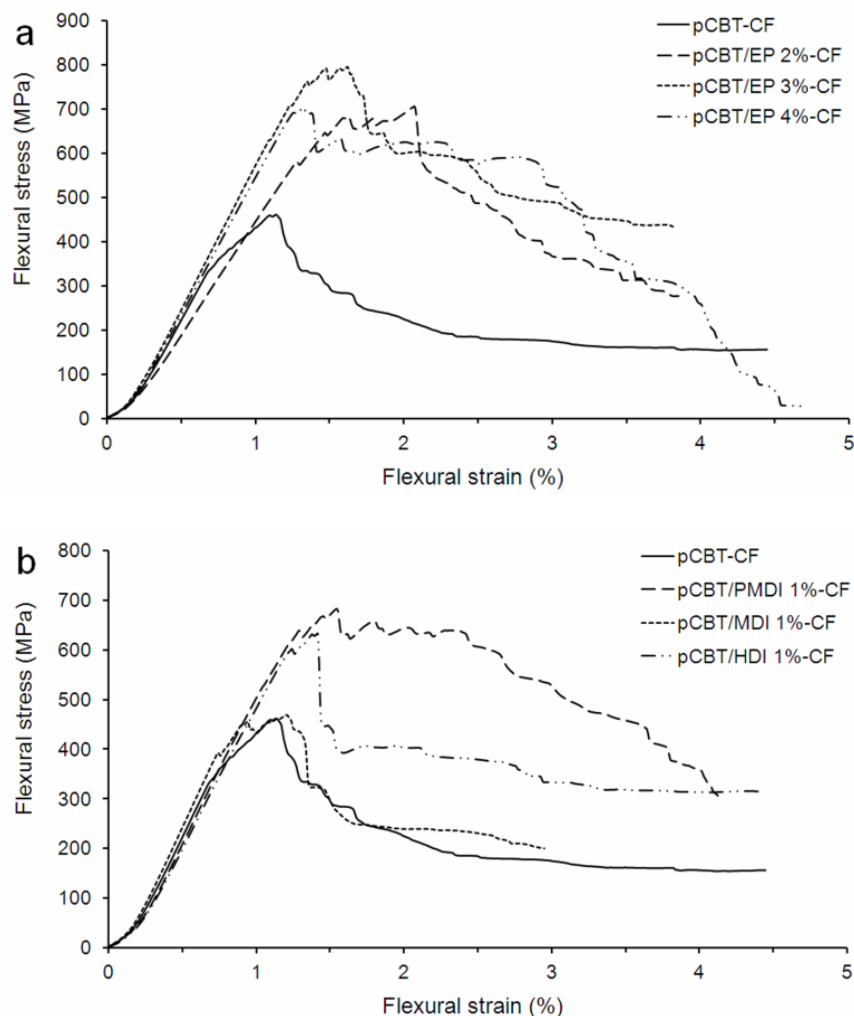


Figure 3. Typical 3-point-bending stress-strain curves for neat as well as (a) epoxy-modified and (b) isocyanate-modified pCBT-CF composites.

Apparently, the maximum composite strength could not be achieved because the unmodified 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 and demonstrate that EP, PMDI and HDI also effectively toughen fibre reinforced pCBT composites.

4. Conclusions

CBT was chemically modified with small amounts of chain extenders, namely bifunctional epoxy resin and bi- or polyfunctional isocyanates. 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. 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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