

## Toughening of polymerized cyclic butylene terephthalate with carbon nanotubes for use in composites

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### ABSTRACT

Low viscosity cyclic butyleneterephthalate (CBT) is a promising material for thermoplastic composites, however after isothermal polymerization (to PBT) and crystallization the material is rather brittle. In the present work, high aspect ratio nanofiller, carbon nanotubes (CNTs), are added to improve ductility. The dispersion of CNTs in CBT is achieved by rotational mixing and appears optimal. Concentrations up to 0.1 wt.%CNT are added to investigate their influence on the mechanical behavior. The addition leads to an increase in stiffness, strength and energy to failure, however, the failure strain slightly decreases. Thermal measurements indicate that the CNTs have no influence on the crystallinity. However, when the mixture of CBT and CNTs is processed in fiber reinforced composites processed by vacuum infusion, the CNTs show a tendency of filtration through the fabric.

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### 1. Introduction

Cyclic butylene terephthalate (CBT) is a low viscosity cyclic oligoester which polymerizes, after adding a catalyst, to the better known thermoplastic polybutyleneterephthalate (PBT) [1,2]. The combination of the low viscosity and its thermoplastic character makes the CBT resin a very promising material for composites. Its low viscosity gives an undemanding impregnation, such as with thermosets, while exhibiting the advantages of a thermoplastic matrix such as recyclability by melting, higher toughness and better impact resistance [3,4]. Due to the low viscosity of the CBT in its oligomeric state it can be processed via resin transfer moulding (RTM)-like processes, which are normally reserved for thermosets [5].

An extra advantage of CBT is that crystallization can start during polymerization because the polymerization can occur already at temperatures below the crystallization temperature of PBT [6–8]. Hence, with this system, isothermal processing under the melt temperature of PBT is possible.

In order to compete with other production methods of PBT, the production cycle of polymerized CBT (pCBT) synthesis must be as short as possible. Therefore, an isothermal production process is usually selected in which polymerization and crystallization occur simultaneously thus allowing demoulding without further cooling. This drastically reduces the overall production cycle time and increases the energy efficiency of the process [9]. However, it was

found that when this resin is processed under isothermal RTM-processing conditions, the polymerized CBT is much more brittle than normal PBT [10,11]. The failure strain of pCBT in bending is 4%, while PBT does not break in a three point bending test. The isothermal production technique of pCBT leads to a perfect crystal structure with few tie-molecules which induces brittleness [6,10,12].

Various potential toughening approaches were attempted to solve this problem with pCBT. Most work was focused on the copolymerization of CBT with another thermoplastic, polycaprolactone (PCL), to make it tougher [13,14]. Another published work involves blending with polyvinylbutyral (PVB) [15]. In all cases a toughening effect is observed, but in the case of PCL the effect remains small. Using PVB, the viscosity increase of the starting mixture is too high for a good impregnation of a fabric for composites.

The influence of carbon nanotubes (CNTs) on standard PBT has been described in literature. It is stated that the addition of single walled CNTs at a concentration of 0.1 wt.% increases the stiffness by 15%, strength by 25% and the failure strain of PBT [16]. In [17] it is stated that oxidized single walled CNTs have no influence on the crystallinity while multiwalled CNTs seem to increase the crystallinity of PBT. This is confirmed in [18] where the microhardness increases when adding multiwalled CNTs. In all these papers, the CNTs are first dispersed in 1,4 butanediol before the polycondensation to PBT.

In this paper, the CNTs are dispersed into the CBT before the ring opening polymerization. The influence of CNTs on the mechanical properties of pCBT is evaluated. Because multiwalled CNTs can act as nucleating agents, a higher crystallinity of the pCBT is expected. However, if these crystals would become less perfect,

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this would have a positive influence on the failure strain and hence on the composite toughness.

## 2. Material and methods

### 2.1. Material

The CBT™ (CBT 100) used in this study is provided by the Cyclics Corporation. The number of butyl groups in the oligomer cycle varies from two to seven, resulting in a melting range of 130–160 °C. Before processing, the oligomers were dried overnight at 110 °C to remove residual moisture, which could interfere with the polymerization reaction. The tin-based polymerization catalyst (Fascat™ 4101, butylchlorodihydroxystannan) is commercially available from Atofina Chemicals Incorporated, this compound is a well established transesterification catalyst.

The reinforcement used is a non-crimp, quasi unidirectional E-glass fiber fabric (1213 g/m<sup>2</sup>) supplied by Ahlstrom. It is composed of a thick 0° layer (1152 g/m<sup>2</sup>) and a very thin 90° layer (61 g/m<sup>2</sup>). The two layers are bound with a synthetic stitch yarn. The fabric was dried overnight at 110 °C before processing.

The carbon nanotubes (CNTs) used in this study are multiwalled nanotubes provided by Nanocyl (Fig. 1), with an average diameter of 10 nm. After the production the nanotubes are milled, which reduced their average length and also narrowed the overall length distribution. This enabled a better dispersion, and is expected to lower the risk of their being “filtered” out when injected through a fabric. Multiwalled CNTs are chosen because of their slight imperfect surface quality like roughness. Such imperfections can be expected to act as potential nucleating sites during crystallization and to improve the adhesion between CNT surface and the matrix.

### 2.2. Production

The process used in this paper is the VARTM (vacuum assisted RTM) process. First the oligomers are heated above their melting point (190 °C). When using CNTs, they are then blended, using a simple rotational mixer, with the molten CBT before adding the catalyst. The catalyst is then added and the resulting mixture is stirred for 20 s. The low viscosity mixture is vacuum infused into a closed mould (at 190 °C) with or without fibers [19]. During this

time, polymerization already starts, resulting in a continuously increasing viscosity. This results in a limited time window for mould filling. Vacuum cannot be kept constant during the resin infusion. If the vacuum is too high, the low initial viscosity will lead to too fast mould filling leaving behind porosities in the fiber bundles. On the other hand, if the vacuum is too low, the slow infusion and the high final viscosity will prevent complete mould filling. Once the mould is completely filled, in- and outlet ports are closed after which sufficient time should be available to complete the polymerization reaction and crystallization simultaneously. Some plates (320\*200\*2 mm<sup>3</sup>) with different weight percentages of CNTs (pCBT-x%CNT) are produced, to characterize the influence of the CNTs on the matrix without reinforcing fibers. Also, flat plates with a fiber volume fraction of 48 ± 1 % and 0.02 wt.% CNTs, are produced using the method described above.

### 2.3. Experimental methods

Differential Scanning Calorimetry (DSC) is used to measure the degree of crystallinity. Melting endotherms were recorded at 10 °C/min. The degree of crystallinity is defined as follows:

$$\chi_c(\text{wt.}\%) = \frac{(\Delta H_m / \Delta H_\infty) \times 100}{\text{wt.}\% \text{pCBT}} \times 100 \quad (1)$$

where  $\Delta H_m$  is the melting enthalpy of the polymer, and  $\Delta H_\infty$  is the melting enthalpy of the fully perfect crystal of PBT, which is found in literature to be 142 J/g [20]. The denominator is the correction for lower amounts of pCBT when mixing with CNT or glass fibers.

The unfilled polymerized CBT (pCBT-CNT) specimens are tested in three point bending according to ASTM D790-M. Samples are 2 mm thick, 10 mm wide and 50 mm long and they are tested using a span of 32 mm. The stress and strain resulting in the sample is calculated according to standard beam theory, using the highest tensile stress and strain in the sample.

Transmission electron microscopy (TEM) is applied on the samples with a LEO 922 TEM operating at 200 kV.

High resolution secondary electron microscopy (HRSEM) is applied on the samples with a Philips XL40-FEG SEM. The samples are sputtered with a thin layer of gold (about 10 nm) to avoid charging. The pictures are taken at a fracture surface applying an electrical potential of 3 kV with a current of 68 pA.

## 3. Results and discussion

The amount of catalyst used for pure pCBT polymerization is 0.45 wt.%. For samples with CNTs, different formulations are prepared, with the results summarized in Table 1. It appeared that with 0.45 wt.% catalyst and 0.05 wt.% CNTs it is impossible to fill the mould because of a very fast increase in viscosity.

Therefore, a lower amount of catalyst is used, 0.2 wt.%. This will decrease the polymerization rate. In [21] it is stated that the amount of catalyst has no influence on the final molecular weight, however, decreasing catalyst concentration induced some ductility seen by an increase in failure strain. Also a plate with 0.1 wt.% CNTs is produced with 0.2 wt.% catalyst (pCBT-0.1CNT).

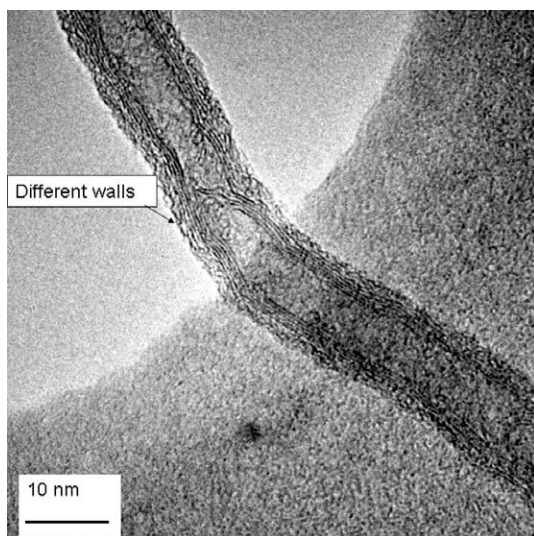


Fig. 1. High resolution TEM image of a multiwalled carbon nanotube, picture from Nanocyl.

Table 1  
Overview of the different plates produced in this research

wt.% CNT	wt.% catalyst	Notation	Comment
0	0.45	pCBT	
0.02	0.45	pCBT-0.02CNT	
0.05	0.45		Mould only partially filled
0.05	0.2	pCBT-0.05CNT	
0.1	0.2	pCBT-0.1CNT	

### 3.1. Dispersion of CNTs

A good dispersion of CNTs is critical in order to improve the mechanical properties. Poor dispersion of CNTs leads to localized, micron sized, agglomerates which can negatively influence the strengthening mechanisms of CNTs such as crack deflection or crack bridging [22]. If the CNTs are well dispersed, they form a three-dimensional physical network, thereby effectively enhancing the overall performance of a material. Additionally, an agglomerate is a stress concentrator in the microstructure and can act as a site for premature debonding or crack initiation.

The CNTs are mixed with the molten CBT for 5 min leading to a visual disappearance of agglomerates. The dispersion is performed only by rotational mixing, which provides high shearing forces, although not as high as in calendaring [23]. However the available calendaring equipment is limited to temperatures up to 70–80 °C. Some optical and TEM images are taken of the pCBT-0.02CNT produced samples. From the micrographs (Fig. 2), it can be seen that there is a multilevel dispersion of the nanotubes. In the optical image, most of the area is visible as a grey area because of finely dispersed CNTs. Then there are also darker spots identified as both micron and submicron sized agglomerates of CNTs. Detail of such agglomerates can be seen in the TEM-micrograph. It is observed that the small agglomerates are homogeneously distributed and are still under 2 μm in size. In fact, a complete exfoliation is not possible because of the strong van der Waals interaction between individual CNTs. The interaction is very high because of the high specific surface area and it requires strong shearing forces to achieve complete exfoliation. Moreover, even after an initially good dispersion, they show a strong tendency to re-agglomerate in low viscosity matrices, which is the case in pCBT. From the micrographs it can be concluded that CBT is a material in which the dispersion of CNTs seems quite easy.

### 3.2. Crystallinity

The addition of CNTs to the polymerizing CBT could potentially have an influence on the crystallization. However, Table 2 shows that only a very small decrease in crystallinity is observed. Upon examination of the DSC graphs, no significant difference is observed in the shape of the melting peak (endothermal) and in the melting temperature, which indicates that there is no significant influence of CNTs on the perfection of the crystals. In Fig. 3 some representative DSC thermogramma are shown, when all of the measurements are analyzed, the scatter is such that no significant difference is seen. From the crystallization peaks, which are

**Table 2**

Degree of crystallinity of the different samples

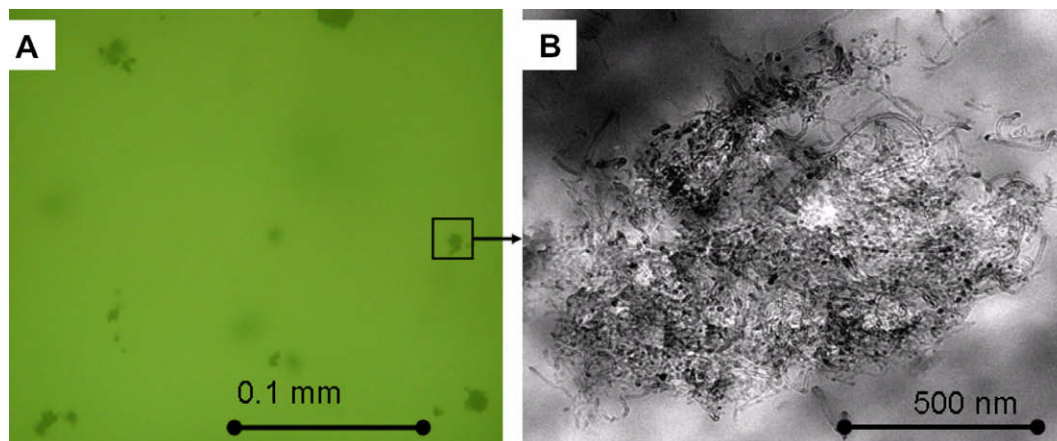
	Crystallinity (%)
pCBT	42.5 ± 0.7
pCBT-0.02CNT	42.9 ± 1.9
pCBT-0.05CNT	40.5 ± 0.5
pCBT-0.1CNT	39.8 ± 0.9

almost identical, it can be concluded that there is also no influence of CNT on the nucleation process, so the CNTs do not act as a nucleating agent.

### 3.3. Mechanical behavior

The influence of the CNTs on the mechanical behavior of unreinforced pCBT is tested in three point bending. The corresponding results can be found in Table 3. After adding 0.05 wt.% CNTs the stiffness increased with more than 30% and also the strength increased with 80%. This increase in stiffness is higher than expected from model calculation using a rule of mixture of Krenchel [24], which predicted a 2% increase in stiffness. An increase significantly higher than expected is also stated in [24]. Additionally a further increase to 0.1 wt.% CNT did not result in any improvement, instead a small decrease in properties is observed. No significant trend is seen between CNT concentration and failure strain. Adding CNTs appears to decrease the failure strain. As explained previously, the influence of micron sized agglomerates, acting as crack initiator, may explain this behavior. The energy to failure, measured as the area under the stress strain curve (Fig. 4), is about 30% higher for pCBT-0.05CNT than for pCBT with the same amount of catalyst. It can be concluded that the addition of 0.05 wt.% CNT has a positive influence on the mechanical properties: the stiffness, the strength as well as the energy to failure.

The mechanical test results show that there is a distinct effect of adding CNTs on the pCBT. The DSC measurements, however, indicate that CNTs do not change the degree of crystallinity and also do not have any influence on the perfection of the crystals. Therefore, the change in mechanical behavior of pCBT when CNTs are added is completely due to the presence of the CNTs which are very stiff (up to 950 GPa) and strong (up to 63 GPa)[25]. The increase in energy to failure of the pCBT-0.05CNT is due to the higher stiffness and strength, since the failure strain does not increase but rather decreases by a small amount. The fact that the failure strain decreases is also an indication that the adhesion between the CNTs and the pCBT is not ideal. With good adhesion there would be



**Fig. 2.** Microscopical images of pCBT-0.02CNT. (A) Optical image, a random distribution of individual CNTs, with different agglomerates of CNTs is visible. (B) TEM-micrograph of one of the agglomerates.

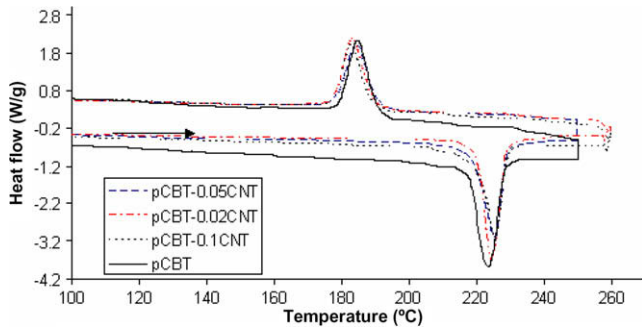


Fig. 3. Typical DSC graphs of the different samples during heating and cooling at 10 °C/min

tendency of localized plastic deformation leading to an increase in failure strain. The HRSEM picture, Fig. 5, in which the smooth surfaces of the CNTs are visible, is consistent with the observation of weak adhesion leading to brittle fracture. The diameter of the nanotubes seem too large in these pictures. This can be explained by the layer of gold which is sputtered on the surface.

3.4. Production of fiber reinforced composites filled with CNTs

CBT is a very promising material for continuous fiber reinforced composites because of its low viscosity. Therefore, the mixture of CBT and CNTs is also tested as a matrix material in fiber reinforced in composites. Since the pCBT-CNT is twice as strong as pCBT (Table 3) it should also have a positive influence on the transverse and shear strength of composites. The higher strength of the matrix should also influence the impact resistance of the composite.

When these composites are produced using the technique described above, there is a risk of the filtering-out of the CNT-agglomerates (with a diameter up to 1 μm) in the small channels between the glass fibers draped in the mould. To avoid this, the length of the CNTs is already decreased by milling them. However after the production of the plate, the resin inlet side shows some black streaks indicating filtration of the CNTs by the complex structure of the fabric, Fig. 6.

This suggests that the CNTs are not equally distributed in the produced composite plate. Also, high and low matrix content regions are seen, indicating inhomogeneous impregnation. This can be explained by the filtered out CNTs forming a network due to entanglement and the already present agglomerates are acting as a secondary filter for the incoming resin flow and hence interrupting the flow behavior of resin between the fibers. The resulting resin holes can be seen in Fig. 6.

From the micrographs (Fig. 7) of the composite, taken in the CNT-rich area, it can be seen that the agglomerates of CNTs tend to be in the matrix rich areas. In the fiber bundles almost no agglomerates can be found. This is probably because of the small spacing between the fibers in the fiber bundles. The presence of thin glass fibers (9–13 μm) forms narrow channels which could concentrate the free flowing CNTs and trigger the reagglomeration. The higher amount of CNTs between the bundles is logical because

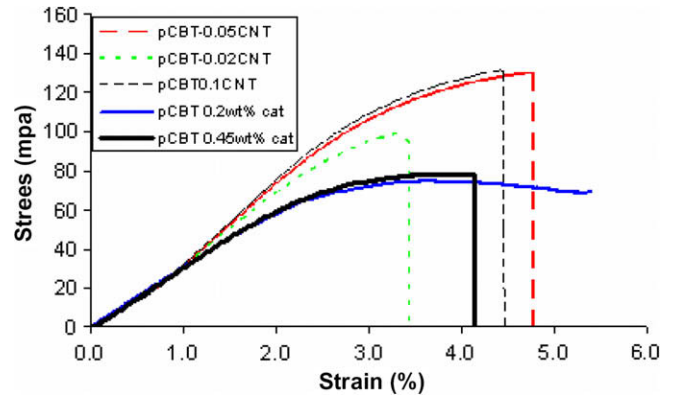


Fig. 4. Stress-strain graph of 3 point bending tests of different unreinforced samples.

of the bigger channels between the fiber bundles than in fiber bundles. A detailed view of an agglomerate is observed by TEM and shows that the size of these agglomerates (several microns) is clearly higher than in the samples without glass fibers (up to 2 μm, Fig. 2A). The agglomerates are bigger because of the higher concentration of CNTs between the fiber bundles, which leads to more reagglomeration. This reagglomeration between fiber bundles is also found in [26]. These big agglomerates hinder complete impregnation by blocking the flow of resin into the narrow channels. The flow pattern also results in orienting the reagglomerated CNTs into elongated bundles as seen in the various micrographs (Fig. 7). In [27] optical observations of agglomerates of CNTs are described, which leads to the conclusion that they form helical bands under shear flow, perpendicular to the flow. The agglomerates found in the composite are of the same magnitude of size as in [27]. The agglomerates between the fiber bundles are all oriented in the same direction, most likely perpendicular to the flow at that place.

The filtering-out of the CNTs during the infusion of the resin into the fabric prevents the use of this production technique for the production of composites with pCBT-CNT as the matrix. Due to its low viscosity during impregnation, the matrix cannot drag the CNTs through the fiber bundles which might be possible with a higher viscosity resin. It might also be improved by altering the CNTs surface, hence making strong covalent bonding between the nanotube and the resin. Another potential solution could be to use additional pressure at the inlet, because in the present case only vacuum at the outlet is the driving force for the resin.

4. Conclusion

Multiwalled carbon nanotubes are mixed with CBT to make a tougher material. This is first tested in pure matrix material. The mechanical properties show a significant enhancement in the stiffness (+ 30%) and the strength by 80% compared to pure pCBT. The increase of these two properties in turn increases the energy to failure, which is linked to the toughness. These enhanced mechanical properties are the direct influence from the CNTs itself, and not

Table 3 Mechanical properties of different unreinforced samples in 3 point bending

	wt.% catalyst	E (GPa)	Strength (MPa)	Failure strain (%)	Energy to failure (MJ/m <sup>3</sup> )
pCBT	0.45	3.17 ± 0.07	74 ± 4	3.9 ± 0.7	2.0 ± 0.6
pCBT	0.2	3.02 ± 0.06	74 ± 2	6.0 ± 0.7	2.9 ± 0.1
pCBT-0.02CNT	0.45	3.6 ± 0.2	97 ± 6	3.6 ± 0.3	1.8 ± 0.2
pCBT-0.05CNT	0.2	4.3 ± 0.2	131 ± 2	4.8 ± 0.3	3.7 ± 0.5
pCBT-0.1CNT	0.2	4.05 ± 0.09	124 ± 4	4.4 ± 0.3	3.1 ± 0.2

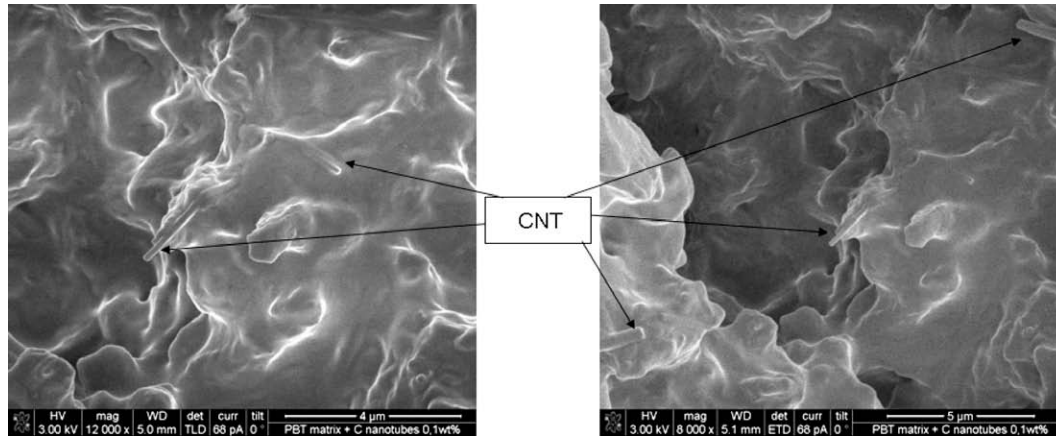


Fig. 5. HRSEM-pictures of pCBT-0.1 CNT. The surface of the CNTs is very smooth.

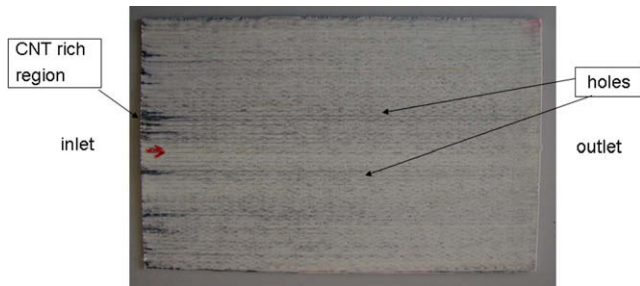


Fig. 6. Picture of a pCBT-0.02CNT plate with glass fibers. At the entrance on the left are clearly more CNT present than at the outlet.

from a modification induced in the matrix such as a change in crystallinity or crystal perfection. This shows CNTs efficiency in transferring the applied load and bridging and deflecting cracks. However, to extract these benefits, a good dispersion is required.

The addition of CNT to CBT is also tried in combination with reinforcing fibers, to make composites. However, with the technique used here, it was impossible to produce a good plate with well dispersed CNTs. The presence of fibers densely packed in a fabric filters out the CNTs from the matrix. Therefore, the CNTs are not homogeneously distributed in the produced plate, but are concentrated and agglomerating in the resin rich areas between the yarns. Therefore, even after seeing a positive influence of the addition of CNTs to CBT, it was not possible to observe similar effects in a produced composite. Therefore the production technique needs to be modified before making any further conclusions.

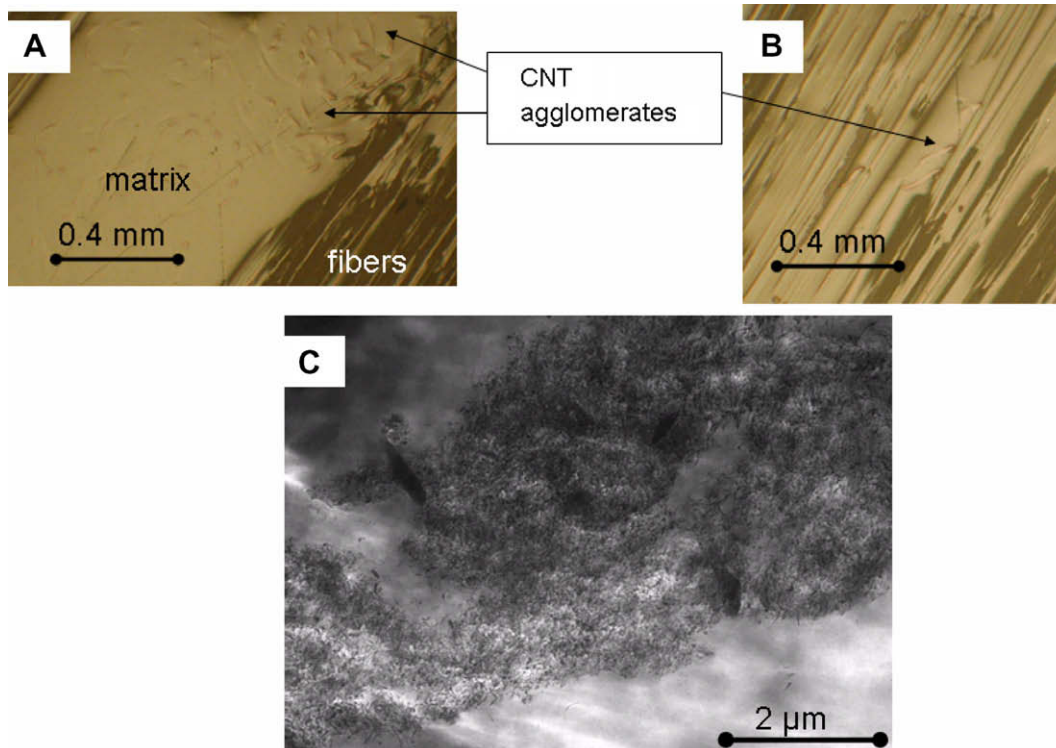


Fig. 7. Microscopical images of a glass fiber-pCBT-0.02CNT composite. (A) an optical image taken between the fiber bundles, different agglomerates are visible, (B) optical image taken in a fiber bundle, only few agglomerates are visible, (C) TEM-micrograph of a CNT agglomerate.

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