

# TOUGHENING OF ISOTHERMALLY POLYMERIZED AND CRYSTALLIZED CBT

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## ABSTRACT

The interest for thermoplastic composites is growing because of the advantages of them over thermosets as well in recyclability as in toughness. The melt viscosity of thermoplastic polymers is very high, which makes fiber impregnation difficult. This can be solved by using cyclic butylene terephthalate (CBT). This low viscous prepolymer polymerizes to the thermoplastic polybutyleneterephthalate (PBT). If this is done isothermally, a too perfect crystal structure grows, which induces brittleness. To solve this problem CBT is mixed with polytetrahydrofurane (PTHF). CBT and PTHF will possibly form a copolymer which leads to a much tougher material, both for unfilled material and for composites. Although the new material is even more brittle than pure polymerized CBT. This is due to low molecular weight and the incomplete copolymerization.

## 1. INTRODUCTION

Cyclic butylene terephthalate (CBT<sup>®</sup>) is a low viscous cyclic oligoester which polymerizes, after adding a catalyst, to the better known thermoplastic polybutyleneterephthalate (PBT) [1]. The combination of the low viscosity and its thermoplastic character makes the CBT resin a very promising material. It combines a rather undemanding impregnation, as for thermosets, with the advantages of a thermoplastic matrix. These advantages are the recyclability by melting, the higher toughness and impact resistance. Due to the low viscosity of the CBT in its oligomeric state it can be used in RTM-like processes, which are normally reserved to thermosets.

For CBT polymerization under the melt temperature of PBT is possible. Crystallization will start during this polymerization. This helps reducing the time of the production cycle [3]. However, it was found that when this resin is used under RTM-processing conditions, the matrix material is much more brittle than normal PBT. This brittleness is induced by the isothermal RTM-production route, where rapid cooling is difficult, if not impossible. Because of the isothermal production process, at which simultaneous polymerization and crystallization occurs, a perfect crystal structure with few tie-molecules arises, which leads to brittleness [4].

Earlier research found that the addition of polycaprolactone (PCL) leads to a copolymer, due to transesterification, which makes the polymerized CBT (pCBT) twice as tough [5]. In earlier work can be found that the addition of PTHF to PBT leads to a copolymer with much higher failure strain [6], although the strength decreases a bit. In this paper PTHF is mixed with CBT before polymerization to investigate of toughening effect is also present in an isothermal production. The addition of PTHF, which should copolymerize, has to induce a lower crystallinity, and therefore lead to a higher toughness.

## 2. Material and Methods

### Material

CBT<sup>TM</sup> used in this study is delivered by Cyclics Corporation. The number of butylgroups in the oligomer mixture varies from two to seven, resulting in a melting range from 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 catalyst (Fastcat<sup>TM</sup> 4101, butylchloridehydroxystannan) is commercially available from Atofina Chemicals Incorporated. Polytetrahydrofuran (PTHF) is delivered by Sigma Aldrich with a number average molecular weight of 2900g/mol and is kept in a desiccator.

### Production

The process used in this paper is based on the RTM process. The low viscous oligomer/catalyst mixture is vacuum infused into a closed mould (190°C). The oligomers are heated above their melting point (to 190°C), the catalyst (0.45 wt%) is then added and the resulting mixture is stirred for 20 seconds. During this time, polymerization already starts, resulting in a continuously increasing viscosity and thus a limited time window for 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. Flat plates (320 × 200 × 2 mm<sup>3</sup>), with different weight percentages PTHF (x), were successfully produced using the method described above (PTHFx).

### Experimental methods

Viscosity measurements are performed on a Rheometrics Dynamic stress Rheometer with a parallel plate geometry. A gap of 0.750mm is used with a constant shear stress of 0.5 Pa.

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

$$\chi_{c(\text{wt}\%)} = \frac{\Delta H_m}{\Delta H_\infty} \times 100 \quad (1)$$

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 [7].

DMTA is used for measuring the glass transition. The single cantilever method is used with a free length of 17,5 mm. The samples are tested at 1 and 10 Hz. The machine that is used is DMA Q800 from T.A. Instruments.

Gel Permeation Chromatography (GPC) is used to determine the molecular weight, its distribution and the conversion. The measurements were performed with a mixture of chloroform/hexafluoro-2-propanol (HFIP) as solvent (98/2 CHCl<sub>3</sub>/HFIP). The flow rate was 0.8 ml/min at a temperature of 20°C. Two Waters PL HFIPgel columns were used in series. The chromatograph was connected to Waters 484 UV detector working at 254 nm. In order to relate retention time to molecular weight, a universal calibration was made using various polystyrene standards. For sample preparation, approximately

1 mg of matrix was dissolved in 80  $\mu$ l of HFIP. After total dissolution, the solution was diluted by 4 ml of chloroform. The degree of conversion is determined from the GPC measurements and is calculated as follows:

$$\alpha = 1 - \frac{A_{oli}}{A_{tot}} \quad (2)$$

with  $\alpha$  the degree of conversion,  $A_{oli}$  the area under the oligomer peaks of the retention time curve and  $A_{tot}$  the total area under the retention time curve.

The unfilled polymerized CBT (pCBT) are tested in three point bending according to ASTM D790-M.

ESEM is used for investigating the microstructure. This is done on a Philips XL30 ESEM. The samples are treated with gold to avoid charging, back scattered electrons are used.

### 3.Results and discussion

If the mixture of CBT and PTHF will be used in composites, the viscosity should be lower than 1Pa.s to get a good fiber impregnation [1]. Pure CBT has a viscosity of  $\pm 30$  Pa.s at 190°C which is far below this limit. Table 1 shows that the addition of some percentages PTHF has only a small influence on the viscosity.

Table 1: Viscosity of mixtures with different weight percentages PTHF

	$\eta$ (Pa.s)
CBT	0.030
CBT + 1wt% PTHF	$0.050 \pm 0.006$
CBT + 5wt% PTHF	$0.05 \pm 0.02$
CBT + 10wt% PTHF	$0.042 \pm 0.009$

The addition of PTHF has as goal an increase in ductility. Therefore the mechanical properties of the different produced plates are measured with three point bending. In figure 1 can be seen that the addition of PTHF does not lead to a tougher material on contrary a more brittle material is produced. As well as the failure strain, the strength and the stiffness did decrease.

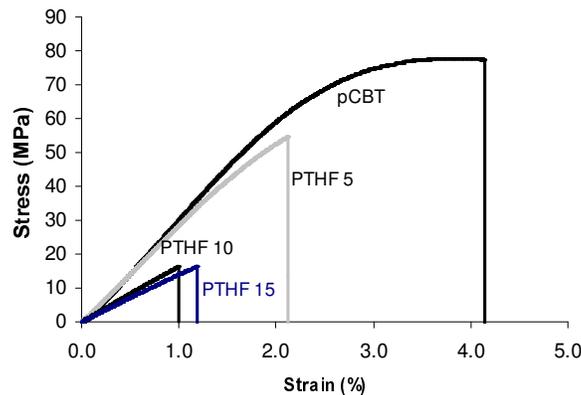


Figure 1: Stress-strain curves of samples with different weight % PTHF.

The strength decreased to less than one third of the original values (19 vs. 75 MPa) after adding 15% PTHF. The failure strain lowered to 1.3 % while the failure strain of pCBT is 4%. This decrease in mechanical properties is not the expected result. There are

different explanations for this. The addition of PTHF can lead to a lower molecular weight, which has a negative influence on the toughness. A molecular weight higher than 50 kg/mol is necessary to have plastic behavior in PBT [7]. Another reason can be found in the microstructure of the polymer. If there stays unreacted PTHF in the material this can lead to brittleness. A third reason can be that the crystallinity did not decrease.

A lower crystallinity should lead to a higher ductility and failure strain. Normally the addition of PTHF should lead to a lower crystallinity because the crystallization of a copolymer is much more difficult than a pure polymer. When the crystallinity is measured with DSC can be seen (table 2) that the crystallinity does not decrease and even increases a bit.

Table 2: Crystallinity in function of percentage PTHF

Sample	Crystallinity
pCBT	40 ± 1
pTHF5	43 ± 6
pTHF10	44 ± 2
pTHF15	42 ± 3

The melting peaks of the different samples do not show a difference (fig. 2). They all have about the same width and lay at the same temperature. When there are more imperfections in the crystals the peaks become broader. Therefore can be concluded that the addition of PTHF has no influence on the perfection of the crystals of the pCBT. Since there is almost no influence of the PTHF on as well the amount of crystallinity as on the perfection of the crystals, this can not be the explanation for the embrittling effect.

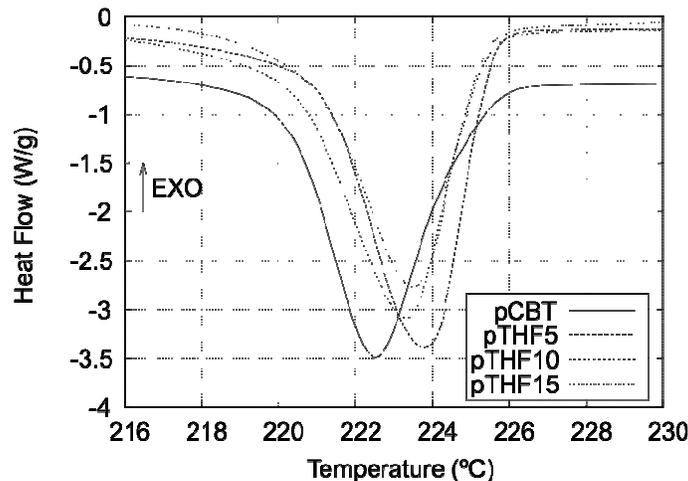


Figure 2: The melting peaks of pCBT with different amount of PTHF added

A higher molecular weight induces a higher failure strain. This also means that a low molecular weight can lead to a brittle material. In [7] is stated that  $M_w$  should be at least 50 for having plastic behavior. With some GPC measurement the molecular weight and also the conversion of the polymerization reaction is measured. Figure 3 shows clearly that the addition of PTHF has a negative influence on the molecular weight after the polymerization. The addition of 5wt% PTHF leads to an  $M_w$  which is half that of pure

pCBT. Adding more PTHF leads to even a lower  $M_w$ . The values of  $M_w$  when PTHF is added are lower than 50 kg/mol, which leads to brittleness.

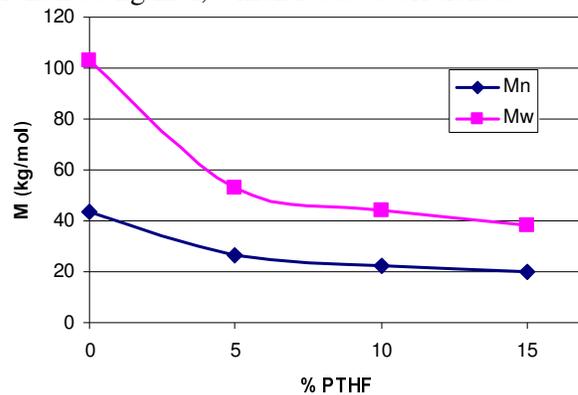


Figure 3: Mn and Mw for pCBT and pCBT with different amounts of PTHF after polymerization for 30 minutes at 190°C

A possible explanation for this lower molecular weight after adding PTHF can be that the polymerization is not yet completed after 30 minutes. However, when the conversion is taken into account, figure 4, it is clear that after 30 minutes the polymerization has finished.

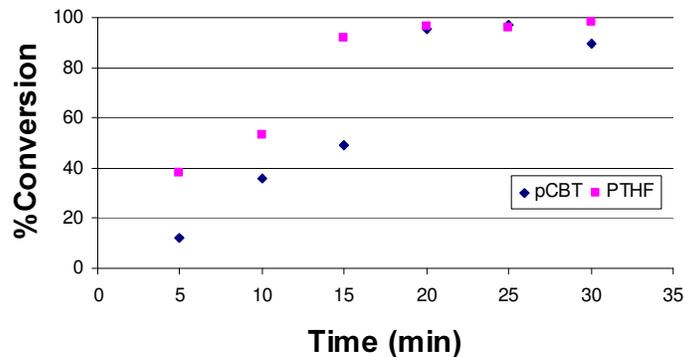


Figure 4: Conversion of the polymerization for CBT (pCBT) and CBT + 10wt% PTHF (PTHF), during the time.

In fact it is normal that the final molecular weight decreases. The final molecular weight is inverse repropotional to the number of end-groups in the mixture. Because the PTHF induces 2 extra end-groups, for every PTHF chain, the weight will decrease. It is this loss in molecular weight that partially explains the decrease in mechanical properties.

The microstructure of the polymer is very important for the resulting properties. Also for the use in composites a copolymer should be formed and not a blend. To know the microstructure, different DSC and DMA measurements are executed. From the DSC measurements (fig. 2) can be concluded that the addition of PTHF does not have an influence on the crystalstructure, and that there is only one crystalline phase, namely pCBT.

The DMA measurements (fig. 5) show an influence of the addition of PTHF. When more PTHF is added, a second peak becomes more visible. The first peak ( $\pm 70^\circ\text{C}$ ) is the glass transition of pCBT. The second peak ( $\pm 0^\circ\text{C}$ ) is not the glass transition of PTHF

(lower than  $-60^{\circ}\text{C}$ ), but is coming from a new second phase appearing in the mixture. This second phase is a copolymer of PTHF with pCBT.

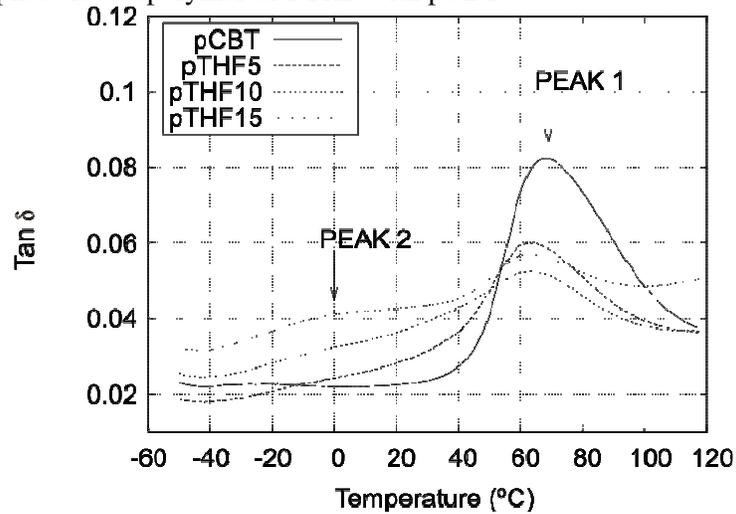


Figure 5: DMTA measurements of different samples

The presence of two phase can be verified with optical light microscopy. In figure 6, of pure pCBT, there is clearly one phase present, while in figure 7, with 5wt% PTHF, a second phase appears. From figures 8 (10wt%) and 9 (15wt%) it is clear that this second phase grows when more PTHF is added.

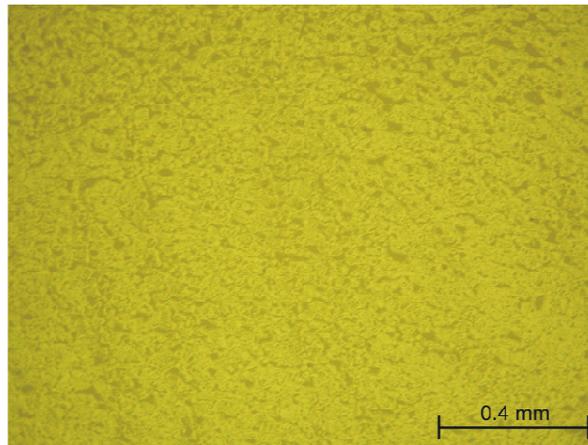


Figure 6: Optical image of pure pCBT after 30 minutes polymerization and crystallization

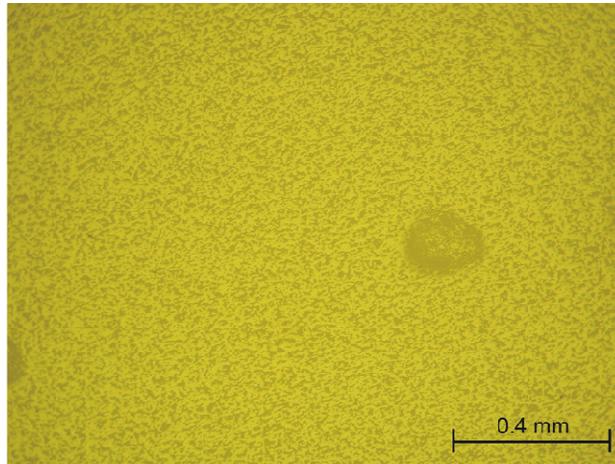


Figure 7: Optical image of pCBT with 5 wt% PTHF after 30 minutes polymerization and crystallization.

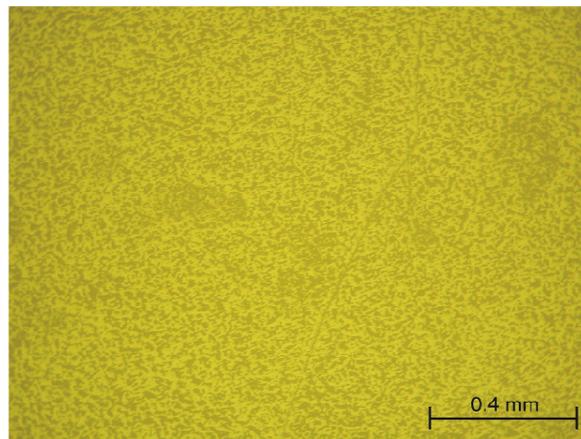


Figure 8: Optical image of pCBT with 10 wt% PTHF after 30 minutes polymerization and crystallization.

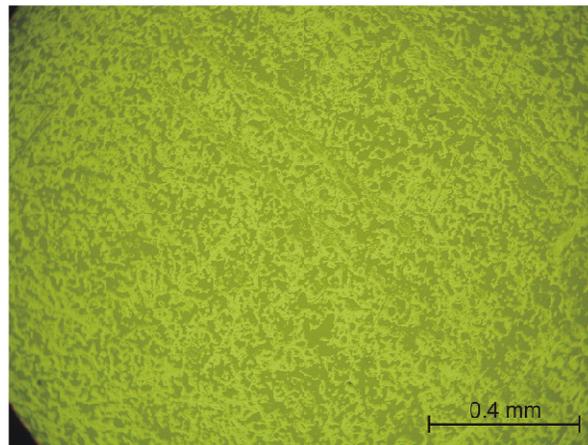


Figure 9: Optical image of pCBT with 15 wt% PTHF after 30 minutes polymerization and crystallization.

To investigate the second phase some SEM images are made of some original samples and some of samples which were treated with dichloromethane for a quarter. Dichloromethane selectively dissolutes PTHF. There is a clear difference between the samples before and after the treatment (fig. 10). When the pure pCBT is treated it is clear that there is no influence of the treatment (fig 11). For the pure pCBT there are some crimp holes visible as well before as after the treatment, due to the fact that

crystals are denser than the amorphous phase. In PTHF15 after treatment (fig. 10) are some clear holes present, coming from unreacted PTHF, which is dissolved. This means that not all the added PTHF reacts due to transesterification with pCBT to a copolymer.

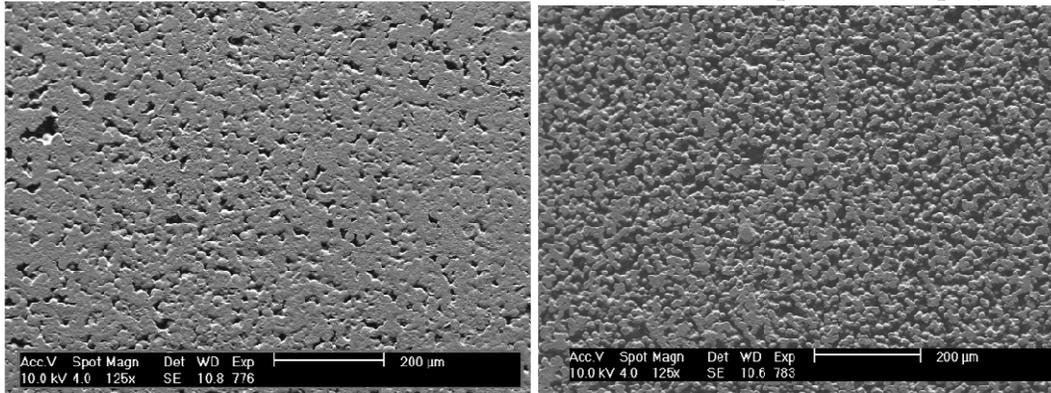


Figure 10: SEM pictures of pCBT-15wt%PTHF (left) and after treatment with  $\text{CH}_2\text{Cl}_2$  (right)

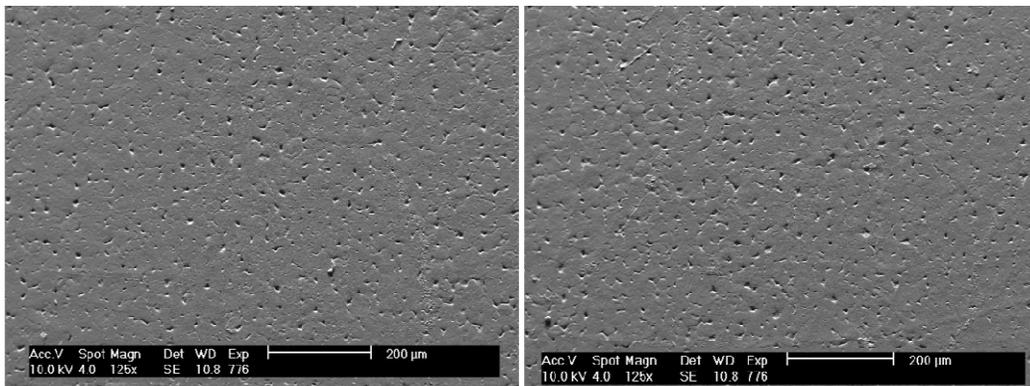


Figure 11: SEM pictures of pCBT (left) and pCBT after treatment with  $\text{CH}_2\text{Cl}_2$  (right).

The microstructure that is present in the material consists eventually of two phases. The first phase is a semi-crystalline pCBT with some very small amounts of PTHF in it. The second phase is a copolymer of pCBT with PTHF with some unreacted PTHF (fig. 12). It is the presence of this unreacted PTHF together with the low molecular weight that is responsible for the brittleness of the material.

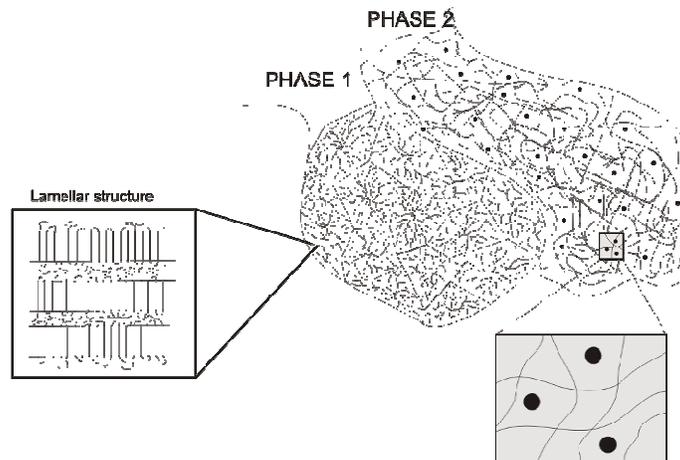


Figure 12: Microstructure which will be formed when CBT is mixed with PTHF. Phase 1 exists of pCBT with some PTHF and Phase 2 exists of a copolymer of pCBT and PTHF with some unreacted PTHF between the chains.

To make a mixture of CBT and PTHF more ductile there are two different solutions.

1. Use less catalyst
2. Change the microstructure

The first solution has as goal to higher the molecular weight. The addition of less catalyst induces less end-groups and should end in a higher molecular weight. This higher molecular weight should increase the failure strain.

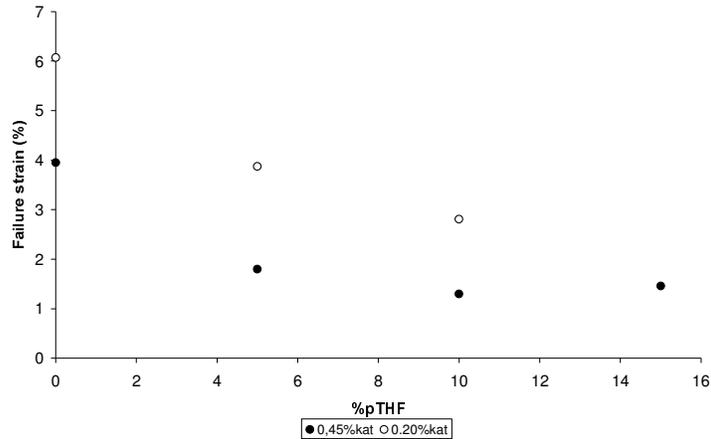


Figure 13: The failure strain for samples with different % PTHF and different amounts of catalyst.

From figure 13 can be concluded that a lower amount of catalyst indeed leads to a higher failure strain. Although the addition of PTHF still has an embrittling effect on the pCBT.

When the molecular weight is considered, table 3, it can be seen that the addition of less catalyst does not lead to a higher molecular weight.

Table 3: The molecular weight after complete polymerization for CBT with 10wt% PTHF and different amounts of catalyst.

amount catalyst	Mw (kg/mol)
0.2 wt%	48 ± 2
0.33 wt%	53 ± 4
0.45 wt%	44 ± 1

The reason for this toughening effect without increasing the molecular weight can be found in the second proposed solution. The addition of less catalyst leads to a slower reaction. This gives the PTHF and the pCBT more chance for transesterification. Therefore less unreacted PTHF will stay in the material. This can be seen on figure 14. In figure 14 the holes of the dissolved PTHF are less present in the sample with 0.2wt% catalyst than in the sample with 0.45wt% catalyst, where more unreacted PTHF is present.

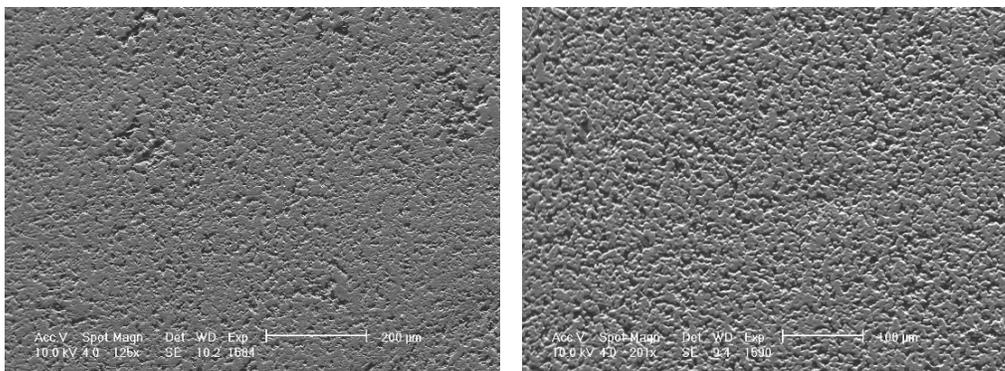


Figure 14: SEM images of samples with 10wt% PTHF. The left picture is with 0.2wt% catalyst and the right with 0.45wt% catalyst.

#### 4. Conclusions

The brittleness of isothermally polymerized CBT can be solved with copolymerization. PTHF is added to make a copolymer of it with CBT. The resulting mechanical properties are not as expected. In fact all the mechanical properties decrease. This decrease in mechanical properties is due to a decrease in molecular weight. Another reason for the worse mechanical properties is the incomplete copolymerization, since unreacted PTHF is present. Possible solutions are proposed and tested. A lower amount of catalyst indeed leads to better properties, but not because of a higher molecular weight, but because of less unreacted PTHF. The lower amount of catalyst slows down the rate of polymerization while the rate of transesterification will stay the same.

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