

Toughening of *in situ* polymerized cyclic butylene terephthalate by addition of tetrahydrofuran

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Abstract

A new method of toughening polymerized cyclic butylene terephthalate (pCBT) with tetrahydrofuran (THF) is proposed. The pCBT was prepared by *in situ* ring-opening polymerization of a commercial cyclic butylene terephthalate, a cyclic form of poly(butylene terephthalate), in the presence of THF. In comparison to conventionally polymerized pCBT, the resultant material was found to be ductile, showing a strain at break of well above 100% in tensile tests. Other matrix properties, such as tensile modulus, tensile strength and glass transition temperature, were not significantly altered by the addition of THF. It was found that the presence of THF enhanced the polymerization reaction, resulting in an increased molecular weight and a narrowed molecular weight distribution. Moreover, remaining oligomers after polymerization were extracted by the THF and a toughened oligomer-free pCBT was obtained. The influence of time and temperature on the long-time toughening action of THF was studied. The results showed that samples became brittle after 3 months when subjected to a temperature of 80 °C, resulting in a reduction of the toughening action.

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Keywords: CBT; pCBT; cyclic butylene terephthalate; THF; tetrahydrofuran; toughening; *in situ* polymerization

INTRODUCTION

Recently, commercialized cyclic butylene terephthalate (CBT) and its applications have become of interest and are the subject of investigation. Cyclic oligomers are small molecules with a ring structure and a low molecular weight. They are precursors for linear high-molecular-weight polymers and consist basically of the same repeat units as their linear counterparts. The low-molecular-weight poly(butylene terephthalate) (PBT) oligomers used in the study reported here are solid at room temperature and melt at relatively low temperatures of ca 120–160 °C.^{1–3} They have a water-like viscosity upon melting,⁴ and thus are able to impregnate fibre reinforcements or to carry high loadings of fillers.⁵ Upon further heating, the molten oligomers polymerize in the presence of a catalyst in an entropically driven ring-opening polymerization into linear high-molecular-weight PBT polyester. The polymerization reaction is athermal and no volatile organic compounds are released. Moreover, the polymerization starts at temperatures below the crystallization temperature of PBT and cold crystallization occurs after polymerization.⁶ This allows isothermal processing below the melting temperature of polymerized cyclic butylene terephthalate (pCBT) without the need of thermal cycling of the mould, which is advantageous from the processing point of view.^{4,5,7–13}

The cold crystallization of pCBT can be hindered when fillers are added prior to polymerization. Working with CBT and organoclays, Karger-Kocsis *et al.*¹⁴ found that the clay can hinder pCBT cold crystallization during the first heating. Lanciano *et al.*¹⁵ suggested in similar research that the presence of montmorillonite shifts the ring-opening polymerization of CBT towards higher temperatures,

therefore preventing cold crystallization. Also non-isothermal processing using high heating rates seems to have a similar effect. When conducting a DSC scan at a heating rate of 5 °C min⁻¹, Mohd Ishak *et al.*¹⁶ also found a reduced melting enthalpy of pCBT. They detected a prominent crystallization peak at 195 °C when a heating rate of 0.5 °C min⁻¹ was used⁴ and deduced that high DSC heating rates hinder the cold crystallization of CBT due to kinetic effects. Nevertheless, both isothermal and non-isothermal processing yield a fully polymerized pCBT when using adequate polymerization temperatures and times.^{1–3,6} These properties make CBT resin a very promising engineering material.

However, pCBT exhibits a more brittle behaviour than conventional PBT when polymerized isothermally. This has been attributed to the growth of large crystals with a high degree of perfection and the presence of only few intercrystalline tie molecules.^{2,3,5,9,10} To overcome this problem, some work was done on the toughening of pCBT, particularly by copolymerization with poly(vinyl butyral),⁷ ϵ -caprolactone,⁸ poly[ethylene-co-(vinyl acetate)]¹⁷ and polycaprolactone.⁵ Polytetrahydrofuran was used by Baets *et al.*⁵ but the resulting copolymers showed

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poorer mechanical properties. The resulting copolyesters showed increased toughness in the case of copolymerization with ϵ -caprolactone, polycaprolactone and poly[ethylene-co-(vinyl acetate)]. Stiffness and strength were found to decrease in these copolyesters due to the properties of the copolymers used. In a further attempt, physical modification was also done by adding carbon nanotubes (CNTs) at up to 0.1 wt%.⁵ In this case stiffness and strength were found to be increased due to the reinforcement of the CNTs. Nevertheless the bulk behaviour of the pCBT obtained was not affected and the CNT-filled pCBT showed a failure strain of ca 4%, well below that of commercial PBT (>50%).¹⁸

In the work reported here, tetrahydrofuran (THF) was used in small amounts (ca 1.5 wt%) to impregnate CBT oligomers prior to *in situ* polymerization. A THF-modified pCBT with an increased toughness was obtained. This toughening effect was found to decrease with time when samples were stored at elevated temperature above the glass transition temperature (T_g). The underlying effect of THF on the properties of the resultant material was analysed using various techniques.

EXPERIMENTAL

Materials

The CBT used was one-component CBT-XB3 and contained 0.3 mol% Fascat® 4105 as catalyst. It was provided in granule form by Cyclics Europe GmbH (Schwarzheide, Germany). The granules were ground in a mortar into a fine powder, vacuum-dried for 8 h at 80 °C and kept in a desiccator until further use. THF (C₄H₈O; molecular weight of 72.11 g mol⁻¹, purity of 99.5%) was purchased from Panreac Química SA (Barcelona, Spain) and was used as received.

Sample preparation

A glass vial equipped with a mechanical stirrer was charged with 100 g of THF, and then 50 g of previously dried CBT powder was slowly added. The CBT/THF suspension was stirred for 5 min and subsequently dried at 80 °C *in vacuo* for 8 h, removing the excess THF. The resultant material was ground in a mortar into a fine powder and again dried until a THF content of about 1.5 wt% was reached. The THF content was determined as follows. The weight of a small sample (e.g. 1 g) of the CBT/THF suspension was carefully determined. Then this sample was dried at 80 °C under vacuum to constant weight. The THF content of the starting material before drying was calculated using the expression

$$X_{\text{THF}} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (1)$$

where X_{THF} is the THF content of CBT/THF, m_{wet} is the weight of the initial CBT/THF suspension and m_{dry} is the weight of CBT/THF dried to constant weight.

The CBT/THF suspension containing 1.5 wt% THF obtained as described above was *in situ* polymerized in a hot press (IQAP LAP PL-15) at 250 °C for 20 min between two polytetrafluoroethylene (PTFE) sheets in ambient atmosphere, leading to pCBT/THF films having dimensions of 120 × 120 mm and a thickness of 0.4 mm. The polymerized samples were then cooled between two water-chilled steel plates. Neat pCBT samples were similarly produced for comparison. Some pCBT/THF films were manually cut into small pieces and subsequently reprocessed in the hot press at 250 °C for 5 min, referred to as pCBT/THF-RP.

Characterization

Gas chromatography/mass spectrometry (GC-MS)

GC-MS was employed to detect volatile THF in the toughened samples. GC-MS was carried out using a Shimadzu QP 2010 with the head space technique for the injection of samples. About 1 mL of sample was heated to 80 °C for 40 min in a 30 mL vial sealed with a PTFE septum and 1 mL of air was injected into the GC-MS system. The GC oven was held at 40 °C for 10 min, then heated to 150 °C at 4 °C min⁻¹ and finally held at 150 °C for 10 min. Injection was performed at 200 °C using helium as carrier gas at a flow rate of 22.1 mL min⁻¹. The column (TRB-624) had a length of 30 m and an inner diameter of 0.25 mm with a film thickness of 0.25 µm. The column flow was set to 0.95 mL min⁻¹. Identification of the compounds was performed using Nist 147, Nist 27 and Wiley 229 as reference libraries.

Differential scanning calorimetry

DSC was carried out using a PerkinElmer Pyris 1 device under nitrogen atmosphere. Polymerized pCBT/THF samples prepared by compression moulding as well as those reprocessed in the hot press were analysed using DSC and compared to neat pCBT. Neat CBT and samples with THF were also *in situ* polymerized during the first heating run of a DSC scan. The first DSC sample was the CBT/THF suspension before drying, containing 2 parts THF and 1 part CBT (referred to as CBT/THF 67%). The second DSC sample corresponded to the dried material with 1.5 wt% THF content (referred to as CBT/THF 1.5%), similar to the one used for compression moulding.

The degree of crystallinity X_c of the samples was calculated from the melting enthalpy of the second heating run according to

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (2)$$

The melting enthalpy (ΔH_m^0) of fully perfect crystalline PBT is found in the literature to be 142 J g⁻¹.^{19,20}

Samples were heated from 30 to 270 °C at a heating rate of 10 °C min⁻¹, followed by an isothermal step of 3 min and then cooled from 270 to 30 °C at a cooling rate of 30 °C min⁻¹. The second heating scan was performed equally and allowed the examination of the conversion from cyclic oligomers into linear polymer. The presence of a melting peak in the range 120–160 °C during the second heating scan can be ascribed to a not fully completed polymerization reaction.

High heating rates in a DSC scan can hinder the cold crystallization of pCBT polymerized during the first heating run.^{4,16} To study this kinetic effect, a heating rate of 1 °C min⁻¹ was used for CBT as well as for CBT/THF 1.5%. The first stage of the heating rate was done at 10 °C min⁻¹ between 30 and 60 °C to prevent premature evaporation of the THF and then changed to 1 °C min⁻¹ between 60 and 250 °C. The results obtained were then compared to those obtained for a scan performed entirely at 10 °C min⁻¹.

Gel permeation chromatography (GPC)

GPC was carried out at room temperature using an Agilent Technologies 1200 Series modular system (Agilent Technologies, Santa Clara, USA) comprising an Agilent 1200 refractive index detector, working at a temperature of 35 °C. A linear Styragel HR5E column from Waters (Milford, MA, USA) with a separation range from 10³ to 5 × 10⁶ g mol⁻¹ was employed. 1,1,1,3,3,3-Hexafluoroisopropanol (Fluka Analytical) stabilized with 6.8 g L⁻¹

Table 1. GC-MS results and molecular weight as determined using GPC

| Sample | Retention time (min) | Area | Area (%) | Compound | M_w (g mol ⁻¹) | M_n (g mol ⁻¹) | α (%) |
|----------|----------------------|------------|----------|----------|------------------------------|------------------------------|--------------|
| pCBT | 9.366 | 1 250 637 | 12.4 | THF | 22 600 | 10 000 | 97.9 |
| pCBT/THF | 9.330 | 56 280 805 | 86.2 | THF | 37 000 | 14 000 | – |

sodium fluoroacetate to prevent polyelectrolyte effect was used as solvent at a flow rate of 0.5 mL min⁻¹. The pressure of the column was 60 bar (6 MPa) and the amount of sample was 1 mg of polymer. Low-dispersion poly(methyl methacrylate) (Fluka, Switzerland) samples were used as internal standards. The degree of conversion α (%) from CBT oligomers to pCBT was determined using

$$\alpha = 1 - \frac{A_{\text{oligomer}}}{A_{\text{total}}} \quad (3)$$

where A_{oligomer} is the area under the oligomer peak of the GPC trace and A_{total} the total area under the GPC trace.

Thermogravimetric analysis

TGA was performed in aluminium oxide pans at a heating rate of 10 °C min⁻¹ with a nitrogen flow rate of 30 mL min⁻¹ using a TA Instruments Q600 device. Weight loss was analysed by heating the samples at a rate of 10 °C min⁻¹ from room temperature to 600 °C. The weight of the samples was 10 mg.

Dynamic mechanical thermal analysis (DMTA)

DMTA was used to study the effect of temperature on the dynamic mechanical properties of neat pCBT and THF-toughened pCBT. A TA Instruments Q800 instrument was used in single-cantilever configuration at a frequency of 1 Hz and a strain of 0.05% for all samples. The temperature range was set from 27 to 220 °C and a heating rate of 2 °C min⁻¹ was selected. Samples were prepared from pCBT processed by compression moulding and had dimensions of 27 × 5 × 0.4 mm³.

NMR spectroscopy

The structure of pCBT/THF was characterized using ¹H NMR spectroscopy. Polytetrahydrofuran (polyTHF; Aldrich, molecular weight of 1000 g mol⁻¹) was also analysed and compared with pCBT/THF in order to clarify whether a copolymer was formed or not. ¹H NMR spectra were recorded with a Bruker AMX-300 spectrometer, operating at 300.1 MHz, with 1% (w/v) samples dissolved in a mixture of CDCl₃/TFA (8/1). A total of 64 scans were accumulated with 32 000 data points and 2 s of relaxation delay.

Mechanical properties

Tensile tests were performed at 25 °C and at a crosshead speed of 10 mm min⁻¹ using a Galdabini Sun 2500 (Galdabini, Italy) tensile testing machine according to ISO 527. Type 1BA specimens according to ISO 527-2 were extracted from sample films. A minimum of five specimens were tested for each reported value.

RESULTS AND DISCUSSION

Previous trials showed that an optimum toughening effect was achieved with a THF content of 1.5 wt%. The toughening effect

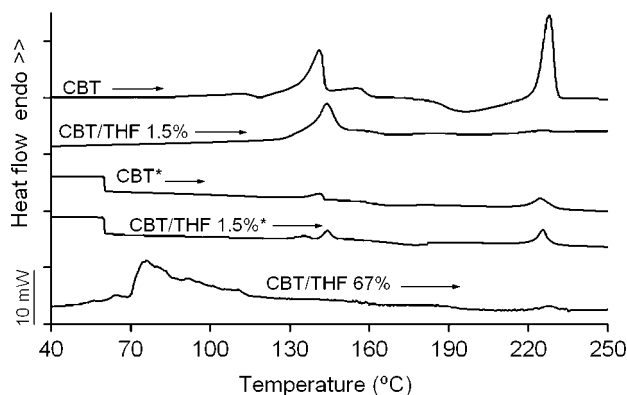


Figure 1. DSC thermograms of CBT, CBT/THF 1.5%, CBT*, CBT/THF 1.5%* (the asterisk indicates a heating rate of 1 °C min⁻¹) and CBT/THF 67%. The traces are displaced on the y-axis for better visibility.

was evaluated in terms of tensile tests. The presence of a yield point with neck formation and post-yield deformation was taken as a criterion for ductility. If the CBT contains less than 1 wt% THF, then the pCBT/THF is equally brittle as neat pCBT. On the other hand, if the CBT contains more than 2 wt% THF, then the pCBT/THF is toughened, but the conventional compression moulding system used does not allow the production of samples without gas inclusions. This is due to the evaporation of the excess THF during processing, which would need a vacuum extraction in order to be removed from the sample.

GC-MS analysis

GC-MS was used to clarify if THF is still present in the pCBT after compression moulding. THF exhibits a low boiling temperature and hence is supposed to completely evaporate during the applied processing at 250 °C. Surprisingly, a large amount of THF is found in pCBT/THF. This result indicates the presence of van der Waals forces between the pCBT matrix and the THF molecules, preventing their complete evaporation. In respect of the peak areas of the analysed samples, pCBT/THF is found to have an 82-fold THF concentration compared to that of neat pCBT (Table 1). A small signal corresponding to THF is also detected in pCBT, as it is known that THF is formed during the degradation of PBT.^{20–22} As a consequence, the THF detected in neat pCBT could come from a possible initiation of degradation during processing.

DSC analysis: CBT/THF

The influence of THF on the *in situ* polymerization of CBT was studied with DSC. The resulting thermograms are depicted in Fig. 1 and the thermal properties are summarized in Tables 2 and 3.

Oligomer melting

Neat CBT non-isothermally polymerized in the DSC pan typically shows a broad melting peak of the cyclic oligomers in the

Table 2. DSC first heating run, heating rate of 10 °C min⁻¹

| Sample | Oligomer melting | | Cold crystallization | | Polymer melting | |
|---------------|------------------|---|----------------------|--|-------------------|--|
| | $T_{m,CBT}$ (°C) | $\Delta H_{m,CBT}$ (J g ⁻¹) | $T_{c,pCBT}$ (°C) | $\Delta H_{c,pCBT}$ (J g ⁻¹) | $T_{m,pCBT}$ (°C) | $\Delta H_{m,pCBT}$ (J g ⁻¹) |
| CBT | 141.2 | 46.5 | 196.5 | -36.5 | 227.8 | 35.1 |
| CBT/THF 1.5% | 141.1 | 46.5 | 202.5 | -10.5 | 228.9 | 15.7 |
| CBT/THF 67% | 144.8 | 6.5 | 200.4 | -3.9 | 227.9 | 4.2 |
| CBT* | 141.1 | 46.0 | 168.7 | -18.5 | 224.4 | 67.0 |
| CBT/THF 1.5%* | 144.2 | 45.5 | 176.2 | -33.6 | 225.5 | 55.0 |
| pCBT | - | - | - | - | 224.2 | 52.8 |
| pCBT/THF | - | - | - | - | 223.1 | 44.0 |
| pCBT/THF-RP | - | - | - | - | 224.7 | 51.6 |

* heating rate of 1 °C /min.

Table 3. DSC cooling and second heating scans, cooling rate of 30 °C min⁻¹, heating rate of 10 °C min⁻¹

| Sample | First cooling | | Second heating | | Crystallinity, X _c (%) |
|---------------|-------------------|--|-------------------|--|-----------------------------------|
| | $T_{c,pCBT}$ (°C) | $\Delta H_{c,pCBT}$ (J g ⁻¹) | $T_{m,pCBT}$ (°C) | $\Delta H_{m,pCBT}$ (J g ⁻¹) | |
| CBT | 176.6 | -41.7 | 223.6 | 42.1 | 29.6 |
| CBT/THF 1.5% | 179.4 | -42.7 | 222.9 | 42.7 | 30.1 |
| CBT/THF 67% | 181.1 | -63.2 | 223.6 | 57.2 | 40.3 |
| CBT* | 172.1 | -36.1 | 225.1 | 37.4 | 26.3 |
| CBT/THF 1.5%* | 175.1 | -40.2 | - | - | - |
| pCBT | 183.4 | -48.8 | 224.8 | 40.7 | 28.7 |
| pCBT/THF | 184.4 | -44.1 | 223.7 | 38.2 | 26.9 |
| pCBT/THF-RP | 183.4 | -48.0 | 223.4 | 47.9 | 33.7 |

* heating rate of 1 °C /min.

range 120–160 °C with a maximum at 141 °C. A subsequent cold crystallization in the range 170–220 °C with a peak at 197 °C is detected as a broad and not much pronounced exothermic signal. The final crystalline melting peak is located at ca 228 °C, as shown in Fig. 1. This is in agreement with the reported values of other researchers.^{2,3,15,16}

However, some differences are detected in the case of CBT/THF suspensions. THF has a boiling point of 66 °C,²³ and therefore evaporates when this temperature is reached during the first heating scan. This phase transition can be observed as a broad endothermic signal with an onset temperature of 53 °C and a peak temperature of 76 °C for the CBT/THF 67% sample. The sample with 1.5 wt% THF content does not show this phase transition, most likely due to a too small amount of THF to be detected with the DSC technique. CBT/THF 67% shows a very reduced oligomer melting enthalpy ($\Delta H_m = 6.5 \text{ J g}^{-1}$), clearly indicating the effect of THF on CBT oligomers. Since the enthalpy is very low, it cannot be observed in Fig. 1, but data are provided in Table 2. This reduction in melting enthalpy of the oligomers may be due to the solubility of CBT in THF. Brunelle *et al.* reported a solubility of CBT up to the heptamer in THF.¹ When CBT is dispersed in 67% THF, part of the crystalline CBT is dissolved and thus the crystallinity is probably lost. This reduction in oligomer melting enthalpy is not observed for the CBT/THF 1.5% sample which has a melting enthalpy of 46.5 J g^{-1} equal to that of neat CBT. Although this sample was also prepared from an initial THF content of 67%, during the drying procedure up to 1.5% of the dissolved CBT may recrystallize and therefore contribute to the melting enthalpy of the oligomers.

Ring-opening polymerization

The ring-opening polymerization cannot be observed using DSC analysis, because it is athermal. The presence of THF does not seem to affect the ring-opening polymerization of CBT to pCBT, because no oligomer melting signal is detected in any second heating scan in the range 120–160 °C. As mentioned earlier, the absence of oligomer melting signals in the second heating scan suggests a complete conversion from CBT to pCBT.

Cold crystallization

The presence of THF affects the cold crystallization and, as a consequence, the subsequent crystalline melting of the polymer formed. Regarding cold crystallization, CBT/THF 1.5% shows only

about one-third of the cold crystallization enthalpy of neat CBT, whereas CBT/THF 67% shows only around one-tenth of the original enthalpy (Table 2). Cold crystallization signals can barely be seen in the DSC traces due to the scale of the thermograms. Peaks can be resolved by focusing on the zone of cold crystallization and calculating crystallization enthalpies by peak integration of the DSC traces using the software included with the equipment. Since the signals of cold crystallization are broad and not very pronounced, for the purpose of analysis more attention is paid to the polymer melting signals, because they are sharp and well defined. The incorporated THF may increase the intermolecular distance and thus the free volume, and as a result the polymeric chains would have a better mobility. But, on the other hand, the molecules cannot crystallize easily because the THF separates adjacent chains. Since ring-opening polymerization, cold crystallization and final polymer melting take place under non-isothermal conditions at relatively high heating rates, the pCBT chains do not have enough time to reach an equilibrium state to cold-crystallize. This explains the lower enthalpy of cold crystallization and melting of samples containing THF compared to neat CBT.

Polymer melting

The aforementioned decrease in cold crystallization enthalpies is reflected in a reduction of the polymer melting enthalpies of THF-modified CBT (Table 2).

Regarding neat CBT, the subsequently formed pCBT has a polymer melting enthalpy of 35.1 J g^{-1} , whereas the corresponding pCBT/THF 1.5% shows, under the same conditions, an enthalpy of 15.7 J g^{-1} . When THF is in great excess, the corresponding enthalpy is reduced to 4.2 J g^{-1} . This decrease in polymer melting enthalpies of polymerized CBT/THF 1.5% and CBT/THF 67% is directly dependent on the amount of crystalline fraction formed during cold crystallization.

DSC analysis: kinetic effects

Effects due to both the incorporated THF and the imposed heating rates were investigated by performing DSC scans with heating rates of 1 and 10 °C min⁻¹ on CBT as well as on CBT/THF 1.5%. For the low heating rate the first stage was performed from 30 to 60 °C at 10 °C min⁻¹ and then decreased to 1 °C min⁻¹ to prevent premature evaporation of the THF from the DSC pan. This sudden

change in heating rate can be seen as a sharp decrease in heat flow of around 3 mW at 60 °C (Fig. 1). A known kinetic effect inherent in DSC analysis when working with high heating rates is a shift of the characteristic peak temperatures of a given polymer towards higher values due to the increasing thermal inertia of the polymer.²⁴ This kinetic effect becomes noticeable when the peak melting temperatures of CBT *versus* CBT* and CBT/THF 1.5% *versus* CBT/THF 1.5%* are compared. For neat CBT and CBT/THF 1.5% both peak melting temperatures decrease by about 3.4 °C (Table 2). Since both samples show the same decrease, it can be fully ascribed to the DSC kinetic effects and not to THF. Another known kinetic effect in DSC analysis is that when high heating rates are used, a better visibility of small signals but less resolution is obtained.²⁴ This explains the observation that the peak heights in the thermograms of both CBT* and CBT/THF* are lower than those of CBT and CBT/THF, respectively.

In comparison to the 10 °C min⁻¹ heating rate, the 1 °C min⁻¹ rate leads to cold crystallization occurring at lower temperatures with a decrease of 28 °C for neat CBT and 26 °C for CBT/THF 1.5%. The enthalpy of CBT at low heating rate is -18.5 J g⁻¹ in contrast to an enthalpy of -36.5 J g⁻¹ measured at 10 °C min⁻¹. On the other hand, the melting enthalpy of the pCBT formed increases from 35.1 to 67 J g⁻¹ when using the low heating rate, although apparently less crystalline fraction is formed than during the previous cold crystallization. In regard to the cold crystallization enthalpy of CBT/THF 1.5% and CBT/THF 1.5%*, one finds similar behaviour. However, in contrast, the increase in cold crystallization enthalpy using the low heating rate is greater for CBT/THF 1.5% as compared to neat CBT, namely an increase from -10.5 to -33.6 J g⁻¹. Also the melting enthalpy of pCBT/THF 1.5% increases from 15.7 to 55 J g⁻¹ when using the low heating rate.

The effect of THF on the melting enthalpy of the pCBT formed is clearly evident from Table 2. When the THF content is increased to 67 wt%, the melting enthalpy shows a continuous decrease from 35.1 to 4.2 J g⁻¹. This fact matches well with the observed decrease in the corresponding cold crystallization enthalpy. The hindering effect of THF on both cold crystallization and melting enthalpy can be observed in the sample containing 67 wt% THF and tested at 10 °C min⁻¹. In this case, the degree of crystallinity decreases to an almost amorphous state, as shown in Fig. 1 and Table 2.

High heating rates hinder the cold crystallization of CBT, which is in accordance with the literature.⁴ When the ring-opening polymerization is conducted at low heating rates, there is more time for the polymer formed to crystallize, whereas at high heating rates the growing crystals do not have time to fully develop before reaching the polymer melting temperature. As a consequence, the enthalpies of both cold crystallization and melting decrease when a high heating rate is used. However, the THF also hinders the cold crystallization to a great extent, depending on the amount of THF present during cold crystallization. When using a large excess of THF and a high heating rate as in the case of CBT/THF 67%, the degree of crystallinity of the pCBT formed can be decreased to an almost amorphous state.

DSC analysis: crystallinity

The degree of crystallinity is taken as the melting enthalpy of the second heating run. Neat CBT polymerizes during the first heating scan and crystallizes during the first cooling scan, showing a crystallization temperature T_c of 176.6 °C and a crystallization enthalpy ΔH_c of -41.7 J g⁻¹. Both T_c and crystallization enthalpy increase with increasing THF content up to T_c of 181.1 °C and ΔH_c

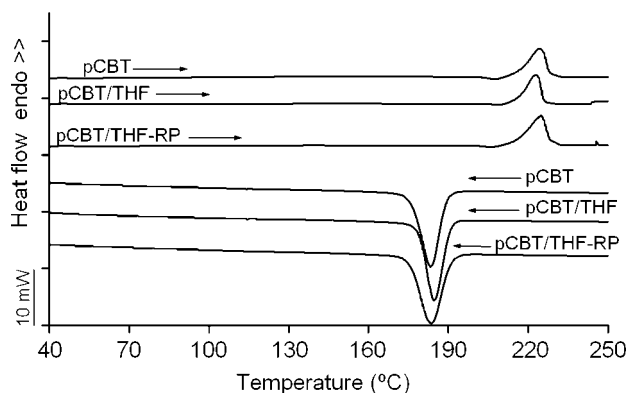


Figure 2. DSC thermograms of pCBT, pCBT/THF and pCBT/THF-RP. The traces are displaced on the y-axis for better visibility.

of -63.2 J g⁻¹ for CBT/THF 67% (Table 3). The THF apparently acts like a nucleating agent, providing heterogeneous nucleation sites for the crystallization of the pCBT as well as increased chain mobility. Moreover, polyesters are known to undergo chemical-induced crystallization.^{25–30} Therefore this increase in crystallinity is likely to be due to a solvent-induced crystallization phenomenon. The degree of crystallinity of neat CBT polymerized during DSC analysis is taken from the subsequent second heating run and is found to be 29.6%, which increases to 40.3% when 67 wt% THF is added.

DSC analysis: pCBT/THF

DSC was also performed on samples produced by compression moulding, particularly on pCBT, pCBT/THF and pCBT/THF-RP. In contrast to the *in situ* polymerization of CBT/THF systems during DSC analysis, thermograms of already polymerized pCBT/THF prepared in the hot press do not show marked differences (Fig. 2). All samples prepared by compression moulding are found to be fully polymerized since none of them show any melting peak of CBT oligomers in the range 120–160 °C. These three samples also show a single polymer melting peak at ca 224 °C of similar shape, but small differences are found in the melting enthalpy, namely 44 J g⁻¹ for pCBT/THF *versus* 52.8 J g⁻¹ for neat pCBT (Tables 2 and 3). This decrease in melting enthalpy for pCBT/THF can be ascribed to the same hindrance effects of the THF on the cold crystallization as discussed before for CBT/THF systems. As a consequence, the degree of crystallinity is slightly lower, namely 3% less than that of neat pCBT. The reprocessed sample (pCBT/THF-RP) gives almost similar results to neat pCBT, namely ΔH_m of 51.6 J g⁻¹ for CBT/THF-RP (Table 2). This may be explained by a loss of the remaining THF in terms of evaporation when the reprocessing of pCBT/THF is carried out. Therefore the degree of crystallinity of pCBT/THF-RP is virtually equal to that of neat pCBT.

GPC analysis

GPC was used to determine the number-average molecular weight (M_n), weight-average molecular weight (M_w) and dispersity (M_w/M_n) of pCBT and pCBT/THF. The results are summarized in Table 1. Neat pCBT exhibits a GPC trace with a main peak at a retention time of 6.3 min and a shoulder peak at 5.6 min (Fig. 3). This shoulder indicates the presence of two fractions of different molecular weight. The peak belonging to the remaining oligomers is seen at a retention time of 7.7 min. The degree of conversion from CBT oligomers to pCBT according to Eqn (3) is 97.9% for pCBT,

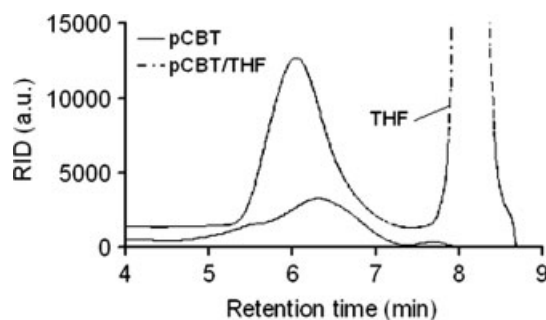


Figure 3. GPC traces of pCBT and pCBT/THF.

which is in accordance with other published results.^{1,6,9} A 100% complete conversion cannot be achieved because polyesters are known to undergo ring–chain equilibrium reactions either in the melt or in solution and oligomers are present in concentrations of about 1–3 wt%.^{1–3,29–32}

The GPC trace of THF-modified pCBT is also depicted in Fig. 3. This consists of a single peak at a retention time of 6.0 min attributed to the pCBT polymer. The results show that the presence of THF during the ring-opening polymerization leads to a higher molecular weight as compared to pCBT without THF modification. Also the molecular weight distribution is somewhat narrower compared to that of neat pCBT. Interestingly, pCBT/THF does not exhibit any peak in the GPC trace attributed to oligomers. The remaining CBT oligomers after polymerization may be dissolved in THF and thus may be removed from the bulk material by solvent extraction. Cyclic oligomers in polyesters affect processing as well as material properties,^{29–32} and therefore efforts are made to remove them from the bulk polymer by various methods. Vermeylen *et al.*³⁰ prepared a cyclic-oligomer-free poly(ethylene terephthalate) (PET) by solvent extraction in a Kumagawa extractor using 1,4-dioxane as the boiling solvent. Also Shukla and Kulkarni³¹ extracted cyclic oligomers from PET using extraction and dissolution methods. Although the oligomer peak in the GPC trace is not present, a prominent peak with a corresponding molecular weight of 73.4 g mol^{-1} is detected, obviously belonging to THF (72.11 g mol^{-1}) and thus demonstrating its presence in the polymer after compression moulding. This peak is one order of magnitude greater in intensity than that corresponding to the polymer and therefore is only partially shown in Fig. 3. It should be pointed out that the molecular weight of all analysed samples is still below the theoretical critical molecular weight for entanglements $M_{w,c}$ of $50\,000 \text{ g mol}^{-1}$.^{2,3}

Higher molecular weight pCBT has been reported by other researchers.^{1–3,5,7–10} A possible reason might be the influence of the environment, where in those other works the ring-opening polymerization was conducted in a well-controlled reaction vessel under nitrogen atmosphere. In the present case, the pCBT was prepared in ambient atmosphere in a more industrial-like process. It is known that humidity inherent in ambient atmosphere partially inhibits catalytic action, leading to an incomplete ring-opening polymerization and hence to pCBT of lower molecular weight.¹¹

Thermogravimetric analysis

The effect of THF on the thermal stability and onset temperature of degradation was investigated using TGA. Mass losses of neat pCBT and pCBT/THF normalized over the initial masses are shown in Fig. 4. TGA plots of both pCBT and pCBT/THF consist of one major decomposition step with maximum decomposition temperatures

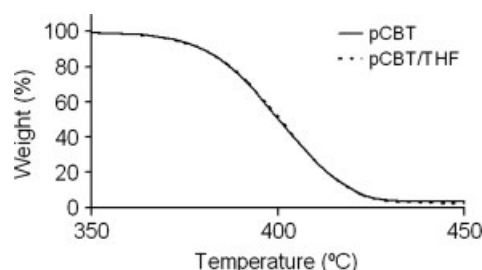


Figure 4. TGA thermograms of pCBT and pCBT/THF, recorded from 20 to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$. For the sake of clarity only the interval between 350 and 450°C is shown.

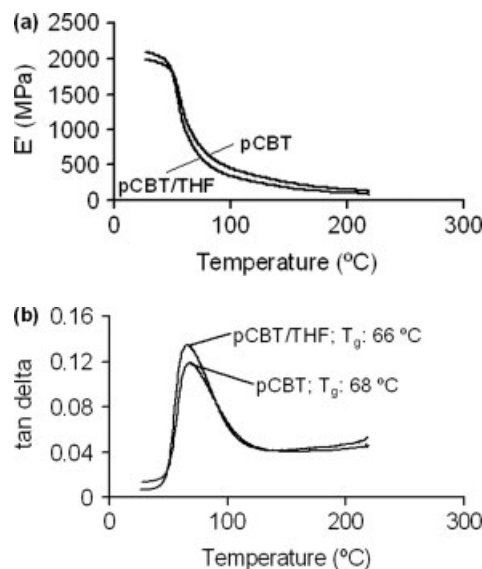


Figure 5. DMTA plots of (a) E' and (b) $\tan \delta$ versus temperature for pCBT and pCBT/THF.

T_{\max} at 406 and 403°C , respectively. The onset of degradation is evaluated from the temperature corresponding to a weight loss of 5% and is found to be 372 and 369°C for pCBT and pCBT/THF, respectively. These results suggest that there is no significant influence of THF on the thermal stability of pCBT. The amount of residue at 600°C is found to be 2.2 and 0.9% for pCBT and pCBT/THF, respectively. The onset temperatures of degradation and amounts of residue are consistent with published values for PBT³³ and pCBT.³⁴ The difference of both residual amounts is very small and is attributed to the inherent experimental error. THF is an organic volatile solvent with a comparably low boiling point and therefore does not contribute to the amount of residues.

Dynamic mechanical thermal analysis

DMTA was employed to study the viscoelastic properties of pCBT and pCBT/THF. THF is found to be present in pCBT/THF after processing, as confirmed from GC-MS and GPC and no evidence for copolymer formation, as suggested by DSC. These results lead to the assumption that the THF may separate adjacent chains and thus increase the free volume of the polymer. This increase in free volume leads to a greater mobility of the amorphous polymer chain segments. The gain in mobility of the amorphous phase is responsible for a greater ductility of the polymer. The dynamic mechanical properties are depicted in Fig. 5. The THF-toughened

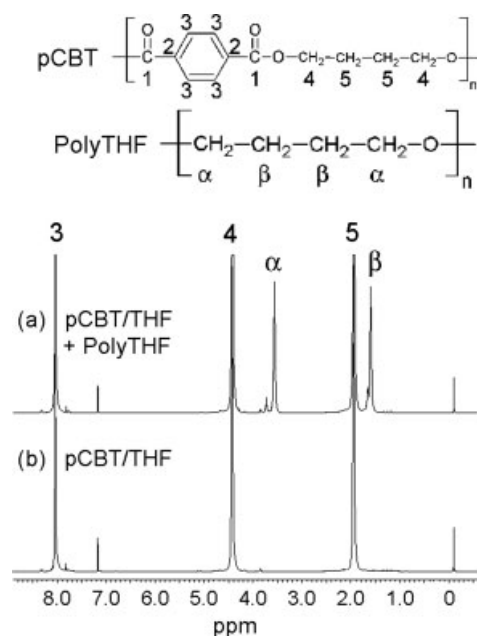


Figure 6. ^1H NMR spectra of (a) a mix of equal amounts of pCBT/THF and polyTHF and (b) pCBT/THF.

sample shows a 5% higher initial storage modulus than neat pCBT, but this decreases more markedly than in pCBT throughout the temperature range. At 50°C both samples reach an equal value of 1.8 GPa (Fig. 5(a)). T_g is considered to be the temperature corresponding to the peak maximum of the dynamical loss factor curve. T_g of neat pCBT is found to be 68°C , whereas that of pCBT/THF is determined at 66°C (Fig. 5(b)). This decrease in T_g for the THF-modified sample can hardly be attributed to a conventional plasticizing effect induced by the THF, because the decrease in T_g is only 2°C . Also the small amount of 1.5 wt% THF added to the matrix is much less compared to conventional plasticizing agent contents. However, the $\tan \delta$ peak height as well as the area under the $\tan \delta$ curve are larger for pCBT/THF than for neat pCBT, indicating greater chain mobility in the THF-toughened sample.

^1H NMR spectroscopy

The ^1H NMR spectrum of pCBT/THF is depicted in Fig. 6(b). Additionally, the ^1H NMR spectrum of polyTHF (molecular weight of 1000 g mol^{-1}) is shown in Fig. 6(a) in order to ascertain if copolymerization between pCBT and THF takes place during processing. Protons in pCBT are labelled 1 to 5 whereas protons of polyTHF are labelled α and β .

For the pCBT/THF system (Fig. 6(b)) the peak at 8.14 ppm is assigned to the aromatic protons (C3). The peak at 4.52 ppm is assigned to oxymethylene protons attached to the ester group. The peak at 2.04 ppm is assigned to the shielded methylene protons (C5).^{7,8,17}

Figure 6(a) shows the ^1H NMR spectrum of a blend of pCBT/THF and polyTHF. In addition to the pCBT/THF peaks mentioned above, this spectrum shows the characteristic peaks of polyTHF. The peak located at 3.66 ppm is assigned to the ($\text{C}\alpha$) methylene protons attached to oxygen, and the peak located at 1.70 ppm belongs to the shielded methylene protons ($\text{C}\beta$).³⁵ When comparing Figs 6(a) and (b), it is evident that no peaks belonging to polyTHF can be

Table 4. Tensile properties

| Sample | Tensile modulus, E (GPa) | Tensile strength, σ (MPa) | Elongation at break, $\varepsilon_{\text{break}}$ (%) |
|----------|----------------------------|----------------------------------|---|
| pCBT | 2.7 ± 0.3 | 56 ± 8 | 6.7 ± 2.9 |
| pCBT/THF | 2.4 ± 0.2 | 52 ± 5 | 227 ± 80 |

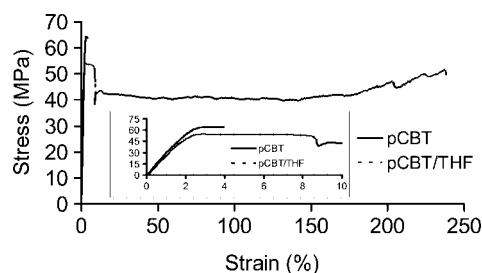


Figure 7. Stress–strain curves for pCBT and pCBT/THF.

detected in the spectrum of pCBT/THF (Fig. 6(b)). This indicates that no copolymer is formed between pCBT and THF.

Mechanical properties

The mechanical properties obtained from tensile tests are summarized in Table 4. The tensile behaviour (Fig. 7) of neat pCBT is of a brittle nature with very low strain at break (*ca* 7%), as confirmed by other researchers.^{2,3,8,9,16,17,36} In contrast, when a small amount of THF is incorporated in the pCBT matrix, a dramatic change from brittle to ductile behaviour can be observed. The mechanical properties of pCBT/THF are typical for a ductile material, having a yield point, neck formation and cold drawing over a large strain range with subsequent strain hardening until fracture. The strain at break is found to increase markedly from 7 to well above 100% with an average value of 227%. It should be pointed out that all pCBT/THF samples tested show the start of necking, but in some cases the neck collapses prematurely due to neck instabilities. Tensile properties of pCBT/THF, namely Young's modulus and tensile strength, are somewhat poorer compared to those of neat pCBT.

In our opinion, the increase in toughness is caused by several factors. On the one hand, the increased molecular weight and the narrower molecular weight distribution account for better mechanical properties. On the other hand, the absence of oligomers in pCBT/THF after polymerization may also contribute to the improved ductility, since cyclic oligomers in polyesters can negatively affect mechanical properties.^{29–32} Moreover, we believe that the THF absorbed by the CBT improves the dispersion and the reactivity of the catalyst during ring-opening polymerization. In addition, as THF is still present in the matrix after polymerization, it may provide greater ease of chain mobility.

Ageing

A set of tensile test specimens were subjected to thermal ageing at 80°C in a desiccator in order to study the migration of THF out of the pCBT. The tensile behaviour of the specimens was then analysed as a function of time. The mechanical properties *versus* annealing time are shown in Fig. 8. Due to the volatile nature and low boiling point of THF (66°C), a rapid migration was expected

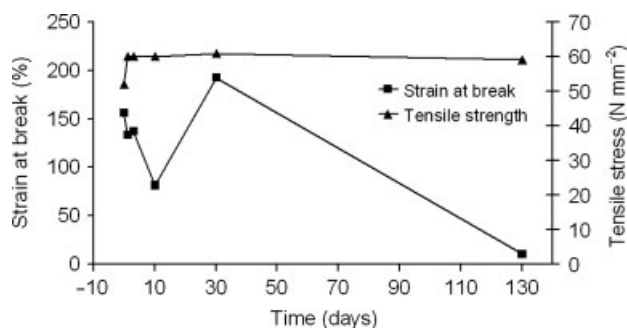


Figure 8. Mechanical properties of pCBT/THF after thermal ageing at 80 °C as a function of annealing time.

when subjected to annealing at 80 °C. Therefore most of the samples were tested during the first few days. The last sample was finally tested after 130 days. Tensile modulus and tensile strength remain relatively unaltered, whereas the strain at break is maintained well above 50% during the first 30 days and finally decreases to ca 10% after 130 days. The lack of data between 30 and 130 days does not allow a determination of the exact time at which the behaviour changes from ductile to brittle. Nevertheless the final sample shows a 1.5-fold ultimate strain compared to neat pCBT, even though the pCBT/THF sample fractures in a brittle manner when tested after 130 days.

It is clear that the THF is attached to the pCBT molecules, because otherwise the brittle behaviour would happen already in an early stage of the ageing procedure. As mentioned earlier, the THF may be attached to the polymer by van der Waals forces, preventing an early migration of the THF.

CONCLUSIONS

THF was used to toughen *in situ* polymerized CBT. It was shown from GPC and GC-MS that the THF is incorporated in the pCBT after processing. The addition of ca 1.5 wt% THF to neat CBT prior to its ring-opening polymerization led to an increase in molecular weight and also a narrower molecular weight distribution. Moreover, no remaining oligomers after polymerization were found. We believe that the THF absorbed by the CBT improves the action as well as the dispersion of the catalyst during ring-opening polymerization. Additionally, as THF is still present in the matrix after polymerization, it may provide greater chain mobility. DSC analysis revealed a hindered cold crystallization when the CBT/THF systems are polymerized *in situ* during a DSC scan. Most importantly, the incorporated THF leads to a complete elimination of the brittleness inherent in pCBT and to a strain at break well above 100% in a tensile test.

Other important properties such as tensile strength, tensile modulus and glass transition temperature were not significantly affected, in contrast to the case where other common methods are used to toughen polymers. The THF was found to migrate out of the polymer matrix, but pCBT/THF remains ductile at 80 °C for at least 30 days.

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