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Toughening of *in situ* polymerized cyclic butylene terephthalate by chain extension with a bifunctional epoxy resin

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ABSTRACT

Cyclic butylene terephthalate (CBT) was polymerized in the presence of a low molecular weight bifunctional epoxy resin. The resultant chain extended polymerized CBT (pCBT) showed an increased ductility compared to that of conventionally polymerized pCBT for all analyzed epoxy concentrations (1–4 wt.%). The best results were obtained with 2 wt.% of epoxy resin. Other mechanical properties remained relatively unaffected by the epoxy resin. ^{1}H NMR analysis suggested an esterification reaction of the carboxyl end groups of pCBT and the glycidyl functional groups of the diepoxide. With increasing epoxy content, the chain extended pCBT showed an increasing molecular weight and a decreasing glass transition. Crystallization and melting temperatures as well as crystallinity also decreased with increasing epoxy concentration.

1. Introduction

Cyclic butylene terephthalate oligomers (CBT®) are an interesting alternative to thermosetting resins for composites. The resulting polymerized cyclic butylene terephthalate (referred to as pCBT to distinguish from conventional poly(butylene terephthalate) (PBT) obtained by polycondensation reaction) can be recycled due to its thermoplastic nature. Unlike conventional thermoplastic resins, cyclic oligomers have an initial water-like melt viscosity prior to polymerization and thus can be employed in processes, such as resin transfer moulding (RTM), which are typically used for thermosets. Cyclic oligomers polymerize quickly in an athermal, entropically driven ring-opening polymerization (ROP) into linear pCBT without releasing volatile organic compounds [1–7].

However, in contrast to conventional PBT, pCBT is brittle. This is due to a high crystallinity and the formation of large perfect crystals with a lack of intercrystalline tie molecules [4,6,8]. Processing CBT below the melting temperature (T_m) of the final polymer may be advantageous because polymerization and crystallization take place simultaneously below 200 °C. This allows isothermal processing below T_m and avoids thermal cycling of the mould. Nevertheless, working at low temperatures may cause a decrease in the polymerization rate, leading to a low molecular weight [6,7]. Between 200 and 225 °C, crystallization is subsequently followed by polymerization. When the ROP is conducted above the melting temperature, only polymerization takes place [4,5]. It was also pointed out in literature that water (coming from humidity) inhibits the catalyst action which also leads to a low molecular weight pCBT [5,8]. Hydrolysis reactions between pCBT and water can also occur, resulting in a molecular weight decrease and brittleness of the material.

Although a high molecular weight is obtained when the ROP is conducted under inert atmosphere, the resulting pCBT is still brittle [4,6,11]. Therefore ongoing research is focussed on the toughening of pCBT. There are many common methods to increase the toughness of polymers and most of them have been applied to pCBT. One method is to decrease

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the degree of crystallinity and thus introducing more tie molecules between crystals which can be achieved by changing the processing conditions, namely by applying a fast cooling after polymerization. Baets and coworkers [8] compared slow cooling to quench cooling in a non-isothermal production process of basalt fiber-reinforced pCBT composites. They found an increased toughness for the quench cooled composites. Another method of toughening polymers is to increase the chain mobility by adding a plasticizer. We previously reported a toughened pCBT by the addition of tetrahydrofuran (THF) prior to polymerization. The resulting pCBT/THF showed a strain at break of well above 100% in tensile tests [9]. Nevertheless, the use of solvents is not environmentally friendly. Another strategy to reduce the brittleness of a polymer is to form copolymers with soft segments. Tripathy and coworkers used this approach and synthesized copolymers of CBT and ε-caprolactone [10]. In a similar way, Baets et al. copolymerized CBT with poly(caprolactone) [11]. Both copolymers gained elongation at break while sacrificing stiffness and strength. Reactive chain extension with low molecular weight bi- or polyfunctional compounds is a common method utilized to improve the properties of polyesters such as toughness, melt viscosity and hydrolytic stability. These multifunctional compounds readily react with the carboxyl and/or hydroxyl terminal groups of polyesters. These so-called chain extenders are preferably bifunctional and should react easily through an addition reaction without the generation of any by-products. For instance, reactive chain extension is widely used in the recycling of poly(ethylene terephthalate) (PET) to compensate for MW loss during melt degradation. Chain extended recycled PET has a higher molecular weight which improves the rheological properties for processes requiring a high viscosity such as low density extrusion foaming or extrusion blow moulding [12–14,20]. Similarly, chain extenders are employed to improve toughness, impact strength and hydrolytic stability of PBT [14,15]. They can also be used as coupling agents or compatibilizers for immiscible polymer blends, such as PET-polystyrene [16], PBT-acrylonitrile–butadiene-styrene [17] or PBT-poly(ethylene octene) copolymer blends [18]. Among the various chain extenders, an effective group proved to be diepoxides. The chain-extension reaction between polyesters such as PET or PBT and epoxides was extensively studied and is well established [12–14,16,17]. Tripathy et al. [19] synthesized a series of copolyesters of CBT and bisphenol A diglycidyl ether (BPADGE) with ratios of CBT/BPADGE from 75/25 to 40/60. Their aim was to improve the flame retardant properties (mechanical properties of the obtained copolyesters were not reported).

In this work a commercial epoxy resin was used in small amounts (1–4 wt.%) as a chain extender during *in situ* polymerization of CBT in order to increase the toughness of the resulting pCBT.

2. Experimental section

2.1. Materials

Cyclic butylene terephthalate oligomers were termed as one-component CBT 160® and contained butyl tin chloride dihydroxide as a catalyst. It was provided as granules by Cyclics Europe GmbH (Schwarzheide, Germany). The CBT was ground into a fine powder in a mortar.

A commercial epoxy resin, Eporai 450/A was purchased from IQRaisa, S.L. (Valencia, Spain) and was used as received. The epoxy resin, referred to as EP, was a low-viscous, bifunctional type characterized by an epoxy equivalent weight (EEW) of 148–155 g/eq.

2.2. Sample preparation

A mortar and pestle were used to create homogenous blends of the previously dried CBT powder and the corresponding amount of epoxy resin (1, 2, 3 and 4 wt.%). The resultant CBT/epoxy blends (referred to as CBT/EP) and neat CBT powder were vacuum-dried for 8 h at 80 °C and kept in a desiccator until further use. Approximately 15 g of the CBT/EP blends were *in situ* polymerized between two PTFE films in a IQAP LAP PL-15 hot plate press at 250 °C in ambient atmosphere. A polymerization time of 20 min was chosen for the compression moulding process in order to assure a complete chain extension reaction. The blends were then rapidly cooled to room temperature in the cold stage of the press. The resulting pCBT/epoxy films (referred to as pCBT/EP) had dimensions of ca. $150 \times 150 \times 0.5\ \text{mm}^3$ and were used to extract samples for further characterization.

2.3. Characterization

2.3.1. Gel permeation chromatography (GPC)

GPC was performed on a Agilent Technologies 1200 Series modular system (Agilent Technologies, Santa Clara, USA) which was comprised of an Agilent 1200 refractor index detector operated at a temperature of 35 °C. A linear Styragel HR5E column (Waters, Milford, MA) with a separation range from 10^3 to 5×10^6 g/mol was used with 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, Fluka Analytical) stabilized with 6.8 g/L sodium fluoroacetate to prevent polyelectrolyte effect. A flow rate of 0.5 ml/min was employed. The pressure of the column was 60 bars, and the sample weight was 1 mg. Low dispersed polystyrene (PS) samples were used as internal standards. The degree of conversion α (%) from CBT to pCBT polymer was calculated using Eq. (1).

$$\alpha = 1 - \frac{A_{\text{oligomer}}}{A_{\text{total}}}, \tag{1}$$

where A_{oligomer} is the area under the oligomer peak of the GPC trace and A_{total} the total area under the GPC trace. Note that Eq. (1) refers exclusively to the soluble fraction of the samples; the insoluble part is not considered here since it has been removed by filtration. The gel content was determined by dissolving around 50 mg of sample in 5 ml of a mixture of $CHCl_3$/TFA (10/1) with agitation for 30 min. The solution was subsequently centrifuged and the soluble part was removed. The insoluble part was washed with 5 ml of the same solvent mixture two additional times and finally with $CHCl_3$. The insoluble part was dried in an oven at 80 °C for 12 h and then weighted.

2.3.2. Nuclear magnetic resonance spectroscopy (NMR)

The structural characterization of the epoxy-modified pCBT samples was performed using ^{1}H NMR spectroscopy. Spectra were collected on a Bruker AMX-300 spectrometer operated at 300.1 MHz at 363.1 K. Sample concentrations were 1% (w/v) and a 1,1,2,2-tetrachloroethane-d_2 solvent was used. A total of 640 scans with 32 k data points were recorded with a relaxation delay of 2 s.

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was carried out on a Perkin Elmer Pyris 1 device under nitrogen atmosphere. Samples prepared by *in situ* ring opening polymerization in the hot plate press were analyzed by DSC and compared to equally processed, neat pCBT. Samples were heated from 30 to 270 °C at a heating rate of 10 °C/min, followed by an isothermal step of 3 min and then cooled from 270 to 30 °C at a rate of 30 °C/min. The sum of both melting enthalpies ΔH_{m1+2} of the second heating run was used to calculate the degree of crystallinity X_C of the samples according to Eq. (2).

$$X_C = \frac{\Delta H_m}{\Delta H_m^0} 100[\%] \tag{2}$$

The melting enthalpy (ΔH_m^0) of fully perfect crystalline PBT is found in literature to be 142 J/g [4].

2.3.4. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis was used to study the dynamic mechanical properties of neat pCBT and chain-extended pCBT, namely the complex dynamic modulus E*, the storage modulus E′, the loss modulus E″ and the dynamical loss factor tan δ (defined as E″/E′). A Q800 TA Instruments DMA was used in tensile mode at a frequency of 1 Hz and a strain of 0.05% for all samples. The temperature range was set from −150 to 220 °C at a heating rate of 2 °C/min. Samples were prepared from pCBT/EP films and had dimensions of 27 × 5 × 0.5 mm^3.

2.3.5. Mechanical properties

Tensile tests according to ISO 527 were performed at room temperature and at a crosshead speed of 10 mm/min on a Galdabini Sun 2500 (Galdabini, Italy) tensile testing machine. A video extensometer was used to measure strain. Type 1BA specimens were extracted from the above described pCBT/EP films. A minimum of five specimens were tested for each reported value.

2.3.6. Scanning electron microscope (SEM)

Scanning electron microscopy was employed to study the morphology of the epoxy-modified pCBT. Therefore, the above described pCBT/EP films were cryo-fractured, and the resulting fracture surfaces were then sputter coated with a thin gold layer using a Bal-Tec SCD005 Sputter Coater. SEM analysis was performed on a Jeol JSM-5610 scanning electron microscope operated at 10 kV acceleration voltage.

3. Results and discussion

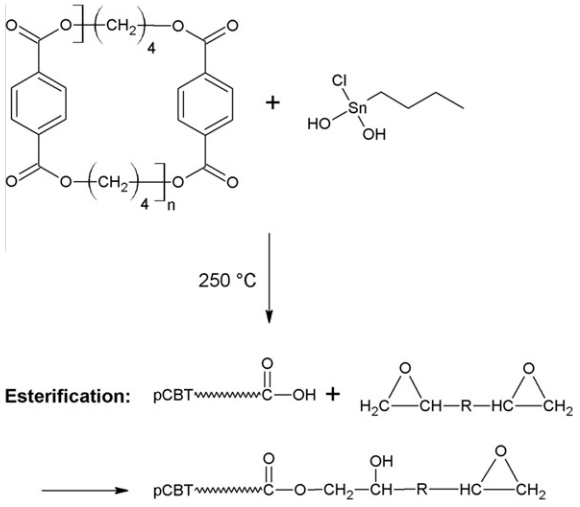
The chain extension reaction between (growing) pCBT chains and epoxy resin is carried out by esterification of the carboxyl end groups of the polyester and glycidyl functional groups of the epoxy resin (Scheme 1).

The epoxy groups react predominantly with the carboxyl groups due to the strong polarization of the hydroxyl bond of carboxylic acids, but are also known to react with the less nucleophilic hydroxyl groups. Secondary hydroxyl groups arise from these chain extending reactions. These hydroxyl groups can further react with the epoxy functional groups, which leads to branching or even crosslinking, as depicted in Scheme 2 [12–17].

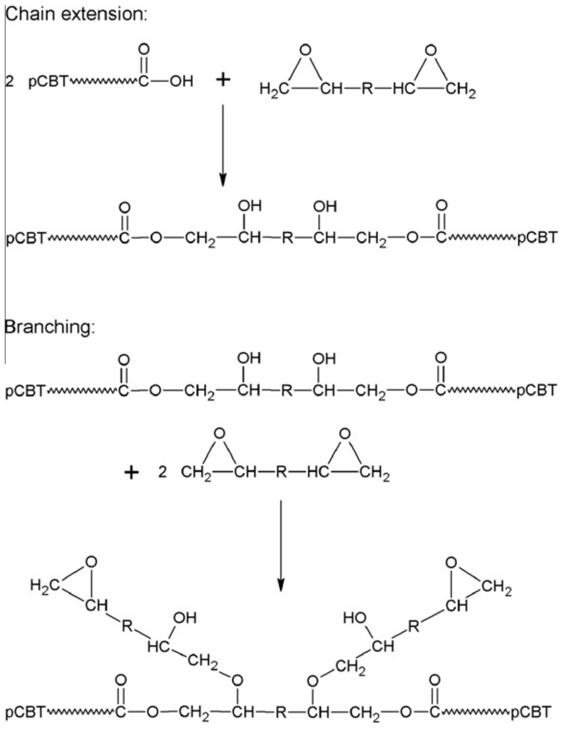
High molecular weights can be obtained with very small amounts of diepoxide because two or more pCBT chains of relatively high molecular weight are linked together with bifunctional, low molecular weight epoxy molecules. One mole of the chain extender reacts with two moles of polymer in order to obtain linear extended chains and prevent excessive branching and crosslinking. Therefore the theoretical amount of chain extender for the reaction can be calculated from [12–14]:

$$\text{wt.\%}_{EP} = \frac{(MW \cdot CC_0)}{2 \cdot 10^4}, \tag{3}$$

where wt.$\%_{EP}$ is the theoretical amount of chain extender to obtain linear chain extension, MW is the molecular weight of the chain extender and CC_o is the carboxyl content of the initial pCBT in equiv/10^6 g. Unlike conventional polyesters with a given carboxyl content, CBT does not exhibit a constant carboxyl content during the ring-opening polymerization until the conversion into pCBT is complete. Since the ROP of CBT starts in the presence of the chain extender, the epoxy may already react during the ring-opening polymerization with the growing pCBT chains.



Scheme 1. Esterification reaction of pCBT and diepoxide.



Scheme 2. Chain extension and branching mechanism of pCBT and diepoxide.

3.1. GPC

Neat pCBT as well as chain-extended pCBT/EP samples produced by *in situ* polymerization in the hot plate press were analyzed by GPC, results are shown in Table 1. The chain-extended pCBT/EP samples may be partly cross-linked, especially at higher EP contents. No insoluble fraction was detected for samples with 0%, 1% and 2% epoxy content. However, samples pCBT/EP 3% and pCBT/EP 4% contained 37% and 63% of insoluble fraction, respectively (c.f. Table 1).

The molecular weight determined by GPC provides an acceptable estimation of the molecular weight increase of pCBT/EP samples. Nevertheless, analysis of branched polymers using a calibration based on linear polymer standards may result in errors. This is due to the fact that the separation is based on the hydrodynamic volume of a polymer. Since linear and branched polymers of equal molecular weight occupy different hydrodynamic volumes, their measured molecular weight will be different and thus the obtained molecular weights of the chain-extended samples may be lower than the true values [20].

Neat pCBT polymerized in the hot plate press exhibited a remarkably low molecular weight. The reason therefore may be a reduced polymerization due to humidity in ambient atmosphere. The polydispersity index (PDI) of pCBT is close to the theoretical PDI of 2.0, typical for ring-opening polymerizations [3,7]. The MW of pCBT/EP 1% was found to be only slightly higher compared to the one of neat pCBT. However, the molecular weight distribution broadened considerably. This confirms the low degree of chain extension reaction. A dramatic increase in both molecular weight and distribution was found for pCBT/EP 2%. The weight-average molecular weight (M_w) and the PDI were three times higher compared to that of pCBT (see Table 1). Regarding pCBT/EP 3%, both PDI and molecular weight further increased to values which were ca. five times higher compared to neat pCBT. When the epoxy content was 4 wt.%, the MW decreased to a value much lower than the samples containing 2 and 3 wt.% EP, but still higher than neat pCBT. Also, the PDI slightly decreased with respect to pCBT/EP 3%. The number-average molecular weight (M_n) decreased for the pCBT/EP samples. As M_n is inversely proportional to the number of end groups, this decrease can be explained by the chain extension reaction of pCBT end groups with epoxy groups. The chain extension reaction leads to stop growing of a few chains, leading to a decrease of the number average molecular mass and a strong increase of PDI. The degree of conversion (α) from oligomers to polymer was calculated from the peak areas of the GPC traces according to Eq. (1). Neat pCBT shows a conversion of 96.6% which is in agreement with reported values and also with the equilibrium oligomer content of PBT, 1–3% [3,4]. No oligomers were detected in the GPC trace of pCBT/EP 1%, which suggests a full conversion to pCBT. Higher EP contents slightly decreased the degree of conversion (c.f. Table 1). These results clearly demonstrate that the diepoxide is an effective chain extender for CBT with an apparent maximum molecular weight up to 100 kg/mol when 3 wt.% diepoxide is used.

3.2. NMR

^{1}H NMR analysis was conducted to analyze the structure of the diepoxide, pCBT as well as of chain extended pCBT/EP prepared by compression moulding. The chemical structures and the corresponding spectra are depicted in Fig. 1. Protons in the pCBT sequence are labeled with numbers. Protons belonging to the diepoxide sequence are labeled with letters.

Regarding pCBT, the signal at 1.9 ppm is assigned to shielded methylene protons (2), the one at 4.4 ppm is assigned to oxymethylene protons (1) and the peak at

Table 1
GPG results of compression moulded pCBT and pCBT/EP samples.

Sample	M_w (kg/mol)	M_n (kg/mol)	PDI (–)	Gel content (%)	Conversion α (%)
pCBT	22.0	10.0	2.26	0	96.6
pCBT/EP 1%	23.7	6.5	3.65	0	100
pCBT/EP 2%	65.0	9.4	6.96	0	92.0
pCBT/EP 3%	104.0	8.5	12.15	37	95.5
pCBT/EP 4%	32.0	3.3	9.78	63	95.4

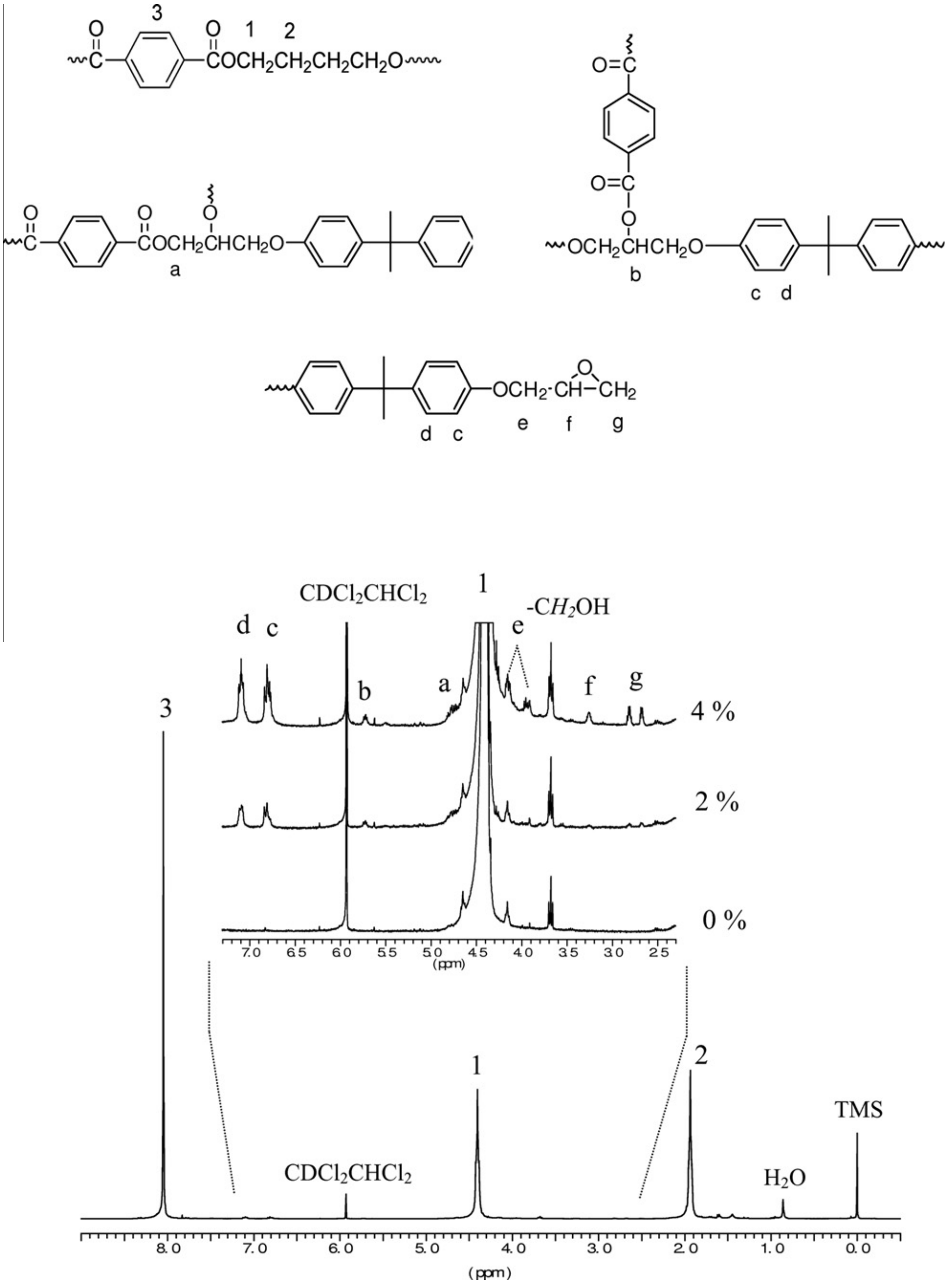


Fig. 1. ^{1}H NMR spectrum of pCBT/EP 2%. Inset ^{1}H NMR spectra of pCBT and pCBT/EP samples in the 2.3–7.3 ppm region with peak assignments.

8.0 ppm is assigned to the aromatic protons (3) [19]. Peaks belonging to the diepoxide are assigned as follows: aromatic protons of the Bisphenol A moieties (c and d) show peaks at 6.8 and 7.1 ppm, respectively. Peaks at 3.9 and 4.2 ppm are assigned to methylene protons attached to oxygen (e) whereas the peak at 3.3 ppm and the doublet at 2.9 and 2.7 ppm are assigned to the glydidyl functional group (f and g).

The peaks around 4.7–4.8 ppm came from an esterification of the glydidyl functional groups with the carboxyl end groups of pCBT (a), resulting in ester groups (R_1–CO–O–R_2). Unfortunately, the corresponding signal of the formed ester group partially overlaps with the peak of –OCH_2 of pCBT. Nevertheless, one may conclude that the esterification is the predominant reaction mechanism. Peaks at 5.7 ppm suggest a connectivity of CH with an ester group (b). This leads to the assumption that some of carboxyl end groups of pCBT are linked (*via* direct esterification) to the secondary hydroxyl groups previously formed during chain extension. The proposed connectivity can be seen as a branch point in the backbone of a chain extended pCBT molecule. Recall that some gel formation was detected in pCBT/EP samples containing more than 2 wt.% of EP, supporting this branching hypothesis.

The presence of glycidyl functional groups in both pCBT/EP 2% and pCBT/EP 4% indicate that not all the epoxy groups have reacted with the pCBT and unreacted diepoxide was dissolved in the pCBT matrix. Note that the corresponding signals of unreacted epoxy resin in the sample containing 2 wt.% EP are weak. The amount of unreacted epoxy groups was calculated to be 17.5 and 32.5 mol% for pCBT/EP 2% and pCBT/EP 4%, respectively. The calculation of the theoretical amount of chain extender according to Eq. (3) is not applicable due to the varying carboxyl group content during ROP, as mentioned above. A chain extension mechanism utilizing 2 mol pCBT of 22,000 g/mol (as polymerized in the hot plate press, measured by GPC) and 1 mol epoxy resin of 361 g/mol (determined by NMR) results in a theoretical amount of 0.8 wt.% epoxy resin, assuming that only carboxyl and glycidyl groups are involved in the reaction.

3.3. Differential scanning calorimetry (DSC)

The compression moulded samples were analyzed in a DSC scan following the heating and cooling rates described in Section 2.3.3. The second heating and cooling runs are depicted in Fig. 2a and b, respectively. The thermal properties are collected in Table 2. Neat pCBT exhibits a double melting peak which consists of a small peak at 213 °C and a major peak at 225 °C. Multiple melting peaks are typical for polyesters, including pCBT. They are attributed to melting and recrystallization processes of less perfect crystallites into thicker crystalline structures with a subsequent melting at the polymer's melting temperature [22–24]. The neat pCBT crystallises during cooling at 184 °C and the crystallinity obtained from the second cooling scan was found to be 32%.

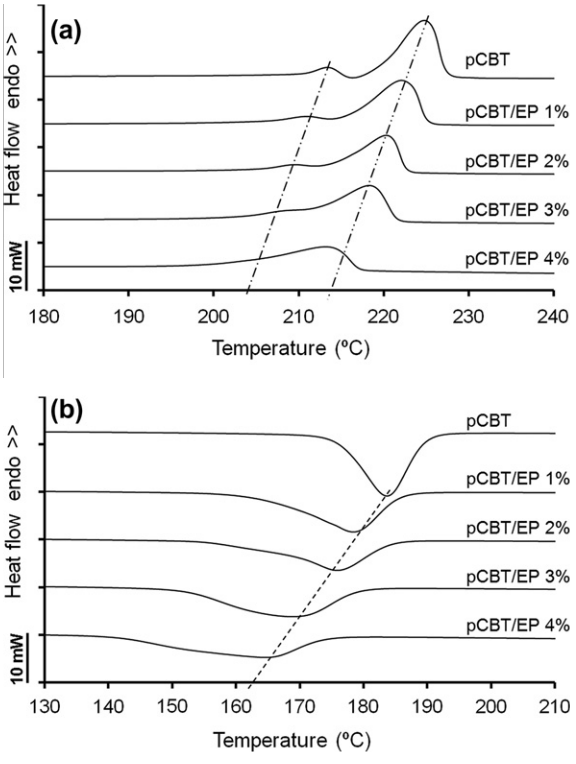


Fig. 2. (a) DSC second heating and (b) second cooling scan of pCBT and pCBT/EP samples polymerized in the hot plate press, DSC heating rate of 10 °C/min and cooling rate of 30 °C/min.

As far as chain-extended pCBT is concerned, it can be observed that the melting endotherms as well as the crystallization exotherms progressively shift towards lower temperatures and increasingly broaden with increasing epoxy content (Fig. 2a and b). The broadening of the melting peaks suggests a broadening of the crystallite size distribution. The depression of the melting temperature is due to the chain extension reaction. With increasing epoxy content, branching and crosslinking takes place. Side branches are thought to be defects which disrupt the local chain symmetry and disturb the crystalline structure. As a consequence, crystallization rates are decreased which results in a decreased degree of crystallinity [29]. Moreover, the lamellar thickness is reduced, which in turn causes a decrease in melting and crystallization temperatures [15,20–22]. At a high epoxy content of 4 wt.%, the two melting endotherms merge together and only one broad melting peak can be observed. This is explained by the hindered recrystallization process of less perfect crystallites below the final polymer melting temperature.

3.4. DMTA

The dynamic mechanical properties of the pCBT/EP samples obtained from compression moulding were determined with DMTA. For clarity only neat pCBT and chain extended pCBT containing 2 and 3 wt.% are shown (Fig. 3). The β and γ transition temperatures and the storage moduli at 0 °C are collected in Table 3.

Three different relaxations can be seen in neat pCBT. The melting transition of pCBT homopolymer is ~225 °C, commonly referred to as the α transition. The glass transition (T_g) of the amorphous phase is termed β relaxation and the sub-T_g relaxation is denoted as γ [25]. It was suggested that the γ relaxation of pCBT may be a secondary relaxation due to the motion of the –O–$(CH_2)_4$–O– group, the glycol (OH) residue in the amorphous phase or the carbonyl (COO) residue [23]. The T_g of neat pCBT was found to be 66 °C which is an intermediate value between the glass transitions reported in [10] and [23]. The sub-T_g relaxation was found to be −83 °C, considerably higher than the one reported by Liu et al. [23].

Regarding the chain extended pCBT, a single glass transition can be observed, indicating the miscibility of pCBT and EP, which corresponds to the miscibility of PBT and epoxy resin [26,27]. It can be seen that the β-relaxation temperature (T_g) decreased with increasing epoxy content (c.f. Table 3). It is known that the glass transition temperature of pCBT and PBT increases with increasing crystallinity [10,25]. Since the degree of crystallinity of pCBT/EP decreased with increasing EP content, the β-relaxation temperature decreased as well. Kulshreshtha and co-workers [26] and Zhang et al. [27] found in PBT/epoxy blends with high epoxy contents, the epoxy did not react completely with PBT; the excess acted as a solvent. Therefore, the decrease in the β-relaxation temperature of the pCBT/EP samples is

Table 2
Thermal properties of compression moulded pCBT and pCBT/EP samples, DSC heating rate of 10 °C/min and cooling rate of 30 °C/min.

Sample	Second heating			Second cooling		Crystallinity
	T_{m1} (°C)	T_{m2} (°C)	ΔH_{m1+2} (J/g)	T_c (°C)	ΔH_c (J/g)	X_C (%)
pCBT	213.4	224.8	45.2	183.9	−48.8	31.8
pCBT/EP 1%	210.8	222.1	36.7	178.6	−40.8	25.8
pCBT/EP 2%	209.3	220.2	34.3	176	−38	24.2
pCBT/EP 3%	207.9	218.4	35.5	168.6	−37.4	25.0
pCBT/EP 4%	–	213.2	29.8	164.5	−36.4	21.0

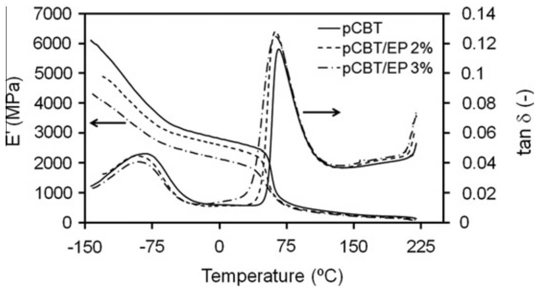


Fig. 3. DMTA plot of E′ and tan δ versus temperature of compression-moulded pCBT and pCBT/EP samples.

Table 3
DMTA storage moduli at 0 °C, γ and β transition temperatures of compression moulded pCBT and pCBT/EP samples, heating rate of 2 °C/min.

Sample	Storage modulus at 0 °C (MPa)	γ-Transition (°C)	β-Transition (°C)
pCBT	2810	−82.9	65.7
pCBT/EP 1%	2072	−88.4	67.9
pCBT/EP 2%	2591	−94.2	62.3
pCBT/EP 3%	2142	−92.9	62.6
pCBT/EP 4%	2209	−86.6	60.3

partly attributed to a plasticizing effect of the dissolved excess of epoxy resin which had not reacted with pCBT, as confirmed by ^{1}H NMR analysis. Nevertheless, the amount of unreacted epoxy resin is low, so the expected plasticizing effect is believed to be negligible. Finally, the influence of branching on the β- and γ-relaxation of the pCBT/EP systems should be taken into account since gel content determination on the pCBT/EP samples indicated an increasing gel formation with increasing EP content. The influence of both long-chain branching (LCB) and short-chain branching (SCB) on the T_g is complex. LCB typically increases the degree of crystallinity due to co-crystallization of the side branches. Since a decreasing crystallinity with increasing EP content was observed, only SCB can be considered. Short-chain branching increases the free volume and thus decreases the glass transition temperature, as reported for poly(butylene succinate), poly(ethylene adipate) and other aliphatic polyesters [20]. Therefore the decrease in the β-relaxation temperature with increasing epoxy content may be due to the sum of all three effects: a decrease in crystallinity, a plasticizing effect of the unreacted epoxy resin, and branching. As far as the γ-relaxation of the chain extended samples is concerned, no clear influence of epoxy content can be observed. The γ-relaxation temperature decreased ∼11 °C when 2 wt.% of epoxy resin was added. Further addition of EP led to an increase in the γ-relaxation temperature. Literature suggests that the γ transition remains relatively unaffected by the degree of crystallinity [25]. The storage modulus (E′) curves of the pCBT/EP samples were lower than the pCBT reference curve. Interestingly, the storage moduli versus temperature of the samples containing 1, 3 and 4 wt.% EP were similar to each other. The lower stiffness of the chain extended samples was more pronounced at low temperature and diminished above T_g. This decrease in stiffness may be attributed to the lower degree of crystallinity of the pCBT/EP samples, as crystallites act as rigid fillers and crosslinks for amorphous segments [23].

3.5. Tensile properties

Tensile tests were performed on the compression moulded pCBT/EP samples, the obtained tensile properties are presented in Table 4. Neat pCBT fails in a brittle manner without yielding and neck formation with an average elongation at break of 7%. In comparison, all tested EP concentrations were found to have increased elongation at break. More than half of all tested pCBT/EP specimens showed neck formation in tensile tests. Brittle failure without necking of pCBT/EP specimens may be explained by inhomogeneities in the CBT/EP blends prior to polymerization due to the low mixing efficiency of the blend preparation. As the diepoxide content in the CBT/EP blends increased, more CBT got in contact with epoxy resin and could react in the subsequent compression moulding process. This is reflected in the heightened percentage of yielded specimens with increased EP content (see Table 4). It was also observed that many of the toughened pCBT/EP specimens showed the onset of necking. However, necking did not proceed due to premature failure. The maximum elongation at break of 49% was observed for samples containing 2 wt.% of diepoxide. When samples contained more than 2% of EP, elongation at break notably decreased. This can be attributed to the increased amount of crosslinked polymer (see Table 1). This crosslinked fraction forms domains that are surrounded by the pCBT/EP matrix. These domains limit the deformation of the system because they are not able to undergo plastic deformation.

3.6. SEM

SEM analysis was conducted to study the morphology of the compression moulded pCBT/EP samples. Micrographs of neat pCBT are provided in Fig. 4(a) and (b)

Table 4
Tensile properties of neat pCBT and pCBT/EP obtained by compression moulding.

Sample	Tensile modulus [GPa]	Tensile strength [MPa]	Elongation at break [%]	% age yielded samples[a] [%]
pCBT	2.8 ± 0.4	57 ± 5	7 ± 3	0
pCBT/EP 1%	2.9 ± 0.1	57 ± 1	12 ± 9	60
pCBT/EP 2%	2.8 ± 0.1	62 ± 1	49 ± 25	80
pCBT/EP 3%	2.9 ± 0.2	60 ± 1	11 ± 6	94
pCBT/EP 4%	2.7 ± 0.2	56 ± 2	11 ± 7	94

[a] A specimen was defined to have yielded if a yield point with subsequent necking was detected.

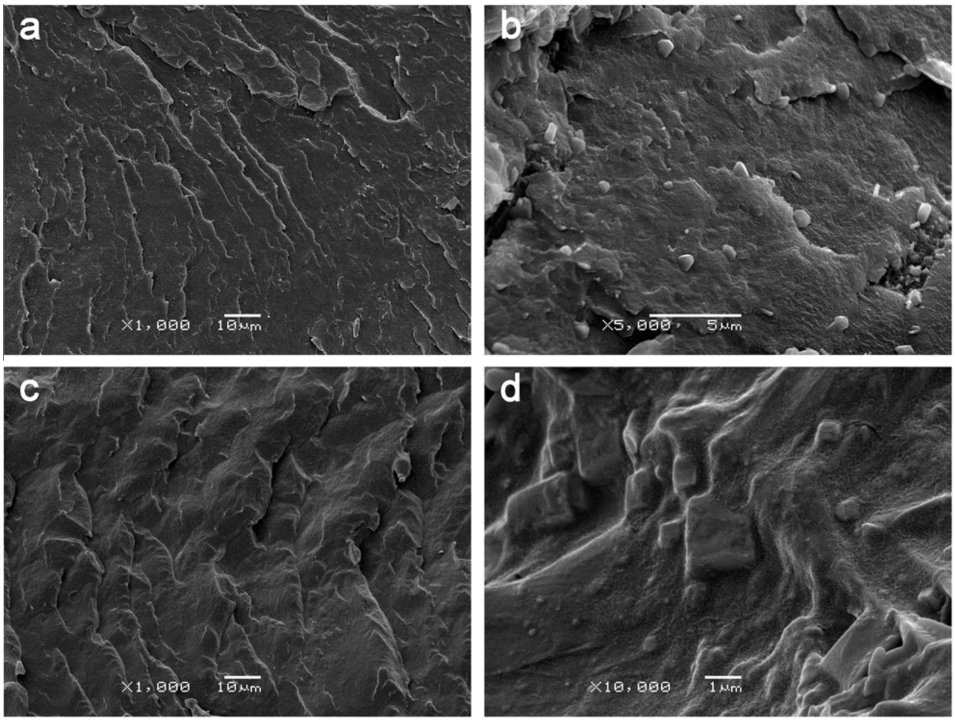


Fig. 4. SEM micrographs of compression moulded neat pCBT (a and b) and pCBT/EP 2% (c and d).

whereas the ones of pCBT/EP 2% are shown in Fig. 4(c) and (d). No significant difference in morphology between neat pCBT and the chain extended samples could be detected. As epoxy resin is miscible with pCBT, a single phase (corresponding to pCBT matrix) was observed in all samples. When CBT is polymerized into pCBT, it does not reach a 100% conversion. This is due to the fact that molten polyesters undergo ring-chain equilibrium reactions and therefore contain an equilibrium content of cyclic oligomers of about 1–3% [3,6–8]. These remaining CBT oligomers form platelet-like or prismatic crystals with sizes up to a few microns upon cooling from the melt [7,28]. SEM analysis revealed the presence of few CBT oligomer crystals in neat pCBT as well as in the chain extended samples. The amount of these oligomer crystals appeared similar in all analyzed samples, as the degree of conversion was found to be relatively unaffected by the diepoxide (as determined by GPC).

The oligomer crystals act as a rigid filler and may therefore contribute to the inherent brittleness of unmodified pCBT. Furthermore, the micrographs of neat pCBT (c.f. Fig. 4b) suggest a poor interfacial adhesion between pCBT matrix and CBT oligomer crystals. On the other side, the oligomer crystals present in pCBT/EP 2% (see Fig. 4d) appear to be covered with polymer matrix, indicating an improved interfacial adhesion between pCBT/EP matrix and the oligomer crystals. This finding also may contribute to the toughening mechanism observed in pCBT/EP samples.

4. Conclusions

Toughening of polymerized cyclic butylene terephthalate has been achieved by reactive chain extension with a difunctional epoxy resin. CBT/EP blends with small amounts (1–4 wt.%) of diepoxide were compression moulded in a hot plate press. Tensile tests were performed and an increase in toughness was observed for all chain extended samples. A sevenfold strain at break was found for a diepoxide content of 2 wt.%, compared to that of neat pCBT. Stiffness and strength was not significantly affected by the epoxy resin. GPC analysis confirmed the low molecular weight of neat pCBT, a possible explanation for brittleness. GPC also showed the remarkable increase in molecular weight when 2 or 3 wt.% epoxy resin was used. Moreover, the degree of conversion from CBT oligomers to pCBT polymer was not significantly affected by the epoxy resin. The diepoxide substantially reacts with the carboxyl end groups of pCBT in an esterification reaction and yields a predominantly linear polymer, as suggested by ^{1}H NMR. On the other hand, when the epoxy content was higher than 2 wt.% some gel formation was detected, indicating a partially branched and crosslinked structure of the chain extended pCBT. Thermal analysis of modified pCBT revealed a decrease in glass transition, melting and crystallization temperature, and degree of crystallinity with increasing epoxy content. This was mainly attributed to decreased crystallinity, branching, and a minimal plasticizing effect of unreacted epoxy resin. SEM micrographs suggested a more favorable adhesion of remaining oligomer crystals to the pCBT matrix when epoxy resin was used. The improved adhesion contributed to the increase in toughness of chain extended pCBT.

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