Effects of thermal history in the ring opening polymerization of CBT and its mixtures with montmorillonite on the crystallization of the resulting poly(butylene terephthalate)

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ABSTRACT

Differential scanning calorimetry was used to study the thermal characteristics and morphological structure of species produced during the ring opening polymerization of cyclic butylene terephthalate (CBT). Thermal programs consisting of a first ramp heating scan and an isothermal step, followed by cooling and a second ramp heating step, were used to study the effects of thermal history, catalyst (butyl chlorotin dihydroxide) at concentrations between 0.1 and 1.3% (w/w), and the presence of a layered silicate nanofiller (montmorillonite at 4.0%, w/w) on the structure of the resulting polymer (poly(butylene terephthalate), pCBT). Wide angle X-ray diffraction was used to monitor the degree of exfoliation of the nanocomposites.

It was found that pCBT is formed in the amorphous state, and crystallizes during the heating step or during the isothermal step at temperatures lower than the equilibrium melting temperature of the polymer (T_m^0). When premixed with the nanofiller, irrespective of whether this was previously intercalated with a tallow surfactant or used in its pristine form, polymerization took place at higher temperatures and most of the crystallization was found to occur during the cooling stage. In those cases where crystallization took place during either the first heating scan, or during a prolonged isothermal step below the T_m^0 of the polymer, the resulting crystals were found to have a higher lamellar thickness, as compared with the same polymer crystallized from the melt during the cooling step from temperatures above the polymer T_m^0.

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1. Introduction

Studies on polymer/layered silicate (PLS) nanocomposites have attracted, in recent years, increasing interest in both academic institutions and industry, owing to the remarkable improvements in properties that can be achieved relative to the pristine polymer or conventional particulate or short-fiber composites. At equal filler content, PLS nanocomposites have a higher modulus and strength, together with a higher thermal oxidative stability, hence a lower flammability and gas permeability than the corresponding microcomposites [1].

To enhance the "compatibility" between the nanofiller and the polymer, thereby improving the extent of exfoliation and the related nanofiller dispersion within the polymer, it is often necessary to modify the chemical structure of the surface layers of natural occurring silicate fillers.

For the case of thermoplastic matrix nanocomposites the intercalation of the nanofiller is usually carried out by conventional melt-compounding methods, which produce intensive mixing and often require high temperatures. Melt intercalation of the layered silicate carried out at high temperatures can induce considerable degradation of the organic modifier through chemical decomposition reactions, which may result in extensive deterioration of the interfacial interactions between the filler and the polymer [1–3]. There are a few cases, however, where polymerization can be carried out during compounding, at substantially lower temperatures or with shorter exposures at higher temperatures, than the corresponding melt-compounding techniques.

There has been considerable interest also on the *in situ* polymerization of cyclic butylene terephthalate (CBT), which is a low viscosity cyclic oligoester, to produce poly(butylene terephthalate) (pCBT) matrix composites capable of being processed at relatively low temperatures [4–7]. These composites, therefore, combine the typical advantages of thermoplastic polymers, particularly toughness, with the low viscosities of thermoset resins which can provide thorough impregnation of fibers, thereby making it possible to produce composites with high fiber contents [8–11].

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Another advantage of pCBT matrix composites is the expected higher toughness, relative to the corresponding PBT-based systems, in so far as the polymerization of CBT does not produce low molecular weight by-products [12].

Not surprisingly CBT has also been used as a precursor for the production of pCBT-based nanocomposite [13,14]. In this case, the low melting temperature of the cyclic oligomer and the very low viscosity of the resulting melt can be exploited to achieve an efficient exfoliation of the nanofiller and dispersion in the polymer matrix, and reduce the degradation susceptibility of any organic surface modifier present.

Despite the great attention paid to CBT and the resulting pCBT, only few of the works reported in literature deal with the characterization of the ring opening polymerization of CBT with a thermal method of analysis [6,11,15]. In the majority of cases the authors have reported results on one-component commercial CBT, usually containing an unknown amount of catalyst. Other workers have reported data for a widely different range of temperatures. For instance, Mohd Ishak et al. [15] have reported data on the TMDSC analysis of CBT polymerization at temperatures that are respectively much higher (260 °C) and much lower (200 °C) than the melting temperature of PBT. No study has been reported on the effect of polymerization temperature within a closer range of the melting temperature of PBT. Furthermore, only one study has been reported in the literature on the thermal characterization of nanocomposites derived from CBT [14]. Even so, the analysis was performed on samples heated to very high temperatures (260 °C), which is not realistic for CBT nanocomposites, due to susceptibility of the modifier to thermally degrade at such temperatures.

The aim of this work is to study the effect of different conditions, particularly catalyst content, polymerization temperature and surface modifier used for the exfoliation of the nanofiller on the structure of the resulting pCBT polymer.

To this end DSC analysis was used to analyze the influence of the different variables on the melting and crystallization of the pCBT obtained. It is worth noting that DSC is particularly suitable for these studies as the ring opening polymerization of CBT is virtually athermal [7] and, therefore, the crystallization and melting transitions can be easily followed without significant interference from the associated heat of conversion.

2. Experimental

2.1. Materials

The materials used were:

(a) Cyclic oligoester CBT100 obtained from Cyclics Corporation.
(b) Butylchlorotin dihydroxide (BCTDH), as polymerization catalyst, supplied by Sigma.
(c) Unmodified montmorillonite (MMT) with a CEC of 128 mequiv./100 g, tradename Dellite HPS, supplied by Laviosa (Italy).
(d) Montmorillonite intercalated with 28% (w/w) dimethyl benzo-hydrogenated tallow (DMBHT-MMT), tradename Dellite 43 B, supplied by Laviosa, Italy.
(e) Commercial poly(butylene terephthalate) known as Pocan B, obtained from Lanxess (Germany).
(f) Acetone, analytical grade, supplied by Sigma.
(g) Distilled water.

2.2. Preparation of oligoester and nanocomposites mixtures

(a) Control samples of oligoester were produced by mixing 10 g of CBT with 100 g of acetone for 30 min with different amounts of

Table 1
Formulations examined.

Sample	CBT content (wt.%)	Catalyst content (wt.%)	Nanofiller type and content (wt.%)
CBT01	99.9	0.1	–
CBT05	99.5	0.5	–
CBT13	98.7	1.3	–
CBT13_MMT	94.8	1.2	4 Dellite HPS
CBT13_DMBHT	94.8	1.2	4 Dellite 43B

catalyst, varying between 0.1 and 1.3% (w/w), and subsequently dried at room temperature for 48 h.
(b) CBT nanocomposites were prepared by first mixing the nanofiller with the catalyst in water at 80 °C for 2 h. After drying in oven at 80 °C for 24 h, the CBT and catalyst/nanofiller were mixed in acetone for 30 min at room temperature. The final mixture contained 94.8% (w/w) CBT, 4% (w/w) MMT and 1.2% (w/w) catalyst. The details of the formulation prepared are summarized in Table 1. This procedure was used in an attempt to confine the catalyst within the galleries of the layered silicate filler, so that polymerization of CBT would take place preferably in these sites, thereby facilitating the exfoliation of the crystal lamellae of the filler.

2.3. Polymerization and thermal characterization

(a) Differential scanning calorimetry analysis was performed on a PerkinElmer DSC 7 instrument under a nitrogen flux at 30 nL/min. The materials were heated at 10 °C/min from room temperature to 220 and 240 °C, i.e. just below and just above the melting point of PBT. After holding the samples at constant temperature for 10 min, they were cooled to room temperature at 10 °C/min and subsequently subjected to a second heating cycle at 10 °C/min to 250 °C.
(b) X-ray analysis was performed on both nanofiller and nanocomposite powders, within the range $2\theta = 1–10°$, using a wide angle X-ray Diffractometer, RIGAKU Ultima+.

3. Results and discussion

The thermogram related to a single heating scan on CBT up to 180 °C, displayed in Fig. 1, shows the characteristic behavior of the commercial oligoester used in the study, consisting of two small melting peaks at 112.8 and 152.5 °C, and a large peak at 137.8 °C. The different melting peaks are due to the existence of oligomers of different size, with the higher melting temperatures characteristic of the lower molecular weight oligomers [7].
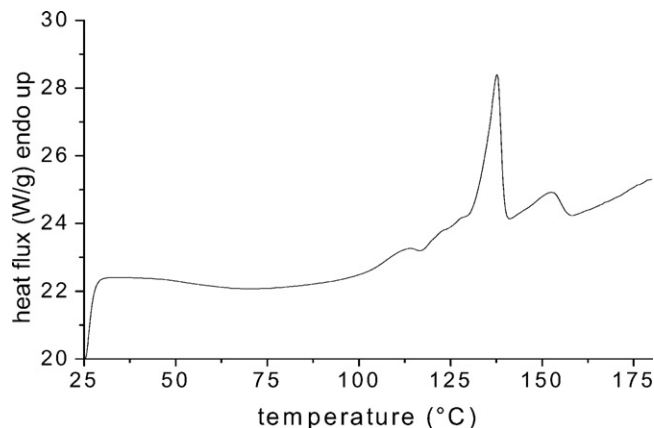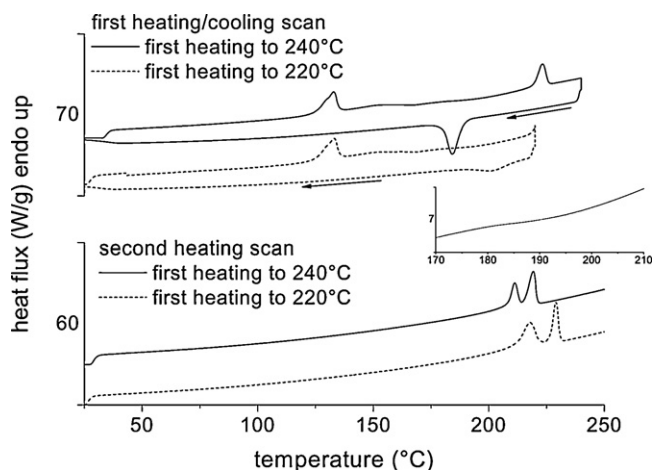

Fig. 1. DSC curve of neat CBT.

Fig. 2. DSC curves of sample CBT01 heated to different temperatures at the first heating scan. The arrows indicate the direction of cooling.

The DSC thermograms on sample CBT01 (containing 0.1% catalyst) heated to 220 and 240 °C, followed by cooling to room temperature (first heating/cooling scan) and subsequently reheated to 250 °C (second heating scan) are shown in Fig. 2.

For the sample CBT01 heated up to 240 °C, three distinct melting peaks can be observed during the first heating scan. The first peak, at about 133 °C, is due to the melting of CBT. After this peak, a second weak peak at about 153 °C is observed, due to the presence of oligomers of different sizes, as previously discussed. The melting peak at 223 °C is associated with the formation of pCBT. Between the two melting temperatures is observed a very weak broad exotherm, with the onset at around 179 °C, which can be attributed to crystallization of the pCBT. In facts, the overall area of the exothermic and the endothermic peak at 223 °C is zero (with an error of ±0.3 J/g). This indicates that pCBT is formed in the amorphous state, which is in concordance with the fact that the starting oligomer CBT is also in the amorphous (molten) state at the temperatures where polymerization takes place. Crystallization can occur in view of the fact that the pCBT is produced at temperatures lower than its equilibrium melting temperature T_m^0. During the cooling step of the scan to 240 °C, the obtained pCBT crystallizes at about 184 °C, releasing a crystallization enthalpy of 49.1 J/g. In a second heating scan, the melt crystallized pCBT shows two distinct melting peaks at 211.2 and 219.2 °C, respectively, with a total melting enthalpy of 49.2 J/g. This is a typical behavior of PBT, showing recrystallization during melting, with a concomitant increase in the thickness of the crystal lamellae [16,17].

For the sample CBT01 heated up to 220 °C, the crystallization of pCBT during the cooling step takes place at higher temperatures (around 202 °C), and displays a much lower crystallization enthalpy (24.3 J/g) compared to the sample heated to 240 °C. This indicates that a significant amount of the pCBT is in a crystalline state at the end of the isothermal step at 220 °C and the crystals act as a nucleating agent for the surrounding molten pCBT. The lower crystallization enthalpy is due to the fact that only the fraction of pCBT melted during the first heating step can crystallize in the subsequent cooling scan. During the second heating scan the melting behavior of the pCBT is characterized by two endothermic peaks, the first at 218 °C and the second at 229 °C. In this case, therefore, two different crystalline structures are present at the beginning of the second heating step. Part of the pCBT crystallizes in the first heating step during the course of the polymerization reaction of CBT or during the isothermal step at 220 °C. Another amount of pCBT crystallizes from the molten phase during the cooling scan. The pCBT that crystallizes during the cooling scan has a melting temperature very close to that observed for the pCBT heated up to 240 °C. The absence of the melting peak at 211 °C can be attributed to the higher crystallization temperature of the molten fraction of the pCBT obtained from CBT01 heated to 220 °C, compared to the crystallization temperature of the pCBT obtained from CBT01 heated to 240 °C. As a consequence, thicker crystals are obtained, and no further lamellar thickening takes place during melting. This can be supported from an examination of the Hoffman–Weeks plots for PBT, reported by Pompe et al. [17]. Accordingly, for sample CBT01 heated to 220 °C, a peak crystallization temperature of 202 °C would result in a melting temperature of 219 °C, which is a value quite close to the measured value of 218 °C. At the same time, the same sample heated to 240 °C gives a crystallization temperature of 184 °C, for which the corresponding predicted melting temperature of 212 °C is also in good agreement with the experimental data.

The second peak observed for sample CBT01 heated up to 220 °C indicates that the fraction of pCBT which was in the crystalline state at the end of the isothermal step at 220 °C has a much higher lamellar thickness, as compared to that of melt crystallized pCBT, in agreement with the predictions of the Thomson–Gibbs equation [18]. The second melting peak results from the combined effect of two melting processes for the pCPBT crystals, corresponding respectively to the crystals formed during polymerization and those formed during the isotherm at 220 °C. The prediction from the Hoffman–Weeks plots for PBT, reported by Pompe et al. [17], for a crystallization temperature of 220 °C is that the melting temperature of the resulting crystals would be around 228 °C, which is in quite good agreement with the experimental melting temperature of 229 °C. However, it is worth noting that the higher melting temperature measured in the second heating scan of the sample heated to 220 °C is higher than the melting temperature measured during the first heating scan of sample heated up to 240 °C, although both melting temperatures are attributed to the crystalline fraction formed directly during ring opening polymerization reaction. The observed difference in melting peaks can be explained by examining the results reported in Fig. 3, which shows the DSC thermogram for the isothermal steps at 220 and 240 °C. For both samples is observed a sharp decrease in the heat flow trace when the actual isothermal step begins. The elbow in the curve, therefore, corresponds to the point at which the heating scan is interrupted and the isothermal step begins. Note that during the isothermal step at 240 °C the heat flow curve is flat due to the athermal behavior of the sample. No evident signal can be observed. A weak and broad exotherm is observed, on the other hand, during the isothermal step at 220 °C, which is associated with the ongoing crystallization of the pCBT during the melting process.
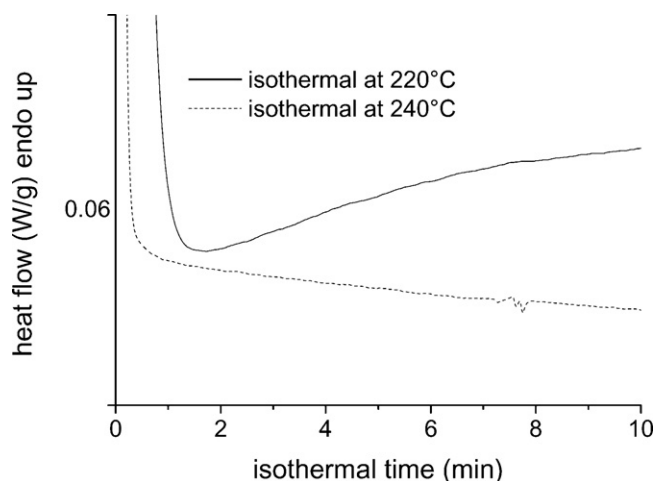

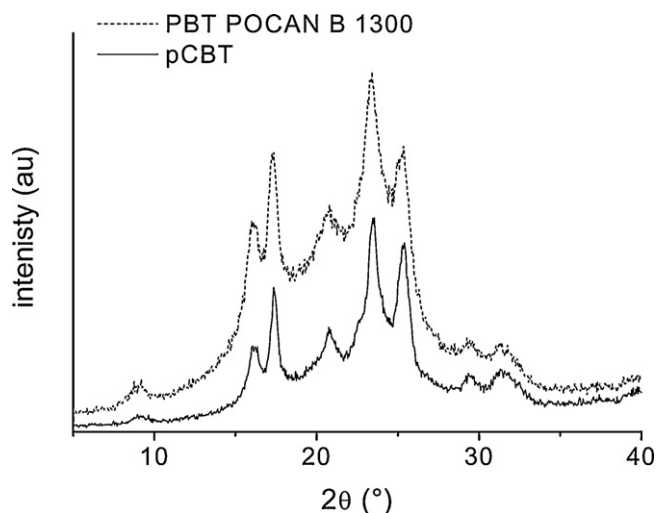**Fig. 3.** DSC signal during the isothermal step at 220 and 240 °C for sample CBT01.

Fig. 4. X-ray traces of commercial PBT and pCBT.

This is a confirmation that the crystallization of pCBT displaces the melting peak to lower temperatures, during the ramp temperature scan through the melting range.

The high lamellar thickness of pCBT crystallized directly during polymerization is confirmed by the spectra obtained by the X-ray diffraction analysis. A comparison between the X-ray traces of commercial PBT and pCBT is shown in Fig. 4. The characteristic diffraction angles of the two materials are the same, which indicates that the crystalline structure of the two materials is essentially the same. However, the width at half-height of the peak at $2\theta = 23.4°$ is 0.80 for the commercial PBT (crystals formed by melt cooling) and 0.56 for pCBT (crystals formed during polymerization). According to the Scherrer equation [19], the ratio of average lamellar thickness of the two polymer crystals is 1.43.

The ratio of average lamellar size for the two systems can also be estimated from the DSC data. The commercial PBT displays a melting peak of 225.7 °C, whereas the pCBT crystallized during polymerization has a measured melting peak of 229 °C, as reported in Table 3. By applying the Thomson–Gibbs equation and assuming an equilibrium melting temperature $T_m^0 = 236\,°C$ [20,21] the extrapolation gives a lamellar thickness ratio for the two systems of 1.47, which is in quite good agreement with the X-ray analysis results.

Also, from a comparison of the results reported in Tables 2 and 3, the higher melting enthalpy measured during the second heating scan for the sample heated to 220 °C (compared to the sample heated to 240 °C) confirms the higher degree of crystallinity of pCBT obtained by polymerization compared to the pCBT obtained by melt crystallization [7].

Results obtained by DSC and X-ray analysis clearly show that the pCBT obtained during ring opening polymerization of CBT crys-

Table 3
Transition temperatures and related enthalpy values for CBT with different catalyst content, corresponding to the first heating scan to 220 °C.

Sample	First heating scan		Cooling scan		Second heating scan	
	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)
CBT01	–	–	202	−24.3	218 229	61.5
CBT05	–	–	204	−21.7	218 229	67.7
CBT13	–	–	205	−23.1	218 229	68.3

tallizes readily into thick crystals. Furthermore, the thickness of the crystals formed during the heating scan is comparable to the thickness of the crystals formed in the isothermal stage at high temperatures (220 °C), despite the much lower crystallization temperature.

Although the results obtained for runs on samples CBT05 and CBT13 appear to be similar to those obtained for runs on CBT01, some small differences can be detected by a careful examination. During the first heating scan the intensity of the exothermic peak between the melting temperature of CBT and the melting temperature of pCBT increases with increasing catalyst concentration. This indicates that, at low catalyst concentrations, polymerization is very slow and takes place mostly at higher temperatures, thereby decreasing the rate of crystallization of the obtained pCBT. Conversely, at higher catalyst concentrations most of the polymerization takes place at lower temperature, which results in a higher rate of crystallization of the pCBT produced. This is confirmed by observing that the melting enthalpy in the first heating scan for samples heated up to 240 °C increases with increasing catalyst concentration, as can be inferred from a comparison of the data reported in Table 2, which also indicates that at low catalyst concentrations there is an overlap of three concurrent events, namely the polymerization of CBT, the crystallization of pCBT and a partial melting of a fraction of pCBT. As reported in Table 2, for all samples heated up to 240 °C, the enthalpy of melting measured during the first heating scan is lower than the crystallization enthalpy measured during cooling and the melting enthalpy measured during second heating cycle. This confirms that in each case the crystallization and melting of pCBT overlap during the first heating scan. The values the transition peak temperatures and related enthalpy obtained from the various runs are reported in Tables 2 and 3.
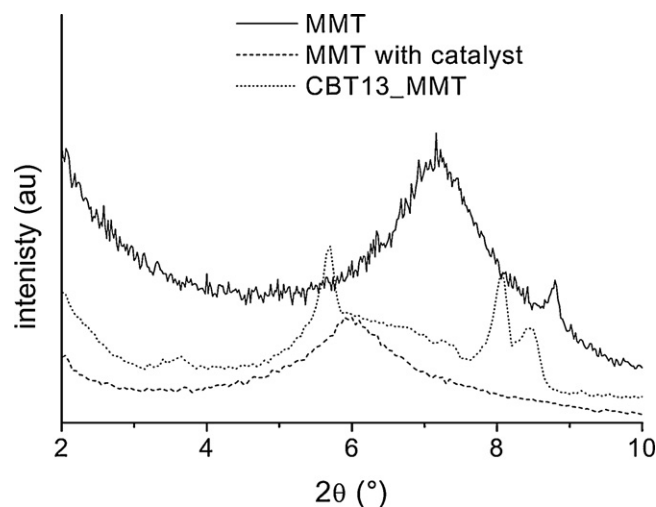

Fig. 5. X-ray traces of commercial unmodified MMT, unmodified MMT mixed with catalyzer and CBT13_MMT sample.

Table 2
Transition temperatures and related enthalpy values for CBT with different catalyst content, corresponding to the first heating scan to 240 °C.

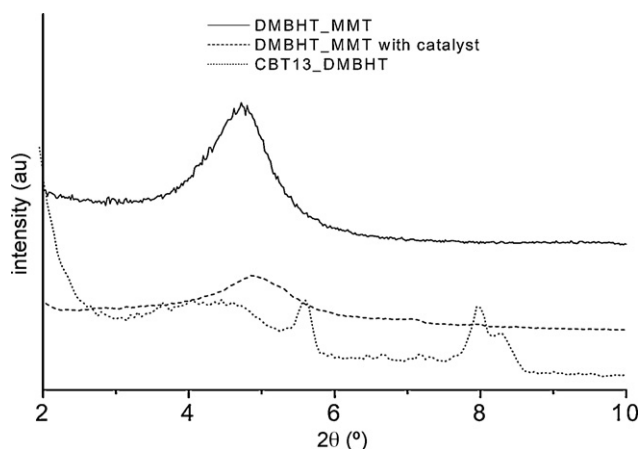| Sample	First heating scan		Cooling scan		Second heating scan	
	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)
CBT01	223	22.2	184	−49.5	211 219	49.2
CBT05	221	43.2	186	−54.1	211 220	54.2
CBT13	221	45.8	188	−54.7	211 220	54.6

Fig. 6. X-ray traces of commercial DMBHT modified MMT, DMBHT modified MMT mixed with catalyzer and CBT13_DMBHT sample.

The spectra obtained from X-ray analysis of samples of CBT mixed with unmodified MMT are shown in Fig. 5. The MMT shows a diffraction angle of 7.2°, corresponding to a lamellar spacing of about 1.22 nm. After mixing with the catalyst, the lamellar spacing increases to 1.43 nm. This indicates that a partial exchange of cations between catalyst and MMT may have taken place. After mixing with CBT the diffraction angle is displaced to 3.65°, corresponding to 2.4 nm lamellar spacing, which indicates that the CBT oligomer, and/or the corresponding polymerized species, can be very effective in intercalating the lamellar spacing of the nanofiller.

The X-ray spectra of CBT mixed with DMBHT modified MMT is shown in Fig. 6. The position of the diffraction angle for the DMBHT modified MMT is at about 4.7°, corresponding to a lamellar spacing of about 1.84 nm. After mixing with the catalyst, the position of the peak diffraction angle remains virtually the same, whereas the subsequent mixing with CBT displaces the peak to lower angles (about 4°). This implies that that some intercalation of the oligomers into the galleries of the silicate filler has occurred.

When the nanofiller is added to the CBT/catalyst mixture significant changes are observed in the three processes, that is polymerization of the CBT, crystallization and melting of the resulting pCBT. The DSC traces of CBT13_MMT are shown in Fig. 7. For the sample heated up to 240 °C only the melting peak of CBT is observed during the first heating cycle. However, since crystallization of pCBT takes place during the cooling cycle, it can be deduced that conver-
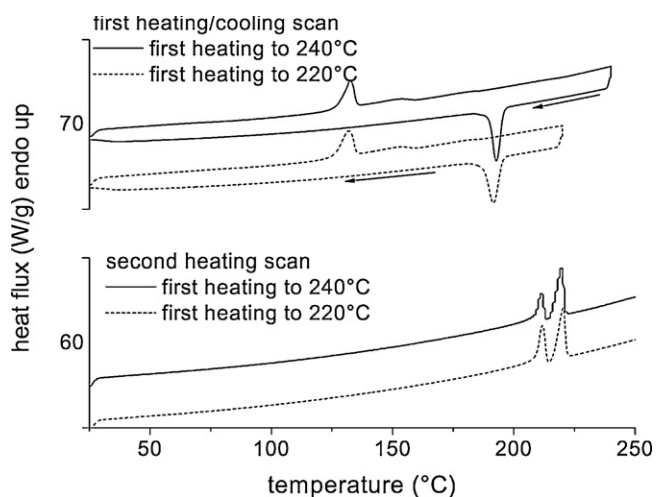
Table 4
Transition temperatures and related enthalpy values for CBT with different nanofiller, corresponding to the first heating scan to 240 °C.

Sample	First heating scan		Cooling scan		Second heating scan	
	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)
CBT13_MMT	–	–	193	−49.5	211 220	49.4
CBT13_DMBHT	–	–	190	−49.8	211 219	49.2

sion of CBT to pCBT has occurred during the first heating scan., and can be also concluded that the presence of the nanofiller within the CBT displaces the polymerization reactions to higher temperatures. Moreover, during the cooling cycle the crystallization behavior of the pCBT formed is very similar for the two heating scans, i.e. to 220 and 240 °C, which indicates that in both cases the pCBT is in the amorphous state before cooling.

The displacement of the polymerization of CBT to pCBT to higher temperatures can be attributed to the reduced catalyst activity. Wide angle X-ray diffraction analysis indicates that the catalyst is intercalated in the nanofiller lamellae, and can form ionic bonds with the lamellar surface.

As can be inferred from the data in Table 4 in comparison with the behavior of pure CBT (that is without MMT) heated to 240 °C, the crystallization exotherms observed during cooling are displaced to higher temperatures. This behavior is indicative of a nucleating effect exerted by the nanofiller within the pCBT matrix. In the second heating scan the occurrence of two melting peaks, at 212 and 220 °C, is typical of melt crystallized pCBT, as previously observed for the system without nanofiller heated above the equilibrium melting temperature of the polymer. The absence of the peak at about 229 °C is a further indication that the pCBT does not crystallize in both the heating scan and the isothermal step of the run.

A significantly different behavior is observed for a CBT13_DMBHT sample, as shown in Fig. 8. In this case, the spectra obtained for the sample heated to 240 °C are similar to those observed for the samples with unmodified MMT, whereas the sample heated to 220 °C shows a double crystallization peak during the cooling cycle.

The difference in the behavior of the two nanofillers can also be highlighted by examining the data reported in Table 5 and the thermograms in Fig. 9 for CBT13_MMT and CBT13_DMBHT held at 220 °C for different time intervals. For the case of CBT13_MMT, no relevant differences can be revealed with respect to the cooling cycle
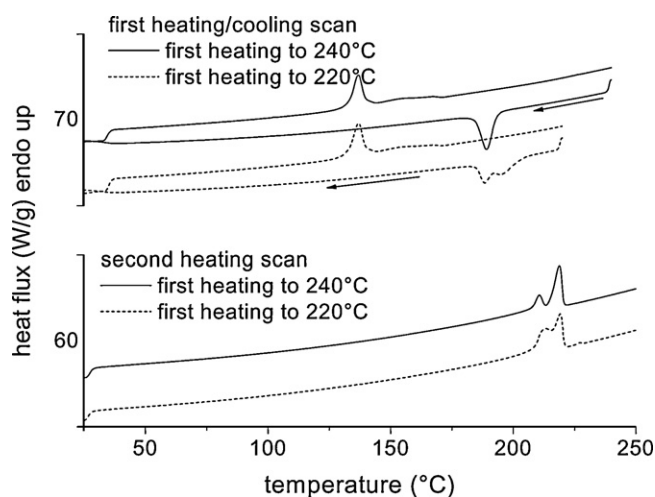

Fig. 7. DSC curves of sample CBT13_MMT heated to different temperatures at the first heating scan. The arrows indicate the direction of cooling.

Fig. 8. DSC curves of sample CBT13_DMBHT heated to different temperatures at the first heating scan. The arrows indicate the direction of cooling.

Table 5
Transition temperatures and related enthalpy values for CBT with different nanofiller, corresponding to the first heating scan to 220 °C.

Sample	First heating scan		Cooling scan		Second heating scan	
	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)
CBT13_MMT	–	–	191	−51.2	212	52.1
					220	
CBT13_DMBHT	–	–	188	−50.7	213	51.2
			195		219	
CBT13_MMT 30 min	–	–	192	−52.7	211	52.3
					220	
CBT13_DMBHT 30 min	–	–	190	−44.7	218	50.3
			197		227	

between the samples held respectively for 10 and 30 min at 220 °C (see Table 5). A significant effect of the holding time, however, is observed in Fig. 9 for CBT13_DMBHT samples heated to 220 °C. In particular, crystallization is displaced at higher temperatures, and the ratio of the intensities of the first crystallization peak to the second crystallization peak increase with increasing holding time at 220 °C. Furthermore, for the CBT13_DMBHT sample held at 220 °C for 30 min, a melting peak at 227.4 °C is observed, due to the fraction of polymer crystallized during the isothermal step at 220 °C. At the same time, for sample CBT13_DMBHT held at 220 °C for 30 min, there is a mismatch between the enthalpy value obtained during the cooling cycle and that obtained in the heating cycle, due to the fact that the melting enthalpy measured during the second heating scan results from the combined effects of the polymer crystallized during the isothermal step and of that crystallized during the cooling cycle. In Fig. 10 are shown the DSC traces for sample CBT13_DMBHT held for 60 and 90 min at 220 °C and then directly heated up to 250 °C. Both samples show the presence of a melting peak at 227 °C, and the intensity of the peak increases with increasing holding time at 220 °C.

These observations indicate that the CBT13_DMBHT sample partially crystallizes during both the first heating cycle and the isothermal stage. Therefore, increasing the isothermal holding time at 220 °C brings about an increment in the fraction of polymer in the crystalline state at the beginning of the cooling cycle, which is accompanied by a displacement of the crystallization enthalpy peak to higher temperatures.
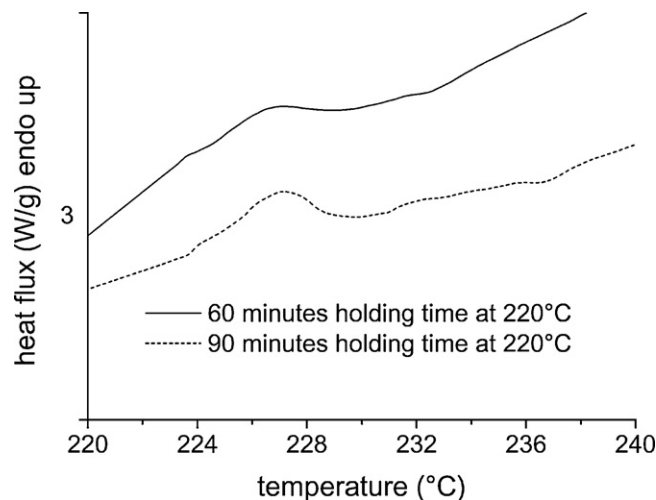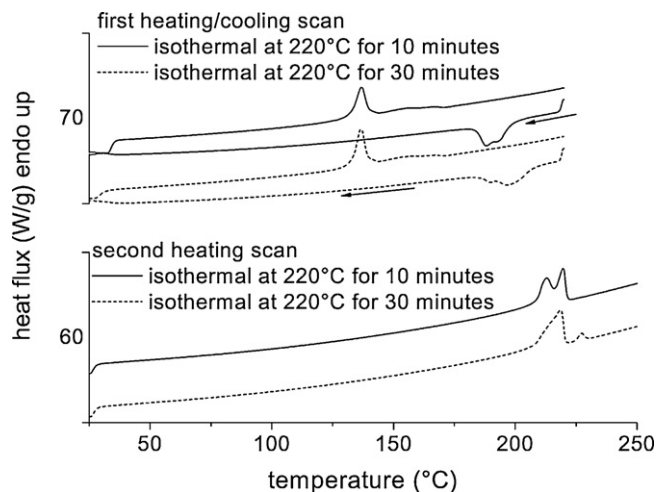

Fig. 9. DSC curves of sample CBT13_DMBHT held for different times at the final temperature of the first heating scan. The arrows indicate the direction of cooling.

Fig. 10. DSC traces for sample CBT13_DMBHT held for different times at 220 °C and heated at 240 °C after the isothermal step.

4. Conclusions

In this work, differential scanning calorimetry and wide angle X-ray diffraction analysis were used to study the thermal characteristics and morphological structure of species produced during the ring opening polymerization of CBT, including the effects of the addition of small amounts of pristine and organo-modified montmorillonite, both imbibed with a tin catalyst.

For the case of CBT, polymerization carried in the heating scan of the DCS apparatus takes place at temperatures above the melting point of CBT, and leads to the formation of a substantially amorphous pCBT. The temperature at which polymerization takes place at an appreciable rate depends on the catalyst concentration. At low catalyst concentrations polymerization of CBT, and crystallization of the obtained pCBT, take place at temperatures very close to melting of pCBT. On the other hand, increasing the catalyst concentration brings about a decrease in the polymerization temperature, and consequently the onset of the crystallization is also displaced to lower temperatures. The pCBT formed directly from ring opening polymerization exhibits a higher melting point and higher degree of crystallinity than the pCBT crystallized from the melt, as a consequence of the formation of thicker crystals.

The addition of the nanofiller has a significant effect on the polymerization of CBT, displacing the onset of the polymerization reactions to higher temperatures. This is attributed to the catalyst being adsorbed in the lamellar galleries of the filler, thus reducing its activity for the polymerization reactions. As a consequence pCBT is formed at higher temperatures, preventing it from crystallizing during the heating scan. However, the nanofiller acts as efficient nucleating agent for the crystallization during the cooling cycle. When long isothermal holding times are used at temperatures lower than the equilibrium melting point of PBT, the resulting polymer can crystallize to some extent and the crystal so produced has a nucleating effect of the crystallization taking place during the subsequent cooling cycle.

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