

# THE EFFECT OF THERMAL HISTORY ON MECHANICAL PROPERTIES OF WOVEN BASALT FABRIC REINFORCED POLY(BUTYLENE TEREPHTHALATE) COMPOSITES

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## Abstract

Fiber impregnation has been the main obstacle for thermoplastic matrix with high viscosity. This problem can be surmounted by adapting low viscous polymeric precursors such as cyclic butylenes terephthalate (CBT) resins, which polymerized to form thermoplastic matrix. Woven basalt fabric reinforced poly (butylenes terephthalate) composites were produced via in situ polymerization. The effect of different thermal history during processing on composites properties was investigated. DSC was used to determine the polymerization and crystallization properties of each condition. Tensile, three point bending, and short-beam shear tests were employed to study the mechanical properties with different thermal history.

## 1 Introduction

Continuous fiber reinforced composite is one of the most promising materials in aerospace, aircraft, automotive and sports industries. Thermoplastics chosen as matrix only has a share of 30% and thermosetting resins of 70% [1], although thermoplastics offer several attractive features over thermosetting resins, such as recyclability, better toughness, unlimited shelf-life, and rapid fabrication cycle [2]. The main drawback which hampers thermoplastic resins is the high melting viscosity (100 to 1000 Pa·s), because of their long molecular chains. Cyclic butylene terephthalate (CBT), used as precursors for polyesters and polycarbonates, could combine both the low viscosity of thermosetting

resins (0.017 Pa·s at 190 °C) [3, 4], and the typical advantages of thermoplastics (after adding catalyst, CBT would polymerize to pCBT).

This particular characteristic has promoted the various explores in polymer blends, micro- and nano-composites. For composites, the resin transfer molding technique, which commonly works on liquid resin of thermosettings, was introduced by Parton [5] to produce unidirectional glass fiber-reinforced CBT-based polymer composites (GFRPCs). Mohd Ishak [6] prepared woven CBT-based GFRPCs using compression molding. In these studies, it was found that the watery melted CBT resin helped markedly to improve the impregnation of fibers. However, the time window for impregnation was quite limited due to the rapid polymerization reaction after catalyst added into CBT resin. And the mechanical strength of the GFRPCs evidenced deterioration, which is presumably ascribed to the brittle c-PBT matrix with relatively high degree of crystallinity [7].

Despite the great attention paid to CBT and the resulting composites, only few papers reported the thermal analysis of the ring opening polymerization of CBT [8-10]. In [11], although different thermal history, in close range of PBT melting temperature, was examined in the ring opening polymerization, it didnot mention how the thermal cycle would affect the resulting composites, especially the mechanical properties.

In this paper, we present a detail analysis of the properties of the pCBT composites under different processing thermal cycle, especially closely above and below PBT melting temperature. The

performance evaluation of the composites includes tensile, flexural and short-beam shear tests.

## 2 Materials and Methods

### 2.1 Materials

The CBT<sup>®</sup> powders (CBT100 and CBT160) used in this study are commercially available from the Cyclics Co. (USA; [www.cyclics.com](http://www.cyclics.com)). CBT100 produced without catalyst is called two-components; while CBT160 containing catalyst is termed as one-component. The number of butyl groups in the oligomer cycle for both kinds varies from two to seven, resulting in a melting range of 140-160°C. Before processing, the oligomers were dried overnight at 105°C to remove residual moisture, which could interfere with the polymerization reaction.

The tin-based polymerization catalyst (Fascat<sup>®</sup> 4105, butylchlorodihydroxystannan) is supplied by the Arkema Co. (USA, <http://www.arkema.com/>), which is a well established transesterification catalyst. The catalyst was kept in desiccators for further use.

The reinforcements are woven basalt fabrics produced by Huaheng High Performance Fiber Textile Co. Ltd (China, <http://www.huahengcf.com/>), with areal density of 272g/m<sup>2</sup>.

### 2.2 Composites Processing

It is known that for temperatures below 230°C (the melting temperature of PBT), polymerization and crystallization occur simultaneously. Once the temperature is above PBT melting temperature, the crystallization would not occur, and only polymerization takes place. In order to investigate the effect of the processing temperature on characteristics of polymerized CBT, the processing temperature was set to be 220°C(CBT160-1), 230°C(CBT160-2) and 240°C(CBT160-3), respectively, just in the close range of the melting temperature.

Because of the long molecular chain, the thermoplastics are always in a high viscosity status even over their melting temperature. Consequently, the fiber content and fiber impregnation have been the main obstacles for thermoplastics composites used as engineering materials. In this study, we chose the CBT, as precursor, to obtain the water-like viscosity for perfect impregnation. After reinforcements were wet completely, the catalyst

began to work so that the in-situ polymerization took place.

Woven basalt fabric (WBF) reinforced pCBT composite samples were prepared by in situ polymerization of CBT compacted by a compression molding press, equipped with temperature and pressure-controlled plates. Laminates containing 10 plies of WBF were molded at certain temperature by using a stainless steel plate of 180×180mm<sup>2</sup>. CBT powder was dispersed evenly between the WBF layers. To avoid moisture as far as possible, the prepared fiber package was kept in an oven at 105 °C for 1h prior to be transferred in the mold.

The process involved pressure control where by the specimens was molded by closing the two heating-plates under a prescribed condition. Finally, the mold was cooled to room temperature outside the hot-press and opened. Flat plates (150×150×3mm<sup>3</sup>) were produced successfully under different thermal cycle. The composite produced at 220°C is designated as pCBT-1, and for 230°C as pCBT-2, for 240°C as pCBT-3.

### 2.3 DSC and SEM Examinations

Differential scanning calorimetry was performed on DSC (Perkin Elmer DSC-7) device. Samples were divided into two groups. One was made of CBT160, and the other was the pCBT from the composites. For part 1, the thermal cycle was determined as follows: heat to 220°C, 230°C and 240°C respectively, followed by cooling to room temperature and then reheated to 250°C. For part 2, there was only one heating scan to 250°C, and then cool to room temperature. All samples were heated to certain temperature and held for 10 min to eliminate the influence of the thermal history with heating and cooling rates of 10 °C/min.

The fracture surfaces after mechanical testing were investigated by the SEM which was taken at a 20-kV acceleration voltage at various magnifications, using a JEOL JSM-6490 scanning electron microscope.

### 2.4 Mechanical Test

Tensile, three point bending and short-beam shear tests were performed on WBF-PBT specimens according to ASTM-D638, ASTM-D790 and ASTM-D2344. All the above tests were conducted on a universal testing machine (MTS series). The test speed was set as 2mm/min.

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## 3 Results and Discussion

### 3.1 DSC

As described above, the DSC samples contain two groups, one is the CBT oligomers, and the other is the pCBT from the composites. The first one is used to detect the thermal history effect on the neat CBT and later polymerized pCBT. The second is used to find out how the thermal history affects the properties of composites, and how the fiber fabrics affect the resin. Figures.1 and 2 show the DSC thermograms of the CBT oligomers in presence of different thermal cycles. As the thermograms for 230°C is similar with that for 220°C, only the 220°C and 240°C are presented.

During the first heating scan, three distinct melting peaks were observed in both cases with at almost the same temperature. The first peak is at 144°C due to the melting of CBT, which is in agreement with other literatures [6, 9, 12, and 13]. The peak, at about 161°C near the first one, may be ascribed to the different oligomer size, as discussed above. While the third weak peak around 188°C is said to be the crystallization of the pCBT, as known that CBT would undergo ring-opening polymerization and crystallization in the temperature range of 170-210°C. So far, the peak temperature is in accordance with both cases. During the cooling scan, the crystallization peaks are at 186°C (CBT160-3) and 192°C (CBT160-1). The CBT160-2 shows a much lower crystallization enthalpy compared to the CBT160-3. At the end of the first heating scan for CBT160-2, more amount of pCBT is in crystalline status than that for CBT160-3. Additionally, the crystals could play the nucleation agent role for the surrounding molten pCBT.

In the second heating scan of both cases, the melt crystallized pCBT shows multiple melting peaks, the values are indicated in Table 1. According to the literature [14], the occurrence of multiple endotherms is a common phenomenon for polymer melting, as reported for other polymers such as PET, PA, and PEEK. This behavior can be ascribed to a number of factors such as the presence of more than one crystal modification, different crystal morphologies, orientation effects, or reorganization processes that occur during the DSC heating scan. It was mentioned in [15] that for PBT, it is generally accepted that the complex fusion behavior is a multistep recrystallization/remelting process: the fusion of a

certain amount of original, less perfect crystals, followed by the recrystallization and final melting of more perfect crystals. This was evidenced by modulated DSC studies as well [10, 11].

The DSC thermograms of pCBT from composites are reported in Fig 3. As the thermograms for 230°C is similar with that for 220°C, only 220°C and 240°C are presented. It is obvious that the multiple melting peaks in the first heating scan disappear for both cases. The composite heat history is the same as CBT160 samples described above, except for the heat holding time. For composites, keep at certain temperature for 2 hours, while for CBT160 samples in the DSC only last for 10min. The catalyst used for the CBT oligomers polymerization calls for at least 45min to obtain the 95% degree of polymerization. The short time window for CBT160 may hinder the polymerization process. The multiple peaks may ascribe to the degree of polymerization.

During the heating scan, the melting peak appeared at about 232 °C for pCBT-1, 224 °C for pCBT-3. Correspondingly, during the cooling scan, the crystallization peak was displaced around 188°C for pCBT-1, and 182°C for pCBT-3 case. It is worth to notice that the melting peak width for pCBT-1 was broadened as compared to the pCBT-3. As the pCBT-3 was produced above the PBT melting temperature, the oligomers went through the polymerization process without the crystallization happened. For the pCBT-1 case, the polymerization and crystallization happened at the same time, which may cause that the part of polymer couldn't polymerized completely, resulting in the broad peak width. Additionally, the thermal history can affect the resulted polymer, as the melting and crystallization temperature are different.

### 3.2 SEM

Good interfacial bonding between fibers and matrix was displaced in the SEM micrograph of composites as shown in Fig. 4. The good impregnation ascribes to two factors. First, the time window is long enough for CBT oligomers with low viscosity which facilitates the penetration of the resin to go through the fabrics, and fully fill the space between the inner fibers. Second, the relative high processing temperature combining the pressure placed on the mould also favors to complete impregnation.

It can be seen from the fracture surface of the composite in Fig. 7a that fibers are well impregnated. The matrix went through the bundle, and wrapped

intro-bundle fibers completely. When fibers broken and pulled out of the matrix, there were a majority of matrix left on the fiber surfaces.

### 3.3 Mechanical Properties

In this paper, the mechanical properties of composites produced under different thermal history were investigated. The relative strength and stiffness are displaced in Table 2 which shows that the pCBT-2 gains the best mechanical strength, pCBT-1 processes similar value of stiffness and strength, while pCBT-3 achieved relative low mechanical properties.

For pCBT-2, the viscosity is lower than that for pCBT-1, resulting in better impregnation for fiber bundles. Various mechanical properties were relatively enhanced since the impregnation was improved. Considering the influence of viscosity, the mechanical properties for pCBT-3 should have achieved the best data, for the lowest viscosity. However, the results show that it gains the lowest properties actually. In spite of the lowest viscosity, the processing temperature for pCBT-3 is near to the depolymerization point. The depolymerization for PBT is said to happen when the temperature exceeds 260-270 °C with vacuum condition. In this study, as the mould was exposed to the atmosphere, the so-called depolymerization may then take place, resulting in poor mechanical properties.

Further more, it can be observed through the tests, that some samples exhibited strong but brittle behaviors. It is known that presence of defects, low molecular weight, high degree of crystallinity and large spherulites can substantially reduce the ductility of a polymeric material [5]. Higher degree of

crystallinity for pCBT-3 was discovered comparing with pCBT-2, which may explain the brittleness of pCBT-3.

The shear strength is a non-fiber dominated property and hence influenced by both properties of matrix and interface. For the intensely stiffness mismatch between the fiber and matrix, the stress concentration always happens at the interface. The perfect impregnation has guaranteed the good interphase properties. In a way, it does favor to eliminate the voids between the fiber and surface, and bring better interface. How the interface affect the mechanical properties will be the subject of our future study.

### 4 Conclusions

In this paper, woven basalt fabric reinforced pCBT composites have been fabricated via in-situ polymerization. The effect of thermal history on the mechanical properties was investigated. The circumstances when the heating temperature below the  $T_m$  of PBT seem to demonstrate similar strength and stiffness value in tensile, bending, and short-beam shear tests. The higher temperature processed, the better mechanical properties achieved due to better impregnation. Once the processing temperature is too high, the mechanical properties declined sharply due to the depolymerization taken place and the high crystalline.

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Table 1 Melting and crystallization parameters of CBT and its composites

	First heat		Cooling		Second heat		
	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_m$ (J/g)	$T_{m1}$ (°C)	$T_{m2}$ (°C)	$\Delta H_m$ (J/g)
CBT160-1	144	36.7	192	29.7	221	234	49.0
CBT160-2	144	37.2	192	29.4	221	233	48.4
CBT160-3	144	46.0	186	35.54	219	226	33.8
p(CBT)-1	232	19.3	188	-15.32	–	–	–
p(CBT)-2	232	18.28	189	-14.69	–	–	–
p(CBT)-3	224	21.54	182	-17.24	–	–	–

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Table 2 Tensile, flexural and short beam shear data

	Tensile modulus (GPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)	Shear strength (MPa)
p(CBT)-1	18.7	321	16.7	446	38.5
p(CBT)-2	23.3	324	17.3	467	44
p(CBT)-3	12.3	277	15.4	305	21.1

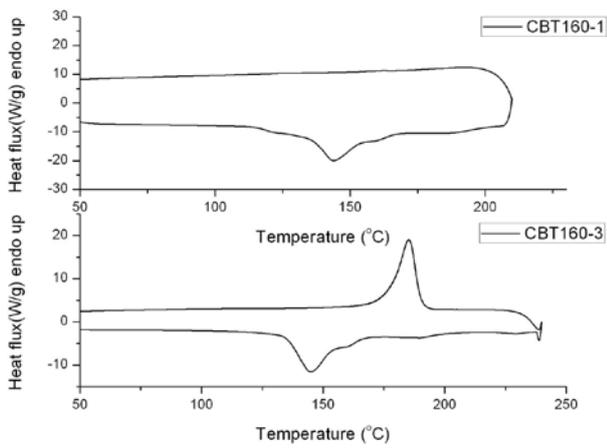


Fig.3 The DSC thermograms of CBT160-1, 3

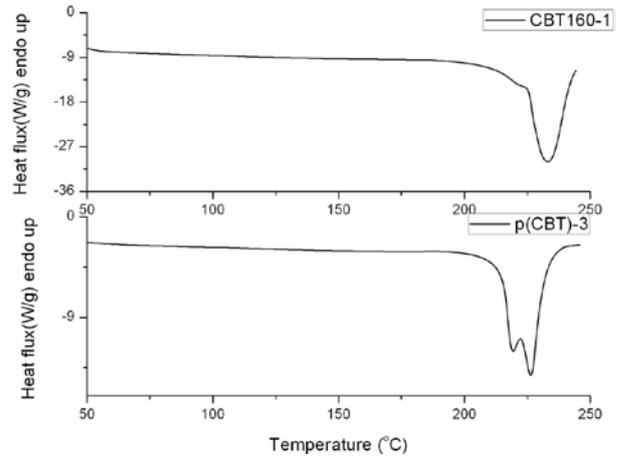


Fig.4 The second heating scan of CBT160-1, 3

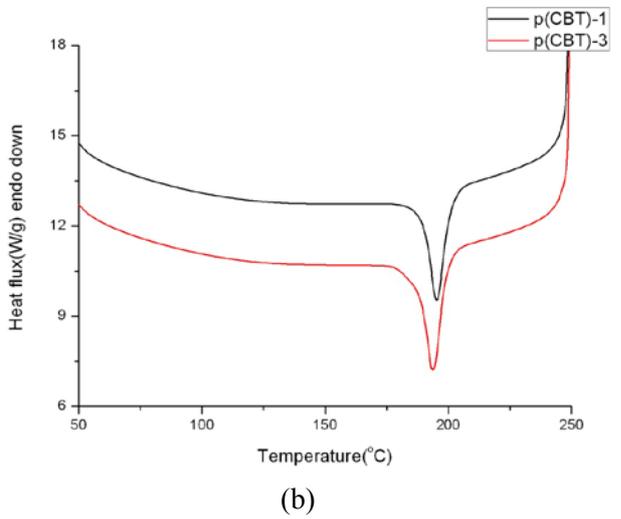
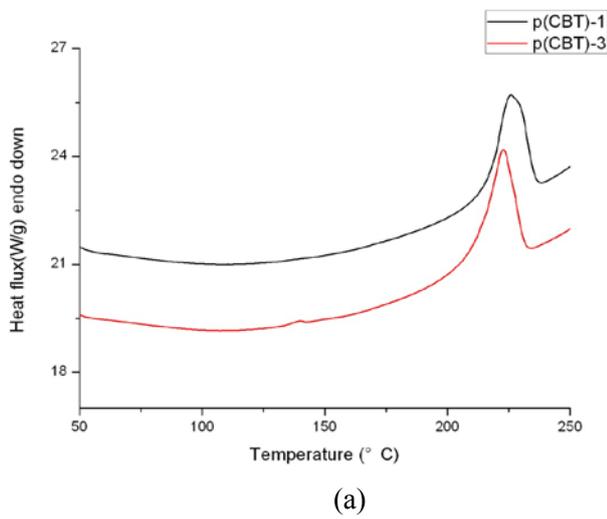
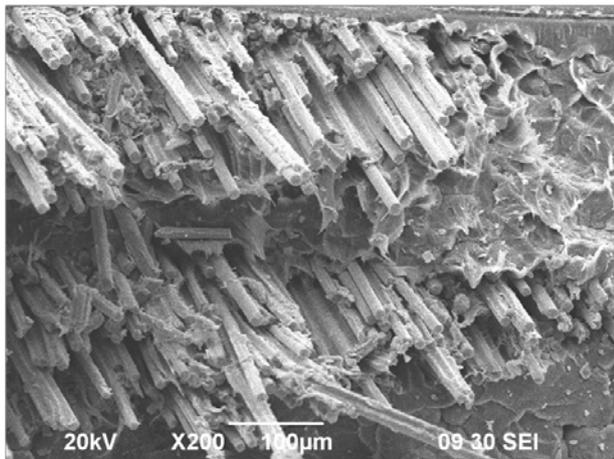
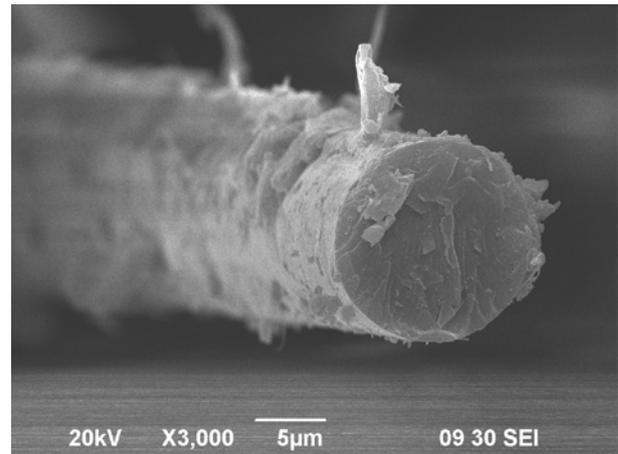


Fig.5 DSC thermograms of pCBT -1, 3



(a)



(b)

Fig.7 SEM photos of fracture surfaces, fiber impregnation

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