Influence of high temperature on the flexural properties of GF/pCBT laminates and their fusion-bonded joints

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ABSTRACT

The glass fiber reinforced poly cyclic butylene terephthalate (GF/pCBT) composite laminates and their fusion-bonded joints were prepared at appropriate polymerization temperature. The connection form of joints was designed and optimized. A series of bending test were conducted to research their mechanical behavior at different temperature. Experimental results showed that flexural properties of laminates and joints decreased as temperature increased. The temperature sensitivity of specimens change at a temperature between 50°C to 75°C as a result of the glass transition of the pCBT matrix. Moreover, the failure modes of GF/pCBT composite joints were investigated at room and high temperature. In addition, the specimens suffered by different high temperatures ranging from 25°C to 200°C were cooled and then tested at room temperature. The results indicated the flexural strength of laminates was nearly a constant after high temperature, and increased slightly when the temperature is higher than 175 °C. The flexural strength of fusion-bonded joints was not affected after suffered high temperature.

Keywords: poly (cyclic butylene terephthalate); polymerization temperature; fusion-bonded joint; high temperature; flexural property.

1. Introduction

Fiber reinforced thermoplastic composites are attractive for use in a wide range of engineering applications because of their improved toughness, impact resistance, rapid fabrication cycle, low manufacturing cost and recoverability of its scrap ^[1]. The superior performance have ensured these composites feature in various fields such as aerospace, marine, automobile and sport industries, and increased substantially. However, one of the main issues that are frequently raised in using thermoplastics as polymer matrices is their melt viscosities which are in the range of 100-10000 Pa.s ^[2, 3]. This creates serious problems in wetting and impregnation of reinforcing fibers, resin flow during fabrication and removal of entrapped air, and therefore thermoplastic composites have the problems involved in fabricating large size and primary load-carrying structures.

Since the advanced cyclic butylene terephthalate (CBT) composites are becoming a viable alternative to traditional engineering materials as a high mechanical strength. CBT resin has a extremely low viscosity like water, when being heated (0.017Pa.s, 190 °C) ^[4, 5]. It can be transformed into poly cyclic butylene terephthalate (pCBT) via entropically driven ring-opening polymerization in a short time. During these processing, there are no gas and volatile organic compound released ^[6]. The pCBT composites with high fiber volume fraction can be prepared using

various processing methods available to thermosettings or thermoplastics because of the low CBT melt viscosity^[7, 8]. As a high strength thermoplastic composite, fiber reinforced pCBT composites are being applied more broadly due to excellent mechanical property. A few researchers focus on the mechanical properties of glass fiber (GF) reinforced pCBT at room temperature^[9-11]. The main obstacle to utilizing these materials as structural members is the general lack of performance data in extreme conditions. At present, research investigating the effects of high operating temperatures on mechanical strength of GF/pCBT composite structures is still lacking. Thus, it is important and necessary to acquire some mechanics performance data for high temperature engineering applications.

Based on the aforementioned statements, this article investigates the flexural properties of GF/pCBT composite laminates and fusion-bonded joints with 70% fiber volume fraction prepared via in situ polymerization of CBT and subjected to temperatures ranging from room temperature (about 25°C) to 200°C. A series of flexural tests have been performed and the failure mode was observed, to determine the influence of elevated temperatures on the mechanical behavior of material.

2. Experimentation

2.1 Materials

Cyclic butylene terephthalate oligomers (CBT 100 resin) used in this study were supplied by Cyclics Company, American. Before processing, the CBT particles were dried overnight at 110°C to remove residual moisture, which could interfere with the polymerization reaction^[12, 13]. The tin catalyst PC4101 was purchased from Canton Yuansu Chemical Corporation, China. The isopropanol was obtained from Tianjin Dekai Chemicals Business Ltd., China, as the solvent of PC4101. The unidirectional glass fabric with surface weight density 300g/m² was purchased from Yixing Fuxing Glass Fiber Ltd., China.

2.2 Sample preparation

Glass fiber reinforced poly CBT composites with high fiber content were manufactured by combining vacuum assisted resin transfer molding and compression molding, the processing sequence is shown in Fig. 1^[14]. Since impregnating the glass fabric will be hampered by the high viscosity of PBT resin melt, the catalyst and CBT resin were sequestered. The catalyst was attached to the surface of fabric by dissolved in the isopropanol solution, then was dried in a oven for about 1h at 130°C. The presulfided glass fabrics were put into a stainless steel mold cavity of 300×200×2.4mm³. The CBT oligomers were heated to the best polymerization temperature. The mold and the injection tube were also heated the same temperature. The ball valve was opened after the mold vacuumized, then the resin was injected, and the glass fabric was impregnated. During this time, in situ polymerization already started on the surface of fiber. The mold was applied 4MPa pressure by the hot press for 20 min, and was cooled to the best crystallization temperature for 10 min. Finally the mold was cooled to room temperature outside the hot press, and the GF/pCBT composite was demoulded. GF/pCBT composite laminates with groove coupling were butted, and were heated to 240°C in a vacuum mould for 30min, and cooled to 190°C for 10 min, then the fusion-bonded joint was demoulded after natural cooling.

Fig.1 Preparation of GF/pCBT composite laminates and their fusion-bonded joints

2.3 Material characterization

2.3.1 DSC analysis

Differential scanning calorimetry investigations used to measure crystallinity were performed on DSC Q2000 device (TA Co., America). Experiments were run with samples ranging from 7-8 mg under nitrogen to prevent moisture and oxidative degradation, and the specimens were subjected to the heating rates of 10°C/min from room temperature to 250°C [15]. The degree of crystallinity is calculated from the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (1)$$

Where ΔH_m is the melting enthalpy of the polymer, and ΔH_m^0 is the melting enthalpy of the fully perfect crystal of PBT, which is found in literature to be 142J/g [16].

2.3.2 Mechanical properties

One of the most common experiments to characterize materials in mechanical properties is the three point bending test [17]. Different polymerization temperatures and fibers volume fraction GF/pCBT composite specimens were manufactured for measuring mechanical strength and the flexural tests according to ASTM-D790 were carried out using Instron 4505 electron universal testing machine at room temperature [18, 19]. As in the flexural tests, there is no standard for static bending at high temperature, so the same standard for laminates at room temperature was used. The high temperature flexural tests of GF/pCBT composite laminates and bonding joints were performed on Instron 5500R testing machine at cross-head speed of 2mm/min and 4mm/min respectively. The connection forms of GF/pCBT composite laminates containing 12 plies of 0° unidirectional glass fabric are shown in Fig. 2, and a single layer thickness is 0.2mm. The geometry size of bonding joints is 190mm length × 15mm width × 2.4mm thickness. There are five specimens for each kind of test [20].

Fig. 2 Connection form and geometry of GF/pCBT composite joints

3. Results and Discussion

3.1 Influence of polymerization temperature on crystallinity and flexural strength

The pCBT and its glass fiber reinforced composite specimens were prepared at different polymerization temperatures (210°C, 220°C, 230°C, 240°C). Fig. 3 shows typical DSC thermograms of pCBT from the heating and cooling scans. From the DSC measurements, the melting point (T_m) of polymer is taken as the maximum of the endothermic melting peak from the heating scans, whereas crystallization temperature (T_c) is considered to be the maximum of the exothermic peak of crystallization from the cooling scans, and the percent of crystallinity (X_c) for pCBT is calculated from formula (1), as shown in Table 1. Table 1 also lists the flexural properties of pCBT samples.

Fig. 3 DSC thermogram of pCBT polymerized at different temperatures (a) heating (b) cooling

The T_m of pCBT due to the polymerization of CBT at different reaction temperature is around 225°C, which is consistent with the melting point of commercial PBT. The crystallization temperature of pCBT is detected at approximately 191.4°C when the reaction temperature of CBT is between 220°C and 240°C. The T_c of pCBT is 185.6°C at the polymerization temperature of 210°C. This can be attributed to incomplete polymerization of CBT at relatively low temperature, so that the little oligomer of small molecular weight constituent remains and the T_c is slightly reduced. The melting enthalpy and crystallinity of PCBT increase with polymerization temperature when the latter are in the range of 210°C~230°C, leading to the flexural strength enhanced. Owing to the CBT molecules linked together chemically to form other polymer at high temperature, the DSC curve

occurs two endothermic melting peaks at the polymerization temperature of 240 °C, and the crystallinity and flexural strength have no obviously increase^[21]. Based on the above, the polymerization process parameters of CBT can be determined. The optimal ring-opening polymerization reaction temperature of CBT is 230 °C, and the crystallization temperature of pCBT is 191 °C.

Table 1 DSC and flexural properties for pCBT specimens

Polymerization temperatures(°C)	T _m (°C)	ΔH_m (J/g)	X _c (%)	T _c (°C)	Flexural strength(MPa)
210	226.4	51.1	36.0	185.6	80.8
220	225.9	54.4	38.3	191.8	93.4
230	224.8	56.9	40.1	191.2	102.6
240	226.0	57.5	40.5	191.3	102.9

3.2 Influence of adhesion structure on flexural properties of joints

The GF/pCBT fusion-bonded joint specimens with three different schemes were manufactured to study their flexural behavior. Fig. 4 shows the mechanical properties comparison of pCBT resin, GF/pCBT composite laminates and fusion-bonded joints. The flexural strength of joints are significantly higher than the resin, especially the joint B exceeds joint A and joint C, and the joint C is the minimum in bending performance. The flexural strength of GF/pCBT joint B can reach 88.6% of its composite laminates.

Fig. 4 Flexural strength comparison of pCBT resin and GF/pCBT composite laminate and joints

The flexural fracture images of the fusion-bonded joints under study are shown in Fig. 5. In this case, the failure modes of joint A and joint B are both compression failure of the matrix near surface and tensile failure of the matrix near bottom^[22]. However, continue to increasing the connection layers, it is conducive to unavoidably interface defects during the fabrication of composite joints. The interface delamination, fiber damage and matrix failure will happen to joint C simultaneously, while the flexural strength exhibits decreasing trend.

Fig. 5 Failure modes of the fusion-bonded joint A, B and C

3.3 Flexural properties of GF/pCBT composites at and after high temperature

Three point bending tests were performed every 25°C from room temperature(25°C) to 200°C. The experimental setup for hypothermal flexural tests using an environmental chamber is shown in Fig. 6. The results of mechanical behavior of laminate specimens are plotted in Fig. 7 with linear curve fits, which shows the effect on flexural strength of GF/pCBT composite at and after high temperature. As expected, the flexural mechanical properties have no obvious variation when the test temperature is 50°C. However, the flexural strength decreases with increasing temperature at higher temperature. Experimental results shows that flexural strength is more temperature sensitive between 50°C and 75°C than between 75°C and 200°C, in view of the fact that the glass transition temperature of pCBT matrix is around 68°C^[23]. Compared with 50°C, the flexural strength decreases by 34.1 percent at 75°C. The flexural strength decreases from 621MPa at 75°C to 95MPa at 200°C.

Fig. 6 Experimental setup for hypothermal three point bending test

With increasing of temperature in the range of 25°C~175°C, the flexural strength of GF/pCBT composites have no obvious change after heating to those temperature and cooling to room temperature. Nevertheless, there is a 6.2 percent increase over untreated laminate specimens when the heating temperature is higher than 175°C and cooling to 25°C. Residual thermal stress is created inside the material in liquid composite moulding process. Now the pCBT resin softened above 175°C, this is equal to annealing treatment of GF/pCBT laminated plates. Since pCBT

polymer molecular chains form slowly after effective relaxation, eliminating residual stress, reducing the linear expansion coefficient, GF/pCBT composites enhance their mechanical properties.

Fig. 7 Flexural properties of GF/pCBT composites at and after high temperature

3.4 Flexural properties of GF/pCBT composite joints at and after high temperature

The fusion-bonded joint B with the matrix of pCBT and glass fiber reinforcement was selected to study the high temperature flexural properties on account of its excellent mechanical performance at room temperature. The range of measuring temperature and test points of joints are the same for the above high temperature testing of laminates.

Fig. 8 Flexural properties of joint B at and after high temperature

Fig. 8 summarizes the results of the measurement of joint B specimens at increasing temperatures, including flexural strength at and after high temperatures. The flexural strength of GF/pCBT composite fusion-bonded joint drops by 38 percent from 50°C to 75°C, which causes by glass transition temperature of pCBT, and its descending rate has 3.9 percent greater than the

degradation of laminates. The joints were manufactured by the fusion bonding technique of pCBT resin, thus the flexural properties of joints are affected greatly by the mechanical behaviors of matrix. The flexural strength of pCBT matrix decreases dramatically when the operating temperature exceeds its glass transition temperature ^[24]. However, the downward trend of flexural strength has slowed when the ambient temperature is between 75°C to 175°C. The flexural strength of joints decreases rapidly over 175°C to 47MPa at 200°C, and the joint specimens has basically no bearing capacity.

Fig. 8 also shows that changing the temperature has no effect on the flexural strength of joints when the fusion-bonded joint specimens were measured after high temperature between 25°C to 200°C and cooling to room temperature. In the preparation process of joints, the GF/pCBT composites had been second heated to 240°C, over the melting point of pCBT resin, and its thermal residual stress had relieved, so that the flexural properties of GF/pCBT composite fusion-bonded joints are almost a constant after high temperature.

The failure mode of GF/pCBT fusion joints is fiber damage and matrix failure of composites at room temperature to 150°C, like the joint B as shown in Fig. 5. The vicat softening temperature of pCBT polymer is around 175°C, therefore, the fusion-bonded joints begin to appear slight delamination damage at 175°C ^[25]. Then the main failure mode becomes interface delamination failure of bonding region at 200°C. Fig. 9 shows the typical failure modes of fusion-bonded joints at 175°C and 200°C.

Fig. 9 Damage patterns of GF/pCBT composite joints at high temperature

The fracture morphology of joints was examined by SEM. Fig. 10 shows typical SEM images of the GF/pCBT fusion joints. Fig. 10a shows the fiber pull-out and fracture near the bottom surface. Fig. 10b shows the compressed resin and concentrated fiber near the top surface. Fig. 10c and 10d show the interface delamination failure at room temperature and 200°C, respectively. At room temperature, the surface of resin is rough, that the brittle fracture of matrix occurs. When the test temperature is 200°C, the little resin coats the fiber. In this state, the cohesive failure of matrix occurs, and the adhesion of resin weakens, so the delamination failure becomes the principal failure mode of joint.

Fig. 10 SEM micrographs of the GF/pCBT fusion joints: (a), (b) and (c) at room temperature; (d) at 200 °C

4. Conclusion

The temperature parameters in the process of preparation were determined via thermal analysis. GF/pCBT composites and their fusion-bonded joints were manufactured to study its flexural properties subjected to temperatures ranging from room temperature (25°C) to 200°C.

The bending bearing capacity of fusion-bonded joints increase with increasing connection layers within limits. Excessive interface may lead to several defects at the junction. Fiber damage, matrix failure and interface delamination occurs simultaneously, and the flexural strength decreases. At high temperature, the flexural strength of GF/pCBT laminates and their joints decrease with increasing temperature, and it is extremely temperature sensitivity of them between 50°C to 75°C due to the glass transition of the pCBT matrix. The flexural strength of joints decreases rapidly over 175°C, possibly as a result of the softened pCBT polymer into adhesive layer. GF/pCBT composite laminates and their joints are temperature independent material after high temperature between 25°C and 175°C and cooling to 25°C. After 200°C and cooling to room temperature, the mechanical properties of joints remain stable, and yet the flexural strength of laminates increase owing to softening annealing of composites.

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