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Effect of fiber surface modification on the lifetime of glass fiber reinforced polymerized cyclic butylene terephthalate composites in hygrothermal conditions

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ABSTRACT

Mechanical performances of polymerized cyclic butylene terephthalate (pCBT) matrix, glass fiber reinforced pCBT (GF/pCBT), and nano-silica modified glass fiber/pCBT composites (nano-GF/pCBT) in hygrothermal condition were investigated. All the materials were aged in hygrothermal environments for up to three months, and then their mechanical strength degeneration ratio (*SDR*) was calculated. To study the aging effect of temperature, specimens with and without nano-silica modification were tested in temperatures ranging from 298 to 500 K. Differential scanning calorimeter (DSC) test, dynamic mechanical analysis (DMA), and fiber pull-out test were adopted to complement the experimental results. It is found that all the *SDR*-time curves follow the linear relationship in hygrothermal environment, while *SDR*-temperature curves follow a bilinear relationship due to the effect of glass transition temperature (T_g) of the matrix. Fibers modified by coating nano-silica on the surface could decrease *SDR* of the composites. This is due to the fact that the fillers on the fiber surface could resist the movement of pCBT molecular chain and diffusion of water molecules in aging conditions. The fiber pull-out test verifies that the interface strength between fiber and matrix is enhanced by the modification.

1. Introduction

Fibrous composites are increasingly being used in many applications owing to their desirable properties such as high strength to weight ratio, high stiffness to weight ratio, and superior corrosion resistance. Unfortunately, both thermosetting and thermoplastic resins used as matrix in fiber reinforced plastic composites (FRP) are susceptible to humidity and temperature when operating in real engineering fields [1]. Mainly due to the uncertainty on the long term reliability of polymer composites, the wider applied scope of composite materials is limited. Thus, it is necessary to investigate the hygrothermal aging behavior of the composites especially in terms of finding out an effective approach by which their long-term mechanical performance can be enhanced.

Numerous works have studied the fiber modification effect on the mechanical properties of FRP. Generally, the modification methods adopted in these works are composed of two approaches [2–4]. Chemical modifications are carried out mainly by treating the fibers with chemical reagents such as coupling agents, while the common physical method used in the modification is heating. Even though it has been verified in these researches that the overall mechanical performance of the composites can be enhanced by the treatments, the strength of the fiber itself is actually reduced mainly due to the damage to its microstructure. Many publications have investigated the mechanical and thermal characterization of FRP under different hygrothermal conditions. The effects of moisture and applied temperature on mechanical properties of FRP are investigated in the literature [5–14]. In detail, Bajracharya et al. [5] reviewed the mechanical properties and durability of glass fiber reinforced recycled mixed plastic waste composites. Information on the behavior of thermoplastic composites at different environmental conditions such as elevated temperature and ultraviolet rays is summarized. Xu et al. [6] performed gravimetric experimental studies on the moisture diffusion process in pultruded FRP composites exposed to the vapor environmental aging condition as well as water immersed condition at temperatures of 20 °C and 40 °C. Their results indicated that high temperature can speed up the moisture diffusion rate, and the moisture equilibrium contents were mainly governed by the humidity of the aging environment. Narendar et al. [7] investigated the coir pith epoxy composites hybridized with nylon fabric/epoxy resin by hand layup technique. Aging of composite panels in moist environment was investigated. Sawpan et al. [8] immersed the FRP composite rebar in alkaline concrete environment for different durations at 60 °C. They found that moisture absorption was a critical factor that controlled the thermal and mechanical properties of GFRP rebar.

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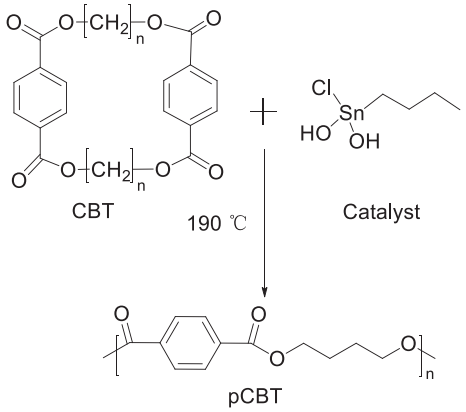
Mohd Ishak et al. [9–11] have done many works on the hygrothermal aging properties of fiber reinforced polymer composites. Tajvidi et al. [12] and Ellyin et al. [13] have investigated the effect of temperature on different composites. Temperature effect on the mechanical properties of glass fiber/PBT (GF/PBT) specimens was studied by Cavdar et al. [14]. Even though some references have verified that the thermal stability of polymers can be enhanced by nanoparticles [15,16], studies on nano-particle modified polymers aiming to enhance the anti-aging property are still limited.

Cyclic butylene terephthalate (CBT) oligomers have the structure of big-ring paucity of polyester with molecular weight $M_w = (220)_n$ (with n = 2–7) g/mol [17]. The melt viscosity of CBT thermoplastic resin is as low as 17 mPa, which makes fiber bundles easily impregnated during the manufacturing process [18]. This advantage provides opportunities to produce fiber reinforced CBT composites with perfect impregnation of fibers using various processing methods that avail of thermoset or thermoplastic resin [19–22]. Meanwhile, the low melt viscosity of the resin further makes CBT micro/nano-composites with excellent dispersion of fillers possible. Scheme 1 shows the ring-opening polymerization reaction process in the presence of S_n-based catalyst. The generated product from CBT resin is polymerized poly(butylene terephthalate), which will be taken as pCBT in this paper. The objective of the present paper is to investigate the effect of fiber surface nano-silica modification on the lifetime of CBT based composites used in the aging environment. Specimens that include pCBT matrix, GF/pCBT and nano-silica modified GF/pCBT composites were aged in hygrothermal conditions for up to 90 days, and then mechanical tests including bending and compression were performed. Additionally, to obtain the relationship between test temperature and hygrothermal aging duration, mechanical tests on the specimens were performed in temperature alone. Afterwards, DSC, DMA and fiber pull-out test were respectively carried out to examine the thermal performance and interface property between fiber and matrix.

2. Experimental details

2.1. Materials

The polymer used as matrix is one-component CBT-100, delivered in granule form by Cyclics Corporation. Tin-based catalyst butylchlorodihydroxytin (PC-4101) with the molecular weight of 245.29 is selected. This compound is an ester catalyst with high catalytic activity and suitable for esterification or polycondensation reactions with temperatures ranging from 210 °C to 240 °C. Unidirectional E-glass fiber cloth (EDW-800) with surface weight of 500 g/m^2 is used as the reinforcement in the composites. Hydrophobic nano-silica (DNS-3) with particle diameter between 5 and 15 nm is used in the experiment. Note that all the materials are used as-received without any further treatment. Because moisture could interfere with the polymerization reaction, all the materials were dried for 10 h in a vacuum oven at 110 °C before processing.



Scheme 1. Ring-opening polymerization reaction of CBT resin.

2.2. Manufacturing process

pCBT casts were prepared by the casting process with CBT resin to catalyst mass ratio 100:0.6. Vacuum-assisted hot-pressing process (VAPP) was used to fabricate the composites in this work. Two categories of composite laminates were prepared via VAPP: GF/pCBT composites and its nano-silica modified fiber reinforced laminates. As pretreatment, glass fibers should be soaked for 1 day into two kinds of isopropanol aqua solution which respectively contained 0.6 wt.% catalyst and 2 wt.% nano-silica, and catalyst (0.6 wt.%) alone. It should be mentioned that all the percentages are relative to the weight of resin used in the experiments. To obtain good dispersion of the solution, the mixture was stirred by a magnetic stirrer for 2 h, and then dispersed in an ultrasonic agitator for 1 h at room temperature. Then the system needed to be dried in a vacuum oven at 140 °C to remove isopropanol aqua and leave the catalyst and/or nano-silica on the fiber surface. The diagram of the VAPP setup is shown in Fig. 1. The hot-pressing machine can provide the heat and pressure to the mold during the manufacturing process. A steel mold was used as the container in which the curing of CBT resin can take place. This steel mold contains a top sheet, bottom sheet, and intermediate frame inside of which the as-prepared glass fibers were placed. The top sheet comprised two ports, one as the resin inlet and the other one as outlet. A rubber seal ring was placed between the top and bottom sheets to maintain the vacuum. In order to remove the air from the mold before injection, the valve was shut and then the mold was vacuumed for approximately 15 min. Both the two composites were processed non-isothermally: 230 °C for 1 h and 190 °C for another hour. The injection started when the temperature inside the mold reached 230 °C, and then demolding when the mold cooled to room temperature.

2.3. Aging conditions

All the specimens were aged in the artificial climatic chambers which could provide the humidity and temperature at the same time. In our experiment, the relative humidity was set at 60% and 90%, while the temperature was respectively set at 50 °C, 60 °C, 70 °C, and 90 °C. It should be noted that the hygrothermal aging duration was up to 3 months, and at least 5 specimens were taken out from the chambers for the next mechanical tests each week. Another group of specimens was tested to evaluate the effect of high service temperature on their mechanical performance. Temperature conditioning for the experiment was performed using an electrothermal furnace (with a temperature range up to 300 °C/573 °F). The conditioning schedules were 5-min at each selected temperature, and it was assumed that the humidity in the furnace was almost zero at set temperatures. Mechanical tests were carried out with the conditioned specimens at six selected temperatures (25 °C, 70 °C, 80 °C, 150 °C, 180 °C and 220 °C, respectively).

2.4. Mechanical tests

Compression and three-point-bending tests were carried out to determine the mechanical strength of the as-prepared and aged casts, GF/pCBT and nano-GF/pCBT laminates, respectively. Test specimens were cut from the prepared square laminate by a low-speed diamond saw blade cutting machine in accordance with ASTM standards. The dimensions of the specimens are listed in Table 1. According to the test results, the strength degeneration ratio (*SDR*) of the specimen was calculated by Eq. (1),

$$SDR = \frac{S_t}{S_0} \tag{1}$$