AGING OF CARBON FIBER/BIS-MALEIMIDE COMPOSITES IN OXIDATIVE CONDITIONS

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Abstract

Bis-maleimide (BMI) resins are widely applied, particularly in polymer-matrix composites for heat-resistant fields, due to their excellent thermal and mechanical properties. The thermal resistance is crucial for the applications of carbon fiber reinforced BMI composites in aerospace fields. The thermo-oxidative aging and its effects on the mechanical properties of carbon fiber reinforced BMI composites were investigated by scanning electron microscopy (SEM) with the combination of flexural strength test and inter-laminar shear strength (ILSS) test at 150°C. The results indicated that the mechanical properties of carbon fiber/BMI composites were affected significantly by testing temperature. SEM results showed that the good adhesion of fiber and matrix resulted in the better mechanical properties. However, some amorphous area of BMI resin were motivated for the internal energy increased at high temperature (150°C). Therefore, the matrix resin showed viscoelastic behavior that resulted in the remarkable dependence of mechanical properties of the composites on temperature, which led directly to the lower flexural strength and ILSS at 150°C.

1 Introduction

Carbon fiber composite materials with high temperature *bis*-maleimide (BMI) resin systems as the matrix component are currently being used on structures for both military and civilian aircraft [1]. Actual application of these materials, however, will depend on their long-term durability under aggressive environmental conditions and high operating temperatures. For example, the operating temperature of the high-speed civil transport aircraft is expected to be around 150 ℃ [2]. A major concern with these materials is the effect of long-term exposure to service environments on their physical and mechanical properties. The extent of mechanical property deterioration as a consequence of thermal-oxidative aging has been widely covered; examining properties of flexural strength, modulus and ILSS [3-5]. There were many researchers investigated the effect of thermal aging on the properties of carbon fiber composites [6-8], most of which were carbon fiber reinforced epoxy resin matrix composite materials.

In this paper, a carbon fiber reinforced BMI composite was evaluated to determine the effect of exposure to a high temperature environment on its flexural and interlaminar-shear strengths (ILSS). The flexural and ILSS properties were tested at 150°C in order to determine the effect of temperature and aging time on the mechanical properties of carbon fiber/BMI composites. The failure modes and microstructures of samples were investigated using a Scanning Electron Microscope.

2 Specimen preparation and experimental methods

2.1 Preparation of composite laminates and specimens

The unidirectional composites, consisting of 16 prepregs (supplied by Beijing Institute of aviation, China) measuring 300 *mm* ×300 *mm* with the fibers in the 0°C direction, were placed in a vacuum bag in an autoclave and cured by heating at 1 *°C/min* to 150 *°C* and then holding for 4 *h* at the pressure of 650 *KPa*. The resin volume fraction in all the laminates was controlled to be close to 0.40. The properties of carbon fiber showed in Table.1. All of the specimens were cut from the composite laminates according to the mechanical tests.

Table.1 Summary of material properties of commercial carbon fibre (CCF300)

Material properties	Symbol	Data
Density	ρ_f	1.78 g/cm^3
Average fibre diameter	d_f	7μm
Elastic modulus	E_f	233 GPa
Tensile strength	σ_{fu}	3864 MPa
Failure strain in tension	γ_{fu}	1.69%

2.2 Thermal aging process

These composites processed a thermal-oxidation aging treatment as follows. Total of 192 specimens for evaluating mechanical properties were exposed in isothermal conditions at 150 ^{o}C for various periods up to 1000 *h*.

2.3 Mechanical tests

The flexural properties were determined by three-point bend test, based on Chinese standard GBT3356-1999 with a 64 *mm* span between the supports, the radius of pusher 5 *mm* and the loading rate 2 *mm/min*. The test samples were of length 80 *mm*, width 12.5 *mm*, and thickness 2 *mm*. 6 samples were tested after each aging time. The ILSS properties were based on Chinese standard JCT773-1996. The test samples were of length 20 *mm*, width 6 *mm*, and thickness 2 *mm*. The span was 10 *mm*, the radius of pusher 2 *mm* and the loading rate 2 *mm/min*. The holder and pusher for measuring flexural strength and ILSS were presented in Fig.1.

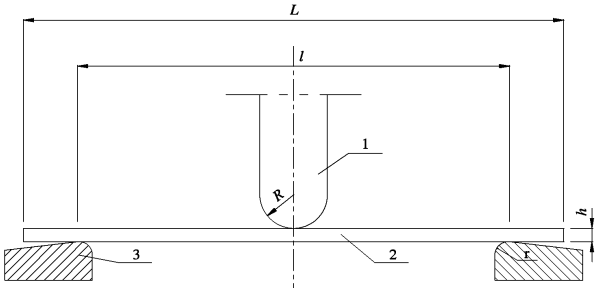

Fig.1. Illustration of the loading methods for flexural and ILSS tests

1—Pusher；2—Specimen；3—Support

For flexural test: L=80mm, l=64mm, R=5mm, r =2mm and h=2mm;

For ILSS test: L=20mm, l=10mm, R=2mm, r =2mm and h=2mm.

2.4 Examination in scanning electron microscopy (SEM)

The failure modes and microstructures in the composites were investigated with a scanning electron microscope (QUANTA-200 SEM). The fracture surface was sputtered with gold before observation. A working distance was about 10 *mm* at 15 or 20 *kV*.

3 Results and Discussion

Fig. 1 and Fig. 2 show the flexural strength and ILSS of carbon fiber reinforced BMI composite materials.

When the mechanical strengths were measured at high temperature (150°C), some chains of BMI resin were motivated for the internal energy increased, especially for the chains within the amorphous area. Therefore, the matrix resin showed viscoelastic behavior, and it is naturally expected that the carbon fiber reinforced BMI composites should show viscoelastic behavior that resulted in the remarkable dependence of mechanical properties of the composites on temperature.

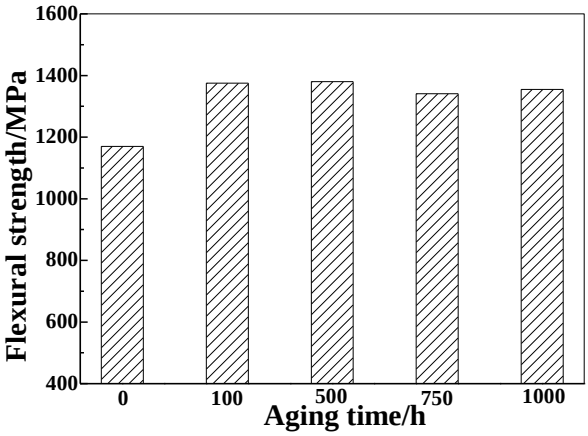

Fig.1. Flexural strength of carbon fiber/BMI composites aging up for 1000h

Figure 1 showed that the flexural strength increased at the internal aging time and then kept almost constant with further increase aging time up to 1000h.This was attributed to the post-curing of BMI resin during the thermal-oxidative aging at 150°C, which could increase the crosslinking density of the polymer matrix. It was reported that BMI composites, as most of other composite systems, only reach around 95% completion during the standard curing cycle; during the initial aging periods, the materials are actually being post-cured, resulting in further crosslinking of the resin, causing the fracture toughness to increase[9]. After aging 500h, the post-curing has basically finished, and the decomposion or degradation occurred subsequently, which led the flexural strength decrease with further thermal aging.

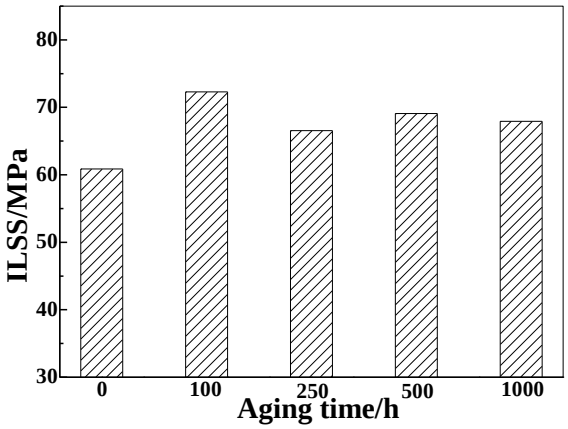

Fig.2. ILSS of carbon fiber/BMI composites aging up for 1000h

The specimen for inter-laminar shearing is a short, flat laminate loaded in 3-point bending with a narrow span with the intent to minimize flexural stresses but to maximize in-plane shear stresses. Therefore, ILSS refers to the maximum shear stress existing between layers of laminated material, reflecting the bond strength between the layers within internal composites; and it depends on both the cohesive strength of polymer matrix and the interfacial strength of reinforcer(fibers)-polymer.

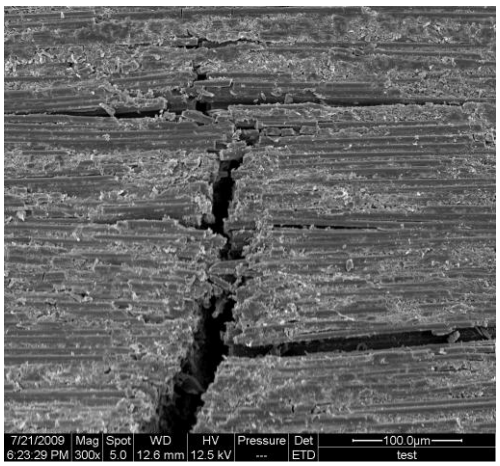

Fig.3. SEM of the flexural sample of carbon fiber/BMI composites before aging

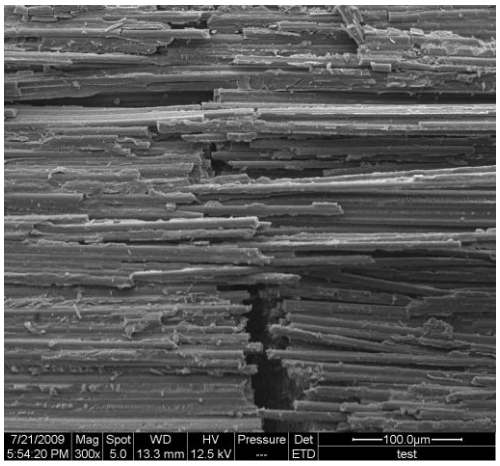

Fig.4. SEM of the flexural sample of carbon fiber/BMI composites after aging 1000h

Figure 2 indicated that the ILSS increased via post-curing with the aging time increased until 500h and decreased until the aging time for 250h, then kept almost constant with aging time further increased. This was attributed to the deteriorations between the reinforcer/resin interfaces caused during the thermal-oxidative aging. When the ILSS specimens were heated up to 150°C, these deteriorations could lead to the debonding or interfacial damage due to the various thermal expanding coefficients between carbon fibers and BMI resin that yielded a strong internal stress. Further increasing aging period, the internal stress generated was released by the viscoelastic behavior of the matrix resin at 150°C for more than 250h.It is show that the resin matrix has significantly viscoelastic behavior (Fig.3 and Fig.5) before aging. There are many resins between the fracture fibers and this phenomenon disappears after aging 1000h.

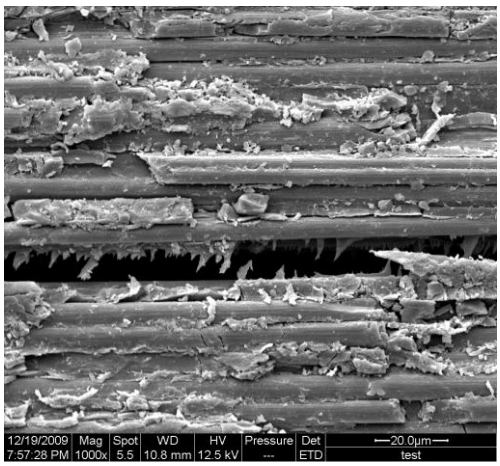

Fig.5. SEM of ILSS of carbon fiber/BMI composites before aging

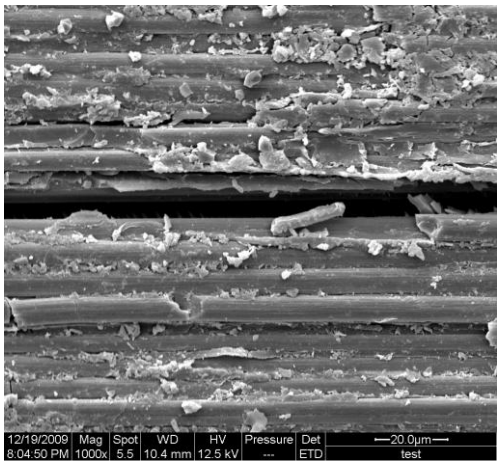

Fig.6. SEM of ILSS of carbon fiber/BMI composites after aging 1000h

The composite presented a tough fracture for the flexural test at 150°C for the flexural specimens didn't break into two due to the viscoelastic behavior of matrix resin, as shown in Figure 3 and 4. SEM micrographs of flexural samples also indicated that the matrix resin, BMI, was tightly adhered to the carbon fibers without breaking into two parts, further indicating that the composites had stronger interfacial adhesion.

Figure 5 and 6 is the micrographs of ILSS of carbon fiber/BMI composites before and after aging 1000h, respectively, which showed that some broken resin fragments remained on the delaminated surfaces, confirming that the cohesive fracture of matrix resin occurred because the matrix resin at 150°C had more motivated chains that led to more viscoelatic behaviors for easy conformation changing. While SEM micrograph in Figure 5 displayed that no resin fragment was observed on the surface delaminated surfaces, implying that the interfacial fracture also occurred during the ILSS test at 150°C because of high internal stress formed by the mismatch of thermal expansion coefficients of fiber and resin after long-time thermal-oxidative aging. In sum, the delamination model of ILSS test at 150°C confirmed the cohesive strength of matrix resin and interfacial strength between fiber and BMI resin at aging 1000h was worse than that before aging.

4 Conclusions

Flexural strength and ILSS testing followed by SEM analysis were performed in order to determine the effects of thermal-oxidative aging on the mechanical properties of carbon fiber reinforced BMI composites. The results indicated that carbon fiber reinforced bis-maleimide composites has good mechanical strengths at 150°C after aging up to 1000h. The slight decrease of flexural strength and ILSS tested at 150°C were attributed to the decomposition of BMI resin on the surface of composites and the visoelastic behavior of BMI resin. SEM shows that there are perfect interfacial bonding between fibers and resin matrix. All these implied that the composites had excellent properties suitable for the application in aerospace field.

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