J Mater Sci (2010) 45:399–404
DOI 10.1007/s10853-009-3954-1

Effects of hydrothermal aging on glass–fiber/polyetherimide (PEI) composites

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Received: 13 August 2009 / Accepted: 5 October 2009 / Published online: 20 October 2009

Abstract The moisture absorption behavior and the influence of moisture on thermal and mechanical properties of glass–fiber/polyetherimide (PEI) laminates have been investigated. The laminates were exposed to hydrothermal aging at two different temperatures and high moisture rates. The properties of as-received and hydrothermally aged samples were compared. The hydrothermally aged laminates contained a large amount of moisture which caused decrease in the glass transition temperature and deterioration in mechanical properties (interlaminar shear strength, flexural modulus, bearing strength, etc.). Fractographic analysis revealed interfacial debonding as the dominant failure mechanism, indicating a strong influence of water degradation on fracture toughness results. Alterations in viscoelastic properties of glass/PEI composite which was exposed to hydrothermal aging were analyzed with the dynamic mechanical thermal analysis (DMTA) method. DMTA tests give evidence of plasticization of the PEI matrix.

Introduction

Various types of polymer–matrix composites are being considered for use in different fields of application, ranging from sporting goods to structural materials for automotive, nautical, and aerospace industries, where the long-term properties are of primary importance [1–3]. In such applications, the composites are exposed to harsh and variable environments ranging from variations in temperature and exposure to moisture, including elevated temperature immersion and "hot-wet" exposures.

The development of a comprehensive understanding of the mechanisms of aging and environmental exposure-related deterioration, for the purposes of prediction of service-life and durability, is of immense importance to extend the service life of such systems [4–7].

In service, failures of glass–fiber-reinforced polymeric composites are commonly attributed to aging of the material in its particular environment, brought about by a combination of the effects of heat, water, and mechanical stresses on the material. Several studies have shown the important effects of absorbed water and aging temperature on the physical and mechanical properties of composite materials [8–13].

When composite materials are used, the environmental aspects have to be carefully considered [14]. This applies, in particular, to the most common phenomenon of moisture penetration in composites, which has become a principal limitation for industrial usage of such products [15, 16].

The absorbed moisture results in more detrimental effects on the mechanical properties of composite materials since the water not only interacts with polymer matrices, physically, i.e., plasticization, and/or chemically, i.e., hydrolysis, as in the unfilled system, but it also attacks the fiber–matrix interface. In fact, it is generally recognized that the glass/matrix interface is the determining factor of the degradation mechanism, especially under wet conditions [17, 18].

Moisture penetration into composite materials is conducted by one major mechanism, namely diffusion. This

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mechanism involves direct diffusion of water molecules into the matrix and, in some cases, into the fibers. The other two common mechanisms of moisture penetration into composite materials are capillary flow along the fiber/matrix interface, followed by diffusion from the interface into the bulk resin, and transport by microcracks [19, 20].

Dynamic mechanical thermal analysis (DMTA) techniques provide a powerful tool to develop insight into structure and viscoelastic response of these materials while simultaneously enabling a high level of sensitivity in the detection of changes in internal molecular mobility [21–24]. Glass transition temperature, T_g, can be determined with significant levels of sensitivity through DTMA by monitoring changes in the storage modulus, E^I; loss modulus, E^{II}; or the loss tangent, tan δ; as a function of temperature [25].

The commonest and simplest method of determining the laminar shear strength of laminated-reinforced plastics is to carry out a bending test by subjecting short, simply supported rectangular beams to the action of a concentrated load applied at midspan to the laminations. This test configuration is known as a short-beam-shear (SBS) test or interlaminar shear strength (ILSS) test. The ILSS thus determined depends strongly on the relationship between the span and the thickness of the beam.

The purpose of this study is to detect the effect of hydrothermal aging at two different temperatures and high moisture rate on ILSS and failure behavior of glass–fiber/polyetherimide (PEI) $[(0°/90°)]_{4s}$ lay-up during pin loadings. Besides, alterations in visco-elastic properties of glass/PEI composite which was exposed to hydrothermal aging were analyzed with the DMTA method.

Experimental method and materials

Continuous glass–fiber/PEI composites with $[(0°/90°)]_{4s}$ stacking sequence were kindly supplied by Ten Cate Advanced Composites (Nijverdal, the Netherlands) in the form of hot-pressed plaques. Plaques were manufactured from eight plies, with total thickness of 2 mm. The volume fraction of the fiber was 48%. Unit weight of each layer was 475 g/m^2.

Hydrothermal aging was carried out in a boiling water container and cold water–ice mixture (0 °C) container. The hydrothermal cycles were performed in the temperature range of min. ~0 and max. ~100 °C. Samples were immersed into the boiling water container for 1 min, and then they were quickly transferred and immersed into the cold water–ice mixture container. One cycle took 2 min and the complete experiment time was 200 min for 100 cycles.

SBS tests were chosen to evaluate ILSS of glass–fiber/PEI composite after hydrothermal aging. The tests were performed at room temperature on an Instron 4411 tester that has a loading capacity of 5 kN. The dimensions of the ILSS samples were $14 \times 6 \times 2$ mm^3. The distance between the supports of the test setup was 12 mm and the support distance to sample thickness ratio was 6. The experiments were performed according to ASTM D 2344-84 standard which imposes 1 mm/min crosshead velocity for the ILSS test.

Bearing strength experiments were performed according to ASTM D 953 standard. The tests were performed at room temperature on an Instron 4411 tester. The crosshead speed was 1 mm/min. In our previous study [26], we used the geometric parameters that result in bearing, shear-out and net-tension types of deformations. These parameters were $E/D = 2$, $W/D = 2$, $D = 10$ mm, and $E/D = 1$, $W/D = 4$, $D = 5$ mm, where D, W, and E stand for diameter of the pin hole, width of the sample, and distance from the upper edge to the pin hole center of the sample, respectively. We have used the same parameters to investigate how the bearing strength of the connection and visco-elastic properties of the samples were changed as a function of thermal cycling loading.

DMTA Q800 type apparatus produced by TA Instruments Company (New Castle, DE, USA) was used for DMTA. Samples having dimensions of $15 \times 5 \times 2$ mm^3 were tested in frequency of 1 Hz, in three-point bending mode, in the range 30–250 °C and 5 °C/min heating rate. A 0.5-N load was used as preload, during the test. Further, the strain rate was defined as 15% for glass/PEI composite.

We investigated the fractographic changes of fractured surfaces of original and hydrothermally aged samples under scanning electron microscope (SEM) (JEOL/EO JSM-6060).

Results and discussion

In Fig. 1a, ILSS values of continuous glass–fiber-reinforced PEI matrix composite are shown, depending on the number of thermal cycles. A rapid decrease in values is observed at the end of the third thermal cycle; in other words, hydrothermal aging has the maximum effect at the end of the third cycle. While the ILSS of original sample is 52 MPa, the strength of three times thermal cycled sample is approximately 45 MPa. ILSS decreased 13.5% through the first three cycles. A decrease of 19% is seen at the end of the 100th cycle. Considering the values, destructive effect of hydrothermal aging appears at the end of the third cycle. In Fig. 1b, flexural modulus values versus number of thermal cycles are given. At the end of the 100th cycle, values decreased approximately 10%.

The decrease is seen in ILSS values as hydrothermal aging cycles increased. There also occurs a decrease in

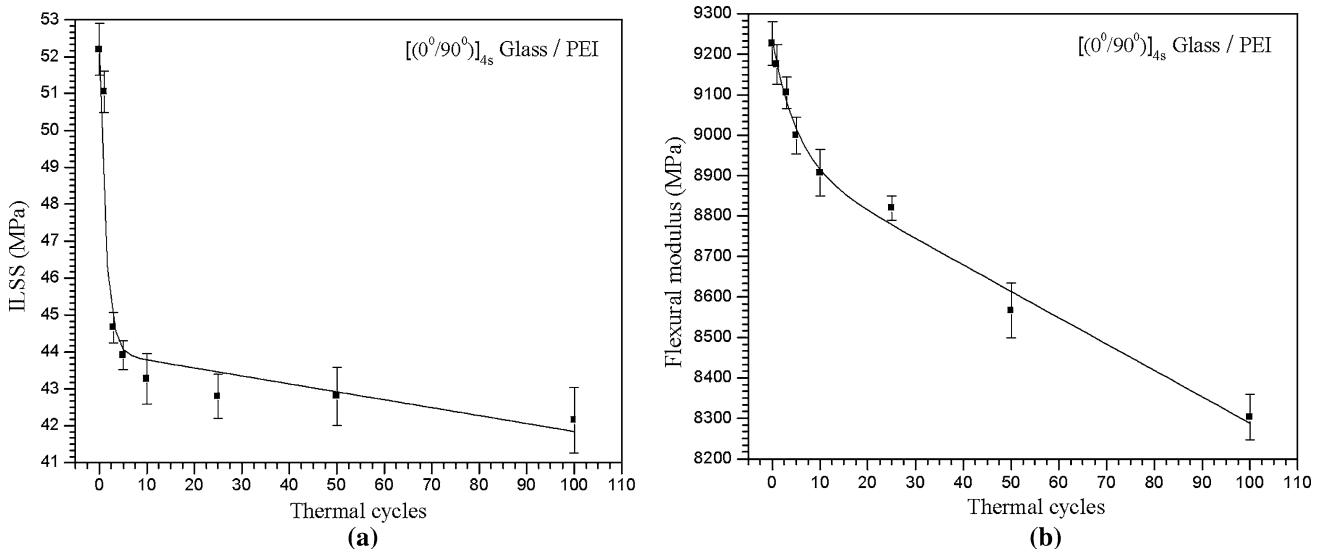

Fig. 1 **a** ILSS versus thermal cycles results for $[0°/90°]_{4s}$ glass/PEI composites. **b** Flexural modulus versus thermal cycles results for $[0°/90°]_{4s}$ glass/PEI composites

ILSS values because of higher stresses (expansion/shrinking) in numbers of high cycles. These stresses cause longer debonding increasing their effect on fiber/matrix interface. The failure mechanisms related with hydrothermal fatigue are mostly matrix cracking, delamination, and fiber/matrix debonding [27].

Load–displacement curves of glass–fiber/PEI composite with different geometric parameters are shown in Fig. 2a ($E/D = 1$, $W/D = 4$, $D = 5$) and 2b ($E/D = 2$, $W/D = 2$, $D = 10$). As seen in figures, hydrothermal aging decreases the load-bearing performance of composites with various geometric parameters. Further, the rate of energy absorbed by pin connection until it is fully damaged also decreased, the reason of which can be the low interface strength between glass–fiber and polymer matrix. The strength of fiber/matrix interface is destructed with the effect of moisture absorption which occurred as a result of hydrothermal aging. The toughness of composite sample diminishes due to decrease in the stress transferred from matrix to fiber. Therefore, stresses occurred due to thermal cycles and moisture absorption on fiber/matrix interface or on matrix weakened the mechanical properties of composite.

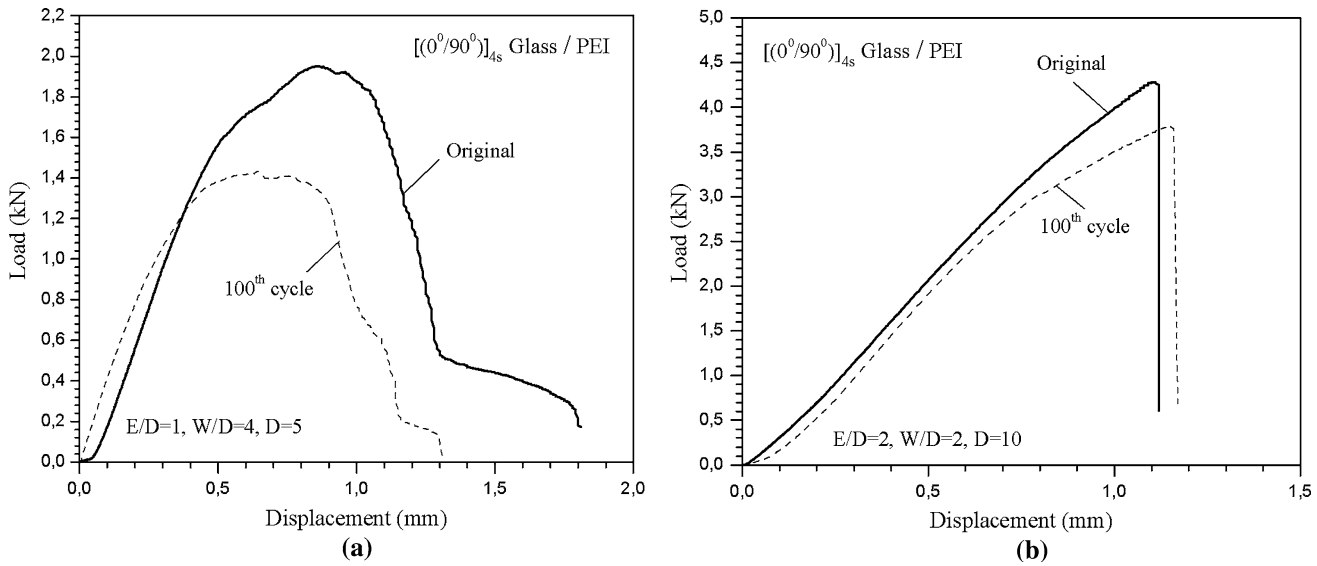

Fig. 2 Load–displacement curves for $[0°/90°]_{4s}$ glass/PEI composites with different geometric parameters

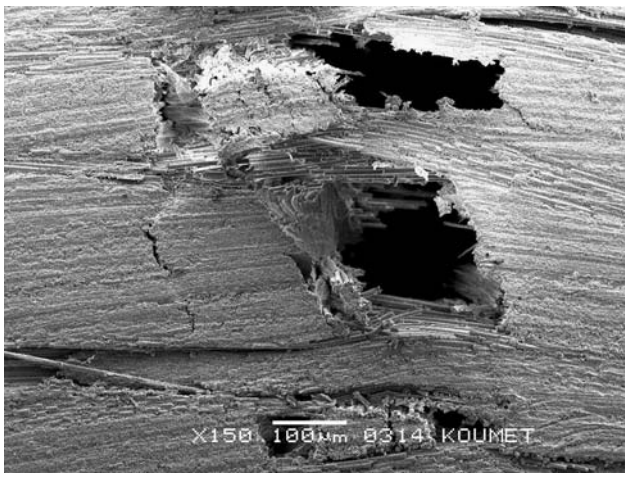

Fig. 3 Fracture morphology of the original SBS test sample

In Fig. 3, the fracture surface of original glass–fiber/PEI lay-up which is obtained after SBS test is seen. Fiber protrusion is not considered for original glass–fiber/PEI composite sample due to high fiber/matrix interface strength. Composite with strong interface and efficient load transfer between fibers tend to fracture with a more brittle appearance as shown in Fig. 3. In composites with weak interface which are exposed to hydrothermal aging, brush-like fractures occurred.

SEM of fibers at fracture surface of failed specimen exposed to hydrothermal aging is shown in Fig. 4. There is delamination between laminates and debonding on fiber/matrix interface due to composite hydrothermal aging. This debonding induces a new water uptake because of the formation of cracks or voids in the bulk material. The existence of differential pressures between the low and the high water content regions induces an osmotic cracking phenomenon. The failed glass–fiber/PEI specimens are more brush-like and rougher in appearance than original samples. This fractographic difference is another indication that debonding is a prevalent fatigue mechanism in hydrothermally aged glass–fiber/PEI composites. Protrusion lengths of fibers in tensile region of matrix happened to be extensive due to weak fiber/matrix adhesion. The mechanisms stated above are the failure mechanisms occurred during crack propagation.

Large fluctuations at tan δ values depend on moisture rate that polymer matrix absorbs through hydrothermal aging [28]. That moisture rate absorbed by polymer matrix causes an increase in tan δ values (Fig. 5) and decrease in glass transition temperature (T_g) of composite samples. Increase in tan δ values may be due to decrease in storage modulus (E^I) values. It is obvious that increase in tan δ values results from decrease in E^I values, as the case is tan $\delta = E^{II}/E^I$. Decrease in E^I values can be comprehended as the degradation of fiber/matrix interface due to formation of residual stresses on this region as a result of thermal expansion coefficient differences between fiber and matrix throughout the thermal cycles, and as the diffusion of water molecules to matrix, moving through fiber/matrix interface (capillary flow) (Fig. 6).

As seen in Fig. 6, the test sample that was exposed to 100 hydrothermal cycles has smaller storage modulus than the original sample, under glass transition temperature. Decrease in curve in the original sample occurs at a higher temperature. This temperature value defines the glass transition temperature. Thermal cycles in glass–fiber/PEI composite influence the elastic behavior of the material. Decrease in storage modulus values of glass–fiber/PEI composite indicates this formation.

T_g values of samples unexposed to thermal cycles are higher. The change in T_g values depends on the reaction of

Fig. 4 Fracture morphology of the SBS test sample exposed to 100 thermal cycles

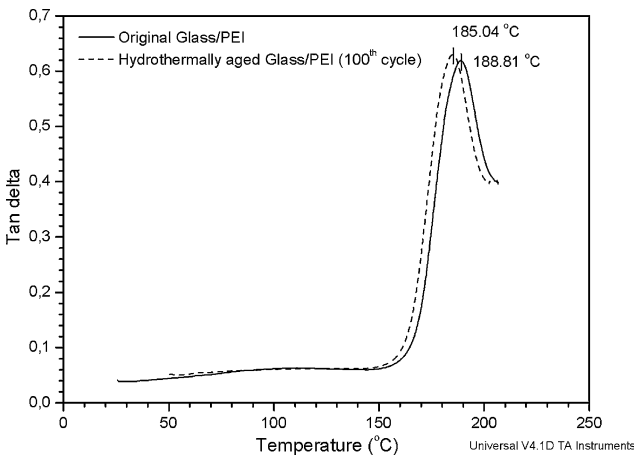

Fig. 5 The characteristic plots of the tan δ versus temperature results of original and hydrothermally aged glass/PEI samples

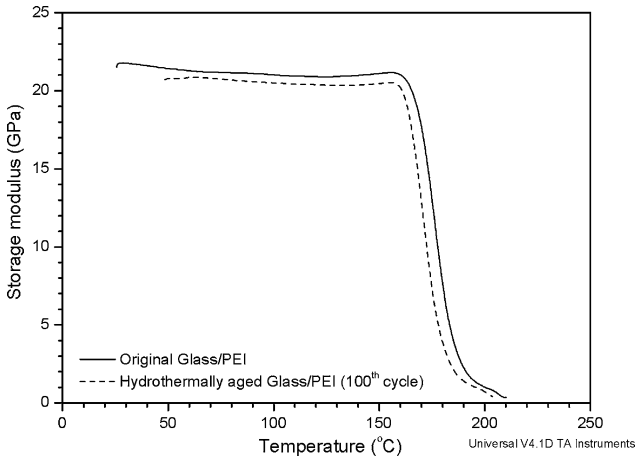

Fig. 6 Storage modulus versus temperature results of original and hydrothermally aged glass/PEI samples

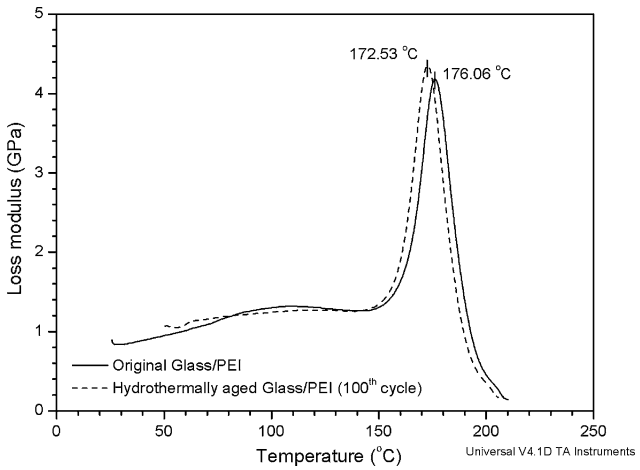

Fig. 7 Loss modulus versus temperature results of original and hydrothermally aged glass/PEI samples

water molecules with polymer chains (Fig. 7). Water molecules decrease T_g by breaking Van der Waals and hydrogen bonds that keep polymer chains together [29].

Conclusions

This article reports moisture absorption behavior and performance of cross-ply glass–fiber/PEI composites (kindly supplied by Nijverdal), and the influence of hydrothermal aging on viscoelastic behavior, ILSS, flexural modulus, and bearing strength.

The main conclusions from this work are as follows.

1. Glass transition temperature (T_g) of samples exposed to hydrothermal aging decreases by increasing number of thermal cycle and absorbed moisture rate. Occurring throughout fiber/matrix interface, moisture absorption causes fiber/matrix debonding and degradation of the structure. Accelerated with temperature, moisture absorption also makes fibers affected from moisture, weakening fiber/matrix interface strength. Decrease in T_g values of samples exposed to hydrothermal aging is likely to be based on plasticization which increases polymer chain mobility in amorphous region.
2. The effect created by hydrothermal aging due to weak glass–fiber/PEI matrix adhesion is a fiber/matrix interface intensive formation. Delamination and fiber/matrix debonding, occurred as a result of hydrothermal aging depending on the number of thermal cycles, restricted the mechanical properties in glass–fiber/PEI composites.
3. There appeared a decrease of nearly 19% in ILSS of glass–fiber/PEI composite sample after 100 cycles of hydrothermal aging. In flexural modulus values, decrease is roughly 10%.
4. In glass–fiber/PEI $[(0°/90°)]_{4s}$ lay-up, ultimate bearing load values diminished 12% in samples with $E/D = 2$, $W/D = 2$, and $D = 10$ mm geometric parameters. The decrease is approximately 26% when $E/D = 1$, $W/D = 4$, and $D = 5$ mm.

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