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Effect of hydrofluoric acid etching of glass on the performance of organic–inorganic glass laminates

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ABSTRACT

Organic–inorganic glass laminates with polyurethane (PU) as an adhesive interlayer were prepared by a warm-pressing method. The hydrofluoric acid etching of glass surface was performed to investigate its effect on the mechanical behavior of glass laminates. Results show that the acidic etching treatment of glass seldom influences the transparency and haze of glass laminates when the etching time is below 30 min. The bonding strength and fracture stress of glass laminates firstly increase and then decrease with increasing etching time. This could be attributed to the formation of three-dimensional interface of glass laminates. The unique interface structure not only increases the contact area between glass and PU layer, leading to the improvement of interface bonding, but also modifies the stress distribution at the interfaces, which is favorable to prevent the crack propagation and delamination failure of laminates.

1. Introduction

Organic–inorganic glass laminates are often used as blast proof safety screen, bullet proof windows or windshield [1,2]. A typical glass laminate construction consists of inorganic glass as the outer layer backed by polymethylmethacrylate (PMMA) with a thin adhesive transparent interlayer (such as polyurethane) in between.

The transparent interlayer plays the roles of adhesive, thermal compensation and buffer layer between inorganic and organic glass. The most common used interlayer materials are polyvinyl butyral (PVB) [1], polyurethane (PU) [3] and organic silicon [4]. Compared to other ones, PU has some advantages for interlayer, such as broad operating temperature range, excellent environmental resistance and good binding power, which makes for improving the durability of organic–inorganic glass laminates. However, because of bad inorganic–organic compatibility and low interlaminar strength, PU interlayer and inorganic glass are susceptible to interlaminar fracture during processing or in service. The presence and growth of delamination may cause severe destruction, which leads to a catastrophic failure. Hence, preventing interlaminar fracture and increasing resistance to delamination growth is of much significance. Many methods have been developed to increase resistance to delamination, such as the use of low profile high strength glass [5], coated glass [6], surface modification [7], and acid etching [8,9]. Among these methods, acid etching is considered as a potentially effective way to significantly improve interlaminar fracture tolerance and suppress delamination.

The focus of this paper is to experimentally investigate the effects of hydrofluoric acid etching of glass on the performance of organic–inorganic glass laminates. Optical transmittance, bonding strength, fracture stress/strain, impact energy and microstructure of organic–inorganic glass laminates treated with different hydrofluoric acid etching processing parameters were studied.

2. Experimental

2.1. Raw materials

Commercial polymethylmethacrylate (PMMA), inorganic glass and PU were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Hydrofluoric acid solution (40 vol.%) was obtained from Kermel Chemical Reagent Co., Ltd., Tianjin, China.

2.2. Preparation of organic–inorganic glass laminates

Inorganic glass was dipped in 10 vol.% hydrofluoric acid solution for several minutes, such as 10, 20, 30, 40, 50, and 60 min. After cleaning and drying, three layers of inorganic glass, PU and PMMA were laminated by warm-pressing at 4 MPa and 100 °C for 30 min.

Hygrothermal aging experiment was performed for organic–inorganic glass laminates under conditions with temperature of 50 °C and relative humidity of 85% for 30 days.

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2.3. Testing

The transparency and haze were measured with a WGW photoelectric haze meter (Tianjin Optical Instrument Co., Ltd., China). The bonding strength was measured by a WDW-50D universal test machine (Jinan Shijin Instrument Co., Ltd., China) on 3-ply unidirectional specimens, 35 mm by 15 mm and 20 mm by 15 mm, at a span to depth ratio of 5 according to GB/T 1450.1-2005. The crosshead speed was 10 mm/min. During the testing, the convex specimen was griped in the clamping fixture. The load was applied perpendicularly to the lateral face of the specimen. The shear testing specimen, device and principles were shown in Fig. 1. The fracture stress/strain behavior in quasi-static loading was measured according to the standard ASTM D790-81 using a WDW-50D universal test machine of 10 kN load in a 3-point flexure mode. The span to depth ratio of testing specimens was maintained to be 16:1. The crosshead speed of 1 mm/min was applied. The fracture stress/strain behavior in dynamic loading was tested by SHPB (Split Hopkinson Pressure Bar) method in Wuhan University of Technology. The tests were conducted at different strain rates, i.e. 100, 1000 and 4000 s^{-1} through applying different gas pressures on the striker bar. The dimension of testing specimens was $\varnothing 70 \times 10$ mm. The impact energy was tested by a CBC-604 charpy impact machine tester (Beijing Guance Test Instrument Co., Ltd., China). The impact velocity of the pendulum was 2.9 m/s and the applied energy was 2 J. The dimension of testing specimens was $40 \times 15 \times 10$ mm with a 2 mm thickness of PU layer. At least twelve specimens of each sample were used and the average values were reported. The entire experimental process was maintained on the temperature of about 25 °C and the relative humidity of about 45%. The surface morphologies of the samples were observed by a JSM-5610LV scanning electron microscope (JEOL Ltd., Japan).

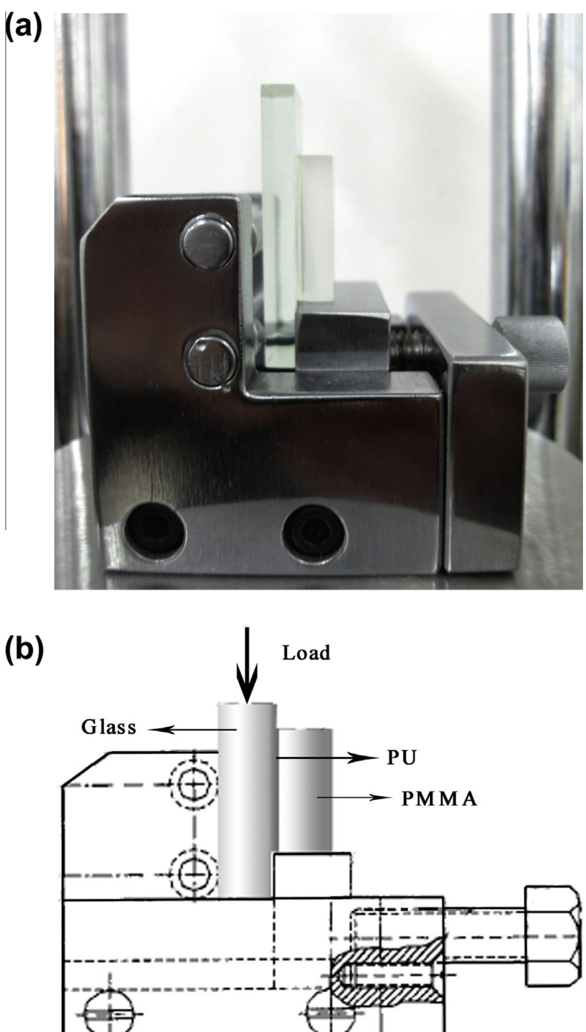

Fig. 1. Shear testing experimental setup on universal test machine (a) shear testing specimen and device, (b) shear testing principles.

3. Results and discussion

3.1. Optical properties

After hygrothermal aging for 30 days, the transparency and haze of organic–inorganic glass laminates were tested. The results are shown in Fig. 2. The dummy without acid etching has almost the highest transparency and the lowest haze. With the increase of etching time, the transparency gradually decreases and the haze gradually increases, especially when the etching time is more than 30 min. However, the transparency and haze of glass laminates change little when the etching time is below 30 min. The transparency of glass laminates that etched for 30 min reaches more than 80%, which maintains 96% of the original transparency of the dummy without acid etching. The haze of glass laminates that etched for 30 min is about 12%. The transparency and haze at this point are still acceptable for windshield.

3.2. Bonding strength

Effect of the etching time on the bonding strength of glass laminates is given in Fig. 3. It is observed that the bonding strength gradually increases with increasing etching time when the etching time is below 30 min. However, the bonding strength suddenly decreases when the etching time is more than 30 min. The bonding strength reaches maximal value (about 1.8 MPa) at the etching time of 30 min, which increases for 33.1% as compared with that of the dummy without etching treatment. This indicates that appropriate etching of glass can increase the bonding strength of glass laminates. Otherwise, it is worthy to notice that the debonding of glass laminates is usually occurred on the interface between inorganic glass and PU layer. This indicates that PU has good compatibility with PMMA but not with inorganic glass although inorganic glass is modified by hydrofluoric acid etching. The reason is maybe PU and PMMA are both organic substance but PU and inorganic glass are not.

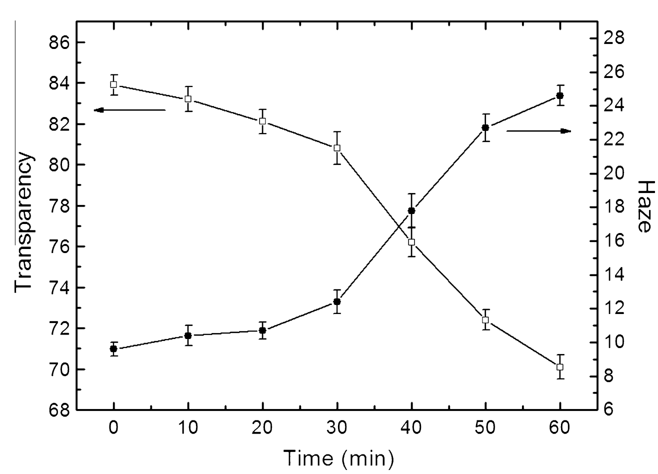

Fig. 2. Relationship between transparency, haze and etching time.