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Adhesion of PBO fiber in epoxy composites

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Abstract A composite of poly *p*-phenylene-2,6-benzobisoxazole (PBO) fiber and epoxy resin has excellent electrical insulation properties. However, it is a challenging issue to improve its mechanical properties because of poor adhesion between PBO fiber and matrix. The relatively smooth and chemically inactive surface of PBO fiber prevent efficient chemical bonding in the composite interface. Here, we report the surface modification of PBO fibers by UV irradiation, O_2 and NH_3 plasma, as well as acidic treatments. We found that the surface free energy and roughness are increased for both sized and extracted fibers after plasma treatments together with maleic anhydride grafting. The sized fiber shows marginal improvement in adhesion strength and no change in fiber tensile strength because of the barrier effect of the finish. For the extracted fiber, however, the tensile strength of the fiber is sensitive to surface treatment conditions and considerable strength reduction occurred, particularly for cases of acidic treatments and UV irradiation. This is because that the treatments increase the surface roughness and introduce more surface flaws. The extracted fiber surface has no adequate wetting and functional groups, which in turn results in coarse interface structures and causes reduction or no apparent variation of the adhesion strength. The fracture surfaces after single fiber pull-out tests exhibit adhesive interfacial failure along the fiber surface, which is further confirmed by similar adhesion strength and interlaminar shear strength values when the fiber was embedded in various epoxy resins with different temperature behavior.

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Introduction

The high mechanical and thermal performance of poly *p*-phenylene-2,6-benzobisoxazole (PBO) fiber provides great potential applications as reinforcement fibers for composites. Recently, in the application of pulsed very high magnetic fields up to 100 T [1], the required reinforcement in coils with a small size has to be electrically insulating and should have sufficient high mechanical strength and stiffness because of extensive radial forces on the conductors arising from Lorentz' force. The PBO fiber is the strongest rigid-rod polymer fiber presently available with a tensile strength of 5.8 GPa and a Young's modulus of 270 GPa. An other organic high performance fiber with a tensile strength of 9 GPa, designated 'M5', was announced by Magellan Systems [2]. Carbon fibers are excluded from the selection due to their conductivity. A composite of PBO fiber and epoxy resin has excellent electrical insulation properties, therefore, it is considered to be the best choice.

However, it is a challenging issue to improve PBO/epoxy composite mechanical properties because of poor adhesion between PBO fiber and matrix. The relatively smooth and chemically inactive surface of PBO fiber

prevents efficient chemical bonding in the composite interface. A substantial improvement of the adhesion strength would open the broad field of composites for the application of PBO fiber. An effective load transfer between fiber and matrix is essential to reach a high yield of the excellent tensile strength and Young's modulus of the fiber. It was reported that oxygen plasma treatment is a suitable method to increase the surface free energy and the interfacial shear strength (IFSS) [3, 4]. Plasma polymerization was also used, but the achieved improvements of the IFSS, however, do not reach the desired requirements [5]. Similarly, a marginal improvement of the surface free energy was reported by acid treatment of the fibers and the adhesion strength remains at a dissatisfying level comparable to that for aramid fibers in epoxy matrices [6]. In this work different approaches of designing the interface are shown, partly built on other author's work and partly based on methods not reported before. It mainly focuses on characterization of fiber-matrix adhesion and besides it emphasizes on the use of different epoxy resins for application in high field coils.

Experimental procedure

Materials

The PBO fiber was received from Toyobo Ltd., Japan with trade name Zylon™. The fibers in HM (high modulus) specification were used with standard finish designated as control state. De-sized fibers were prepared by removing the finish with acetone in ultrasonic bath. Composites and pull-out specimens were prepared using five different epoxy resins. The composition and the curing procedures of the resins are listed in Table 1. Unidirectional epoxy composites were prepared by wet winding of the fibers and subsequent curing under pressure in a hydraulic press with temperature control.

Surface treatment

On the as-received control state sizing was applied by coating the fibers in a bath of the sizing formulation and subsequent squeezing to reduce the amount of the adhered sizing. Wet sized fibers were dried at 130 °C for 3 h. Plasma treatments were applied for 10 min in a lab microwave plasma chamber with a plasma power of 600 W. Oxygen and ammoniac were used as plasma gases at a working pressure of about 10 mbar and a gas flow of 50 sccm. Maleic anhydride grafting was performed by immersion of the oxygen plasma treated de-sized fibers into a bath of a 5% solution of maleic acid anhydride in acetone. Subsequently, a second oxygen plasma treatment was applied. Furthermore, a UV-treatment was carried out at various de-sized samples at 222 nm (KrCl lamp) in air and Argon with diallyl phthalate (DAP), glycerine-1-allyl ether (GLY), and allyl glycidyl ether (AGE). After acetone extraction of control PBO fibers amino acids, specifically 4-aminobutyric acid (PP42) and 11-aminoundecanic acid (PP43) were used as modifiers. The reaction temperature was kept at 200 °C and 210 °C, respectively.

Characterization

Single fiber tensile tests were conducted in accordance with EN ISO 5079 using the Fafegraph ME testing device (Fa. Textechno) equipped with a 100 cN force cell. The fineness of each selected fiber using a vibration approach in a Vibromat testing equipment (Fa. Textechno) in accordance with EN ISO 53812 and ASTM D 1577. Assuming a circular cross-section, a relation between the resonant frequency υ and the fineness T_t at known pre-load F_v, gauge length L and Young's modulus of fiber E_f is defined as

$$T_t = \frac{F_v}{4 \cdot \upsilon^2 \cdot L^2} \left(1 + \frac{d_f^2}{4L} \cdot \sqrt{\frac{E_f \cdot \pi}{F_v}}\right)^2 \quad (1)$$

The tensile test is conducted with a cross velocity of 10 mm/min using a gauge length of 20 mm, at 65% RH and 20 °C temperature. Fifty samples were tested for each treatment condition.

The surface topography of the fibers was characterized with atomic force microscopy (AFM) by using a Digital Instruments Dimension™ 3100. Compression shear tests were performed with unidirectional composites of 2 mm thickness and a sample size of 10 × 10 mm. The force was applied in fiber direction with a testing speed of 1 mm/min. Details of the self-constructed testing device are described elsewhere [7]. The contact angles between PBO fibers and water, *n*-hexadecane, toluene, ethylene glycol and glycerin

Table 1 Epoxy resin formulations and curing conditions

Resin	Hardener	Mix ratio	Curing cycle
Stycast 1266 Part A	Stycast 1266 Part B	100:28	65 °C, 2 h
Stycast W19	Catalyst 11	100:17.5	100 °C, 4 h
Araldite LY 564	XB 3403	100:36	100 °C, 4 h
Huntsman XB 3292	XB 3473	100:34	100 °C, 2 h + 140 °C, 1 h + 200 °C, 2 h
Bakelite EPR L20	EPH 960	100:34	60 °C, 4 h + 130 °C, 3 h

as model liquids were determined using a sensitive tensiometer (K14, Krüss GmbH) applying the Wilhelmy method. The surface free energy of fibers was estimated using the geometric mean approach. The unidirectional composite specimens were undertaken a dynamic mechanical analysis (DMA, Texas Instruments DMA 2980, single cantilever bending, frequency of 10 Hz, heating rate of 2 K/min). Single fiber pull-out tests were performed with a self made apparatus as described elsewhere [8], where single filament was embedded in droplet of the resin and cured according to the cycle given in Table 1 and the force-displacement curves were recorded during the tests. The data treatment to determine the local adhesion strength τ_d, the frictional strength τ_f, the critical energy release rate of the interface G_{ic}, and the apparent adhesion strength τ_{app} (or IFSS like often referred to in literature) was described elsewhere [9].

Results

Tensile strength of the modified fibers

Figure 1 displays the average tensile strength of PBO fibers and the effects of various surface treatments. The control PBO fiber showed a tensile strength of ~6 GPa, in good agreement with the manufacturers information. The oxygen plasma treatment of the control fiber led to a marginal decrease of tensile strength. Additional sizing reduced the strength probably due to squeezing and heat exposure during the drying. An extraction of the fibers significantly decreased the fiber strength. Additional oxygen plasma treatment led to further slight reduction of tensile strength. Exposure to UV radiation also reduces the tensile strength by 35%, in agreement with reported results [10]. Acid treatments led to the strongest reduction of tensile strength observed in this set of treatments. The PBO fiber is formed from microfibrils (preliminary 10–50 nm in diameter) highly oriented to the fiber axis and the very surface of the fiber is void-free region [11]. We proposed a possibility that the surface treatments affect mostly the chain end of PBO crystal induced onset of microstrain, resulting in roughening of the surface and enhanced stress concentration which contribute to the reduction of the tensile strength. The control fiber and oxygen plasma treated control fiber showed similar Weibull-curves (Fig. 2) revealing that there is no change in failure mechanism of the fibers, because the finish was not removed and can heal the surface flaws. After extraction the curves shift to lower tensile strength and the slope (Weibull modulus) is decreased. The reduction of average strength indicated that the fiber surface defects introduced by the treatments have a strong influence on the fiber strength. A subsequent treatment in oxygen plasma further enhanced this effect. The extraction of the sizing bares the fiber surface which is then sensible to degradation by the plasma treatment, whereas the finish shields the aggressive effect of the oxygen plasma so that the plasma treatment does only marginally reduce the tensile strength of the control fibers. Acid treatments caused the strongest change in the failure behavior, arising from roughening of the surface associated with enhanced stress concentration at surface flaws.

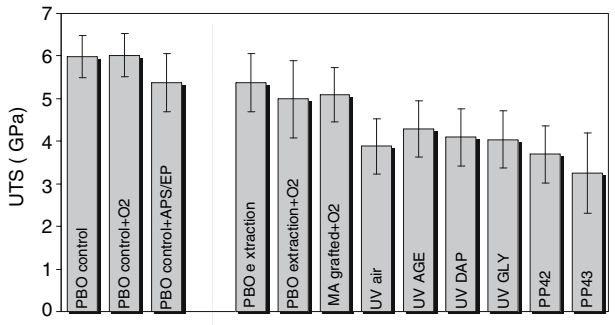

Fig. 1 Effects of the fiber treatments on single fiber tensile strength

Surface and interface properties of the modified fibers

Figure 3 shows the effect of the applied surface treatments on the interfacial shear strength IFSS and the surface free energy γ_f of the PBO fibers. IFSS of the untreated fiber is about 35 MPa and there is only marginal increase after oxygen plasma treatment. The surface free energy increased by 40% but this positive effect does not contribute to improve the adhesion strength. An increase of γ_f was also achieved by other treatments, especially when oxygen plasma was involved. Nevertheless, the IFSS stayed at the same moderate level or even decreased.

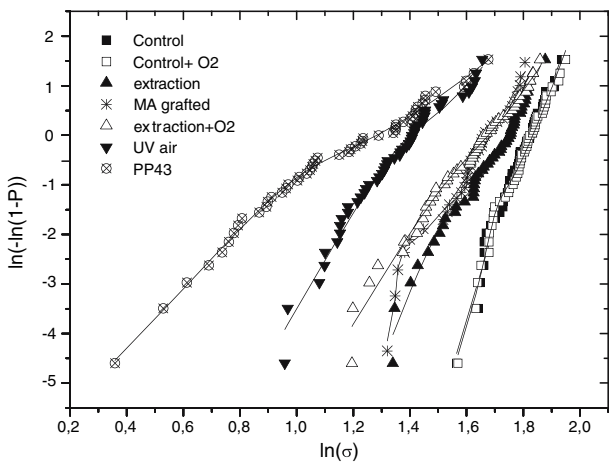

Fig. 2 Bimodal Weibull distribution analysis of single fiber tensile strength of differently surface treated PBO fibers

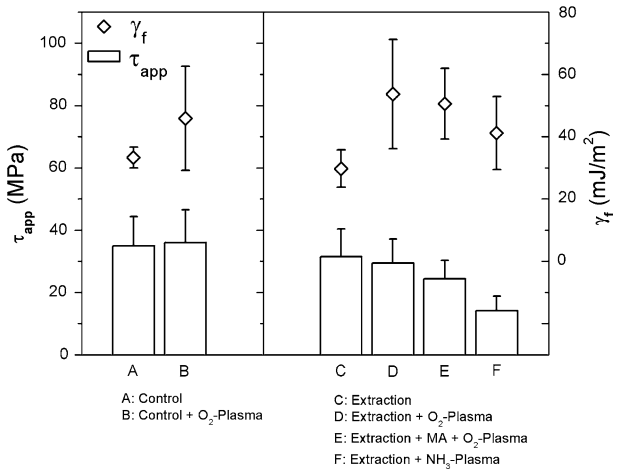

Fig. 3 Interfacial shear strength τ_{app} (from resin Bakelite L20) and surface free energy γ_f of differently surface treated PBO fibers

In addition, the influence of different epoxy resins on the interfacial adhesion strength and simultaneously different temperature characteristics were tested for the actual application. The results of the single fiber pull-out tests are summarized in Table 2 for both resin variation and surface modification of PBO fibers embedded in Bakelite L 20 resin. All interfacial characteristics underline similar values for different epoxy resins, whereas the surface modifications mainly decrease the interfacial properties. This is in accordance with the surface morphology after pull-out investigated by AFM. Two examples of pull-out fracture surfaces are shown in Fig. 4. Independent of the resin used, smooth fracture surfaces after pull-out indicate adhesive failure at the interface.

Composites with different epoxy resin matrices

The bulk composite testing is important to develop the appropriate manufacturing route. Unidirectional composites have been prepared with five different epoxy resins and were undertaken compression shear tests and DMA (Table 3). The interlaminar shear strength is independent of the epoxy resin used. This agrees well with the results of the single fiber pull-out tests. Adhesive failure occurs at the fiber-matrix interface and there is a high interface content in the composite so that differences in the fiber volume content within the observed thresholds do not influence the shear strength.

Dynamic mechanical analysis reveals the temperature dependence of mechanical stiffness of the material in the case of oscillating bending load. It is of particular interest for operation temperatures in high magnetic field coils differing from liquid nitrogen temperature of –196 °C up to 125 °C. Figure 5 shows the storage moduli of pure epoxy resin specimens analyzed in the temperature range from –130 °C to 250 °C. Stycast W19 holds the highest level of stiffness in a wide temperature range till approximately 70 °C. The strong decline of the storage modulus in this area arises from the glass transition of the thermoset material. The glass transition temperature T_g indicates the

Table 2 Interfacial properties of PBO/epoxy composites fiber derived from single fiber pull-out tests with different matrix resins and differently surface treated fibers

Fiber	Resin	τ_d (MPa)	τ_f (MPa)	G_{ic} (J m^{-2})	τ_{app}(MPa)	γ_f (mJ m^{-2})
PBO control	Stycast W19, 11	48.5	29.4	18.3	35.7	
PBO control[a]	Stycast 1266 A/B	54.9	30.5	31.0	41.2	
PBO control + corona[a]	Stycast 1266 A/B	51.8	31.2	24.5	39.3	
PBO control	Araldite LY564, XB3403	40.4	23.2	16.6	45.6	
PBO control	Huntsm. XB3292, XB3472	38.8	16.6	19.5	33.2	
PBO control	L20	47.0	31.9	17.0	35.0	33
PBO control + APS + epoxy	L20	35.8	25.6	9.2	30.5	36
PBO control + O_2 plasma	L20	39.6	28.4	11.7	35.9	46
PBO de-sized	L20	37.5	27.8	9.8	31.4	30
PBO de-sized + O_2 plasma	L20	40.1	20.9	15.3	29.4	54
PBO de-sized + NH_3 plasma	L20	24.3	9.3	7.1	14.2	30
PBO de-sized + MAH plasma	L20	32.9	20.4	8.6	24.4	51
PBO de-sized acid treated PP 42	L20	33.4	13.1	11.9	19.5	
PBO de-sized acid treated PP 43	L20	41.0	20.5	14.9	27.2	
PBO de-sized UV, AGE grafted	L20	38.0	29.3	10.0	32.1	
PBO de-sized UV, DAP grafted	L20	34.2	27.1	7.8	29.7	
PBO de-sized UV, GLY grafted	L20	33.5	21.9	9.3	25.0	

[a] Improved wetting by Stycast 1266 A/B achieved increased embedded length and in turn more reliable data treatment

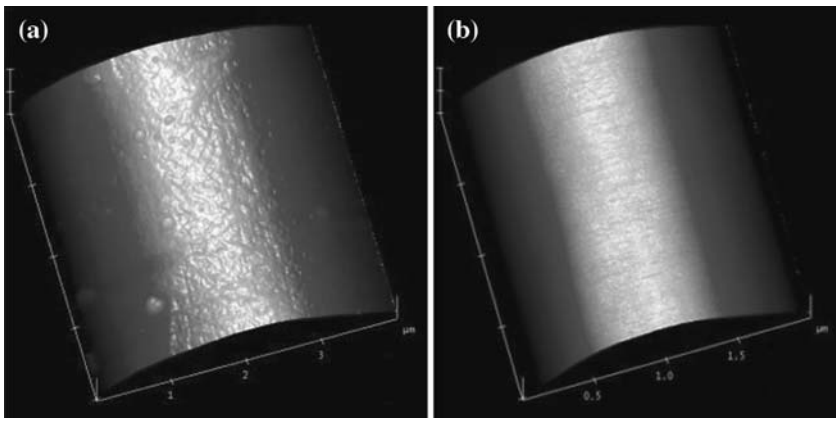

Fig. 4 PBO fracture surfaces after pull-out from (**a**) Stycast W19 and (**b**) Stycast 1266 A/B

Table 3 Interlaminar shear strength of PBO control fiber composites with different epoxy resin matrices

Resin	Fiber content φ (vol%)	$\tau_D \pm$ s.d. (MPa)
Bakelite L20	46.8	30.0 ± 3.9
Stycast 1266	46.8	28.7 ± 2.0
Stycast W19	63.8	31.7 ± 3.9
Huntsman XB3292	61.0	30.3 ± 3.2
Araldite LY564	51.0	28.4 ± 0.9

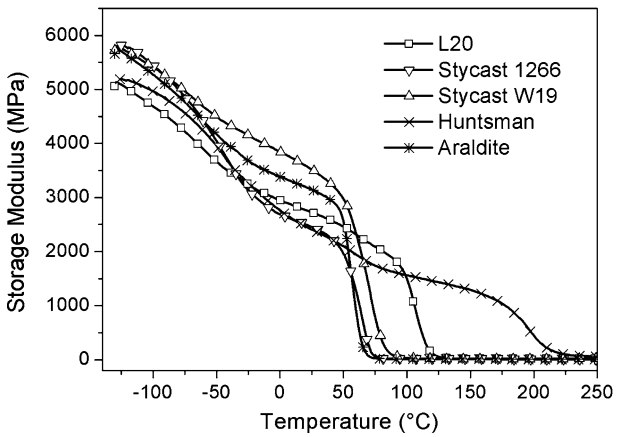

Fig. 5 DMA curves of storage modulus of different epoxy resins

maximum application temperature since no shear load will be transferred above this point. Huntsman resin has the highest T_g value. Figure 6 shows the loss modulus of the composites with different resins, where T_g is represented by the maximum of the loss modulus which corresponds with the first derivation of the storage modulus. The composites having a T_g below 125 °C cannot be recommended for the coils. Also the composite having a T_g at the critical temperature limit is not suited. Stycast W19 and Huntsman XB3292 resins achieve the best temperature resistance for the specific application.

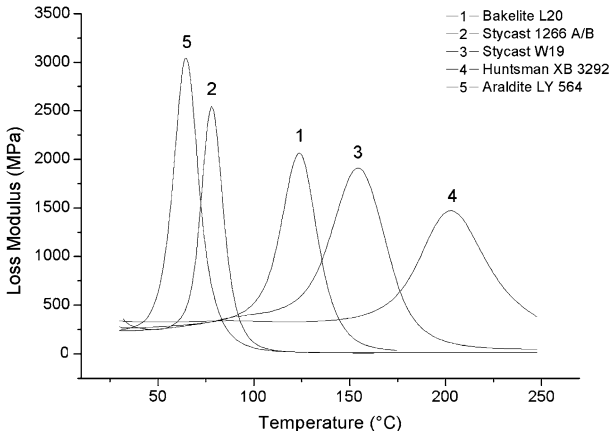

Fig. 6 Temperature dependence of loss modulus derived from DMA for composites of control PBO with different epoxy resin matrices

Conclusions

A series of PBO fiber surface treatments were analyzed either as control fiber treated or after extraction surface treated fibers with respect to their effect on interfacial adhesion to epoxy resin, surface free energy and single fiber tensile strength. Plasma treatments were found to increase the surface free energy, however the IFSS either remained at the control level without finish extraction or decreased for surface treatments of the de-sized fibers. The tensile strength of finished fibers have minor changes due to surface treatments, whereas plasma, UV radiation and acid treatment of de-sized fibers had a damaging impact on the fiber strength. Micromechanical tests as a sensitive tool for the characterization of fiber-matrix adhesion strength showed similar tendencies compared with tensile strengths. Treatments resulting in a high strength loss showed a reduced adhesion strength and vice versa. Smooth fracture surfaces of the fibers after the single fiber pull-out indicated that failure occurs at the interface, although the roughness of fiber surfaces was differently influenced by surface

modifications. More comprehensive studies conducting with AFM and micromechanical investigations on the relation of fractal geometry of fracture surfaces on the nanometer scale and the interfacial micromechanical properties are needed to verify the validity of this assumption in a wider range. Variation of the matrix resin did neither improve the interfacial adhesion strength nor change the failure mode. Based on DMA results a selection of the appropriate resin can be taken with respect to the occurring temperatures in the particular application.

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