Supplementary Information

Synthesis of a fully bio-based self-catalyzed hyperbranched waterborne polyurethane as sizing agent for enhancing the interfacial properties of CF/PA6 composites

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1. Experimental

1.1 Preparation of HWPU sizing agent and modification of CF

In a three-necked round bottom flask equipped with a condenser and mechanical stirrer, Amine-ESBO and LDI were combined in calculated amounts to prepare HWPU sizing agents. The mixture was stirred continuously at 80 °C for 3 hours,

followed by addition of TA and stirring for an additional hour at 75 °C. y–VL solvent was introduced during the reaction for fluidity control. Upon completion of the reaction, as determined by analyzing the isocyanate group content, TEA was gradually added to neutralize carboxyl groups. The resulting mixture was stirred at room temperature for 25 minutes. Deionized water was then added to obtain waterborne sizing agents with varying concentrations (0.5 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt%). These sizing agents exhibited a particle size of 193.2 nm (Fig. S1) and remained stable at room temperature for up to six months without precipitation. The synthesis process is illustrated in Fig. 1b. Commercial CF fabrics were treated by soaking in acetone for 48 hours to remove the existing sizing agent, followed by drying at 60 °C for 1 hour to create unsized CF. These unsized CF fabrics were then immersed in different concentrations of HWPU sizing agent for 5 minutes. Subsequently, the treated CF fabrics, each with dimensions of 100 mm \times 100 mm, were dried at 100 °C for 3 hours. The resulting CF fabrics, treated with varying concentrations of HWPU sizing agent were labeled as CF-0.5 wt%, CF-1.0 wt%, CF-1.5 wt%, CF-2.0 wt%. Unsized CF fabrics and CF fabrics treated with epoxy (EP) sizing agent were served as control samples to highlight the reinforcing effect of the HWPU sizing agent.

1.2 Preparation of CF/PA6 composites

The composites were prepared via hot compression method using sized fabrics and PA6 films (100 mm \times 100 mm \times 0.3 mm). CF/PA6 laminates (100 mm \times 100 mm \times 2 mm) were constructed by alternately layering eight plies of PA6 films with seven plies of treated CF plain weave fabrics. These laminated composites were then subjected to heating at 250 °C under 5 MPa pressure for 30 minutes, followed by a 20 minutes cooling phase. The fiber volume fraction was determined through a matrix digestion method, involving immersion in concentrated sulfuric acid to dissolve the PA6 resin. The average of three repeated tests revealed a fiber volume fraction of 36.5%, with a measured void content of 2.7%.

2.1 Characterization

The Fourier-Transform Infrared Spectrometer (iS-50, Thermofisher Nicolet, USA) was employed to capture spectra in the wave number range from 500 to 4000 cm⁻¹. ¹H-NMR and ¹³C NMR of ESBO and Amine-ESBO were performed on a Bruker Avance III-400MHz spectrometer with CDCl₃ as solvent. The mass spectrometry analysis was conducted using a High Resolution Mass Spectrometer (HRMS, Thermo Fly Thermo-QE Plus, USA). X-ray photoelectron spectroscopy (XPS) was performed using equipment from Thermo Electron Corp in the USA. XPS spectra were obtained using Al K α radiation (hv = 1486.6 eV) and a pass energy of 20 eV. All XPS spectra were calibrated using the C1s peak at 284.8 eV to account for any hydrocarbon contamination. Thermogravimetric analysis (TGA, METTLER TOLEDO, 10 °C/min heating rate under N2 atmosphere) was employed to test the thermal stability of HWPU. The average particle size of the HWPU sizing agent was determined using dynamic light scattering (Zetasizer NanoZS-90, Malvern, UK) with samples diluted to a concentration of 0.1 mg/L in deionized water. For sizing agent samples (20 mL), we recorded the precipitation period at room temperature in glass bottles.

To assess CF wettability, a dynamic contact angle meter (DCAT25, Dataphysics, Germany) was used by averaging five measurements. Deionized water (γ = 72.8 mJ/m², $\gamma^{d} = 21.8 \text{ mJ/m}^{2}$, $\gamma^{p} = 51 \text{ mJ/m}^{2}$) and diiodomethane ($\gamma = 50.8 \text{ mJ/m}^{2}$, $\gamma^{d} = 50.8 \text{ mJ/m}^{2}$, $\gamma^{d} = 50.8 \text{ mJ/m}^{2}$, $\gamma^{p} = 0 \text{ mJ/m}^{2}$) were set as test liquids. The dispersive and polar components were calculated using equations (1) and (2), where γ_{1} represents the liquid surface tension, while γ_{1}^{p} and γ_{1}^{d} denote the polar and dispersion components, respectively.

$$\gamma_1$$
 (1+cos θ)=2($\gamma_1^p \gamma_f$ p)^{1/2}+2(γ_1^d γ_f^d)

(1)

 $\gamma_{\rm f} = \gamma_{\rm f} p + \gamma_{\rm f}^{\rm d}$ (2)

The surface analysis of composites and varying concentrations of HWPU–sized CF was conducted using a Field–Emission Scanning Electron Microscope (JSM–7610F, JEOL, Japan). To evaluate the interfacial shear strength (IFSS) of the composites, we employed evaluation equipment from Tohei Sangyo (Model HM410, Japan). The flexural strength and interlaminar shear strength (ILSS) of the composites were determined following ASTM D7264 and ASTM D2344 standards, respectively, utilizing a universal mechanical tester (Z100, ZwickRoell, Germany). Each specimen's results were averaged from five sets of measurements.

3. Results and discussion

3.1 Chemical structure of Amine-ESBO

The results from the ¹H nuclear magnetic resonance (NMR) measurements

provide valuable insights into the chemical structure. Epoxy group protons are observed within the δ 2.8–3.1 region (refer to Fig. S2a–b), while the methyne proton from the $-CH_2CH-CH_2$ backbone appears at δ 5.1–5.3 and the methylene proton of the $-CH_2CHCH_2$ backbone is seen at δ 4.1–4.3. Additionally, the CH₂ proton adjacent to two epoxy groups is detected at δ 1.7–1.9 ppm. Furthermore, the α –H of the carbonyl group are found at δ 2.2–2.3. The β –H of the carbonyl group emerge at δ 1.55–1.75, and the β –CH₂ to epoxy group protons are visible at δ 1.4–1.55. Saturated methylene groups exhibit signals at δ 1.1–1.4, and terminal –CH₃ groups are detected in the region of δ 0.8–1.0. Fig. S2a and S2b illustrate that the product largely preserves the characteristic peaks of ESBO, with the exception of protons in the δ 2.8–3.2 and 1.4–1.55 regions, corresponding to protons attached to epoxy groups and methylene groups adjacent to the epoxy group, respectively. Additionally, two multiplet peaks at δ 0.9–1.2 are indicative of the ethyl groups introduced by diethylamine. Importantly, the addition of diethylamine results in a reduction of protons at δ 3.2, which can be attributed to the opening of epoxy rings and the subsequent modification of protons attached to the epoxy groups.

3.2 The ¹³C NMR and mass spectra of Amine–ESBO

The ¹³C NMR (100 MHz, CDCl₃) of ESBO were δ 173.2, 173.2, 172.8, 68.9, 62.1, 57.2, 57.2, 57.0, 57.0, 56.7, 56.7, 54.4, 54.3, 54.2, 34.1, 34.0, 34.0, 31.9, 31.9, 31.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.2, 29.2, 29.1, 29.0, 29.0, 27.9, 27.9, 27.8, 27.8, 27.2, 26.9, 26.6, 26.6, 26.6, 26.5, 26.5, 26.3, 26.1, 24.9, 24.8, 24.8, 22.7, 22.7, 22.6, 14.1, 14.1, 14.0. The ¹³C NMR (100 MHz, CDCl₃) of Amine–ESBO were δ 173.0, 172.9, 172.5, 68.8, 64.9, 62.0, 57.0, 56.9, 56.8, 56.7, 56.5, 56.5, 54.2, 54.0, 44.1, 34.0, 33.9, 33.8, 31.8, 31.7, 31.5, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.2, 29.1, 29.0, 29.0, 28.8, 27.8, 27.7, 27.1, 26.8, 26.5, 26.3, 26.1, 26.0, 24.7, 24.7, 22.5, 22.5, 22.4, 14.9, 14.0, 13.8. The new peak at 44.1 ppm and 64.9 ppm in the Amine–ESBO spectrum was assigned to the $-CH_2-$ and -CH- adjacent to Nitrogen. HRMS (ESI) m/z: [M]⁻ calculated for $C_{73}H_{146}N_4O_{10}$ 1239.1039; found 1238.9733.

3.3 Thermal stability of HWPU

The performance of CF composites is intricately linked to the thermal stability of the sizing agent. As illustrated in Fig. S5a, the thermal decomposition temperature at a 5% weight loss (T_3) is determined to be 264.5°C. This value aligns with a notable decline in the curve, signifying the degradation of carbamate bonds and ester groups. Moreover, as shown in Fig. S5b, HWPU experiences a thermal weight loss of 1.4% at 250°C. After maintaining this temperature for 30 minutes, the weight loss for HWPU increases to 4.9%. Consequently, the processing temperature of PA6 (250°C) can be effectively sustained, owing to the constructed hyperbranched structures, thereby enhancing the thermal stability.

3.4 Surface chemical properties of CF

The XPS was employed to quantitatively assess the elemental composition of the CF surface, elucidating alterations induced by the sizing agent. Fig. S6a illustrates the wide–scan XPS spectra, while Table S1 delineates the elemental proportions of carbon (C), oxygen (O), and nitrogen (N) on the CF surface across various stages. On

the desized CF surface, the predominant elements are C and O, with a minor presence of N. After sizing treatment, there is a discernible decline in the C proportion, juxtaposed against a notable increase in O, suggesting an enhancement in oxygenic groups on the CF surface. Upon application of the HWPU coating, the C proportion diminishes from 84.7% to 74.6%, while both O and N proportions exhibit an obviously increment, substantiating the effective integration of the sizing agent. The evolution of functional groups on the CF surface at different stages was meticulously evaluated via peak fitting and integration of the C1s spectrum, as depicted in Fig. S6(b-c). In Fig. S6(b), the desized CF exhibits a relatively straightforward functional group composition, primarily comprising C-C bonds (284.8 eV) interspersed with a minority of -C-OH (286.0 eV) functionalities. As illustrated in Fig. S6c, sizing treatment witnesses a reduction in C-C proportion from 82.4% to 54.7%, accompanied by a surge in -C-OH from 17.6% to 34.7%. Additionally, upon HWPU sizing agent application, distinct -COOH and N-C=O peaks emerge at 290.1 eV and 287.7eV, further corroborating the successful modification and coating of the CF surface. This modification renders the CF surface compatible with the PA6 resin matrix, owing to their analogous amide structures.



Figure S1. The particle size distributions and PDI of HWPU sizing agent.



Figure S2. The (a) proton NMR of amine-ESBO with proton area integration, (b)



proton NMR of ESBO with proton area integration.

Figure S3. ¹³C NMR spectra of (a) Amine–ESBO and (b) ESBO.





60

70

5min

40

20

0

100

200

300

Temperature (°C)

400

500

250 °C 1.4% weight lost

180°C 230°

10min 15min 20min 25min 30min

130°C

4.9% weight lost

40min 45min

50mir

keen 250 °C for 30

35min



isothermal thermogravimetric curve of synthesized HWPU.

Figure S6. (a) Wide-scan XPS spectra and (b-c) C1s peak spectra of desized CF and

HWPU sized CF.

Samples	Element proportion (%)					
	C1s	O1s	N1s			
Desized CF	84.7	11.1	4.2			
Sized CF	74.6	18.7	6.7			

Table S1. Analy	ysis of	surface	element	proportio	n of	carbon	fiber.
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