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A simple way to synthesize nano-scale stable epoxy emulsion for sizing CF/epoxy composites

Yifan Chen[a], Lei Ding[a], Chao Cui[a], Zhengxiang Zhong[a], Li Liu[*,a,b] and Yudong Huang[*,a]

[a] School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, PR China

[b] State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, PR China

[*] Corresponding author: Yudong Huang; Li Liu

E-mail: ydhuanghit@163.com; liulihit@163.com

The homogenizing emulsifying machine was purchased from Gongyi Yuhua Instrument Co., Ltd., and the model is FA-25. The speed of the homogenizer emulsifier ranges from 10000 to 28000 r/min. When the rotating speed is 10000 r/min, add water and stir for 1min. When the rotating speed is 14000 r/min, conduct high-speed shear for 2min. The two speeds keep switching until all distilled water is added.

The standard curve of hydrophile-lipophile balance (HLB) value was determined by water titration method [9]. First, isopropanol and toluene with mass ratio of 100:15 were mixed as solvent. The compound emulsifier of Span 80 (HLB = 4.3) and Tween 20 (HLB = 16.5) was prepared according to different mass ratio, and the HLB value was calculated according to the Formula (1). Then the compound emulsifier was evenly dispersed into 5.8 ml solvent and titrated with distilled water. The standard curve of HLB value was drawn with the mL of water consumed as the ordinate and the HLB value of compound emulsifier as the abscissa, as shown in the Fig. S1. Then, the prepared emulsifier and Span 80 were mixed according to different mass ratios and titrated. The volume of water consumed was recorded, and the corresponding HLB value of the compound emulsifier was obtained from the standard curve. The HLB value of the compound emulsifier was substituted into the formula to calculate the HLB value of the prepared emulsifier.

$$HLB_0 = (W_A HLB_A + W_B HLB_B)/(W_A + W_B) \quad (1)$$

HLB_0 is the HLB value of the compound emulsifier. W_A and W_B are weight fraction of components A and B, respectively. HLB_A and HLB_B are the HLB value of A and B, respectively.

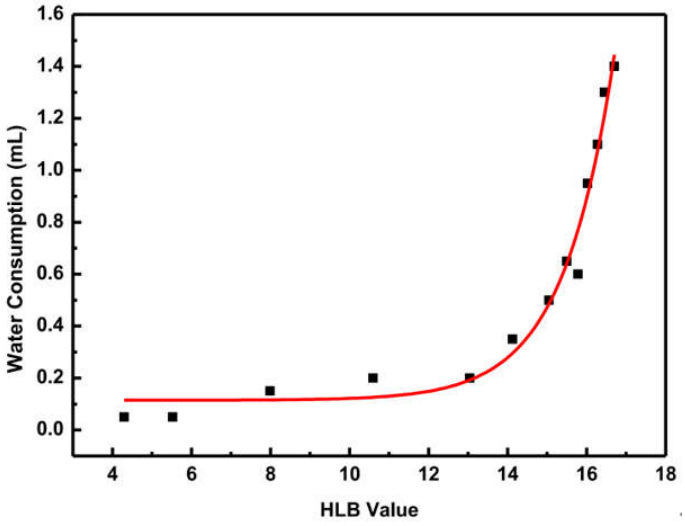

Fig. S1. HLB value standard curve.

The single fiber tensile test was carried out with universal testing machine (5569, Instron, USA), and testing speed was 10 mm/min. Tensile strength of single fiber was then analyzed by Weibull statistical methods. The dynamic contact angle between the CF and the test liquid was measured by a dynamic contact angle meter (DCAT21, Germany). The test liquids were deionized water (γ^d = 21.8 mJ/m^2, γ = 72.8 mJ/m^2) and diiodomethane (γ^d = 50.8 mJ/m^2, γ = 50.8 mJ/m^2). The polar and dispersive components could be obtained by the equation (2) and (3).

$$\gamma_l(1+\cos\theta) = 2(\gamma_l^p\gamma_f^p)^{1/2} + 2(\gamma_l^d\gamma_f^d)^{1/2} \quad (2)$$

$$\gamma_f = \gamma_f^p + \gamma_f^d \quad (3)$$

where γ_l represents the surface tension of the test liquid, γ_l^d represents dispersive component, and γ_l^p represents polar components. γ_f^d and γ_f^p are dispersion component and polar component of the CFs, respectively.

In addition, the change of the contact angle between the surface of the sizing agent films and the water drop with time was also recorded. According to the temperature and time of the sizing process, the sizing agent is made into a film with a

thickness of 0.02 um. Record the image of water droplets falling on the surface of sizing agent film on the contact angle instrument (Dingsheng Tester, JY-82). The contact angle was measured using the height method.

In order to characterize interfacial shear strength (IFSS), monofilament debonding test between CF and matrix resin (EP) was carried out with fiber pull out tester. Micro composites were prepared according to the process of composites. The difference was that the matrix resin was dropped on a single fiber for curing. The micro composites samples were tested at a speed 150 um/min. IFSS values were calculated according to the formula (4).

$$IFSS = \frac{F_{MAX}}{\pi dl} \tag{4}$$

where F_{MAX} is maximum horizontal pull (the maximum load recorded), d is CF diameter of matrix resin embedded CF, and l is length of matrix resin embedded CF.

The electronic universal material testing machine (INSTRON 5569, USA) was used to characterize the interlaminar shear strength (ILSS) of the CF composites according to the ASTM D2344. The samples with the dimensions of 20 mm× 6.5 mm × 2 mm were tested at a speed of 2 mm/min. ILSS values were calculated by the formula (5).

$$ILSS = \frac{3P}{4bh} \tag{5}$$

where P represents the failure load (the maximum compression load recorded, N), b and h represent the sample width (mm) and thickness (mm), respectively.

In different characterization of CF tests, each group of samples were measured several times, and then the average value was calculated.

Table S1 HLB values of four emulsifiers

Samples	HLB Value
EE	16.54
EE-P4	16.30
EE-P20	16.08
EE-P40	16.28

Fig. S2. The apparent state of four kinds of white emulsion.

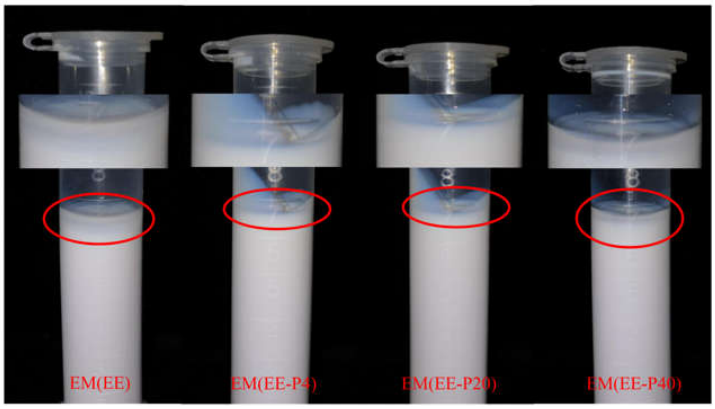

Fig. S3. Stratification state of four emulsions after centrifugation

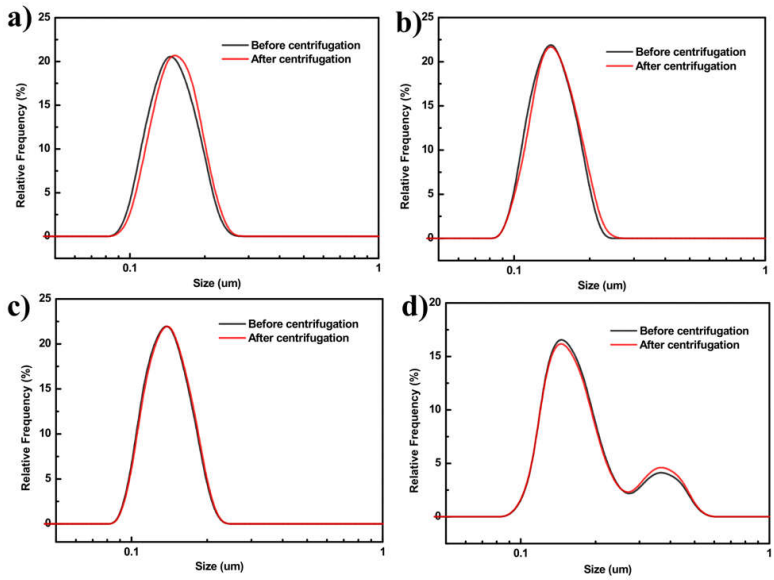

Fig. S4. Particle size distribution curves of four emulsions after centrifugation: (a)EM(EE); (b)EM(EE-P4); (c)EM(EE-P20); (d)EM(EE-P40).

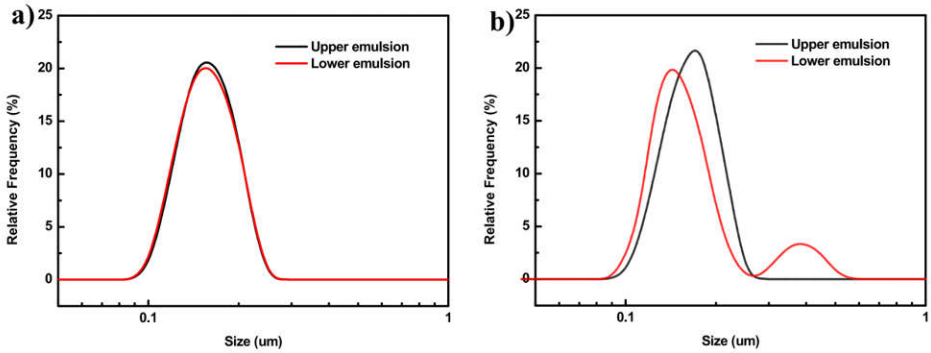

Fig. S5. The upper and lower particle sizes of EM(EE): (a) initial and (b) after standing for 7 days.

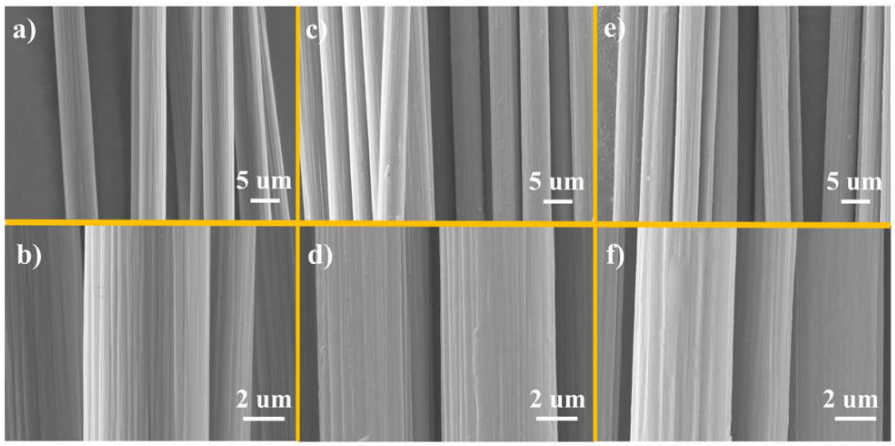

Fig. S6. SEM image of bare CF (a-b), CF(EE) (c-d) and CF(EE-P20) (e-f).

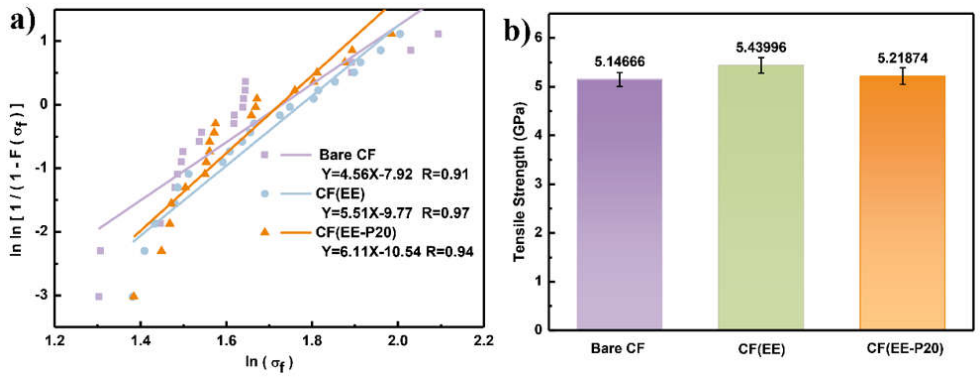

Fig. S7. (a) Weibull distribution of mechanical properties and (b) tensile strength of CF before and after sizing.

Fig. S7a showed the Weibull distribution of mechanical properties of CF before and after sizing, and Fig. S7b showed the tensile strength.

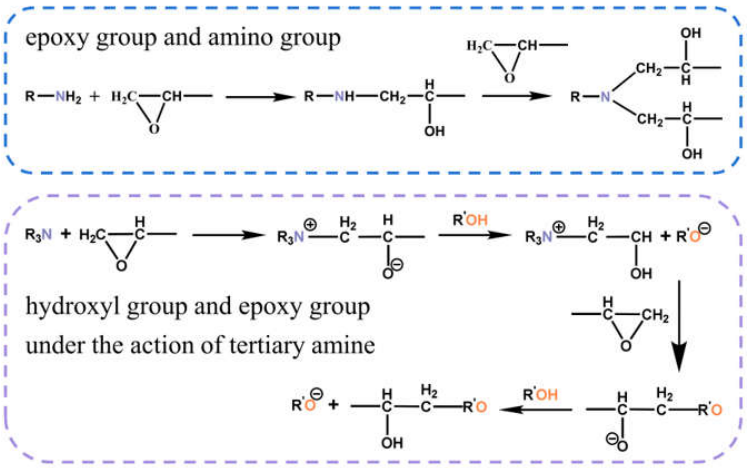

Fig. S8 The reaction process of epoxy group with amino group and hydroxyl group respectively.

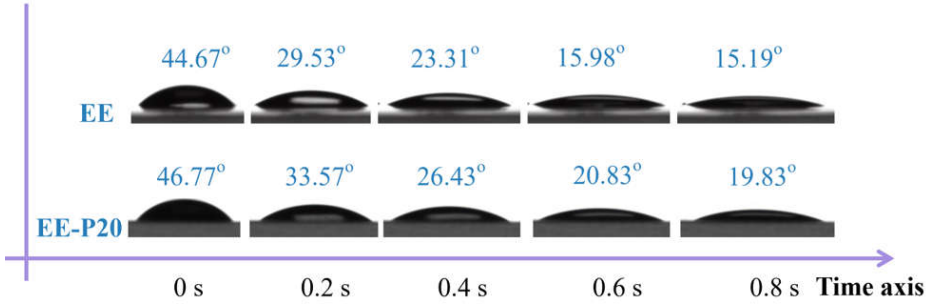

Fig. S9 Variation of contact angle of water droplets on the surface of sizing agent films with time.

It can be seen intuitively from the figure that water droplets always have a larger contact angle (initial: 46.77°, 0.8 s: 19.83°) on EM (EE-P20) film at the same time

interval. Compared with EM (EE), the hydrophilicity of EM (EE-P20) is weaker, and the moisture absorption of CF (EE-P20) is weaker.