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Improving the interfacial properties of carbon fiber-reinforced epoxy composites by grafting of branched polyethyleneimine on carbon fiber surface in supercritical methanol

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ABSTRACT

We report on a new application of branched polyethyleneimine as a coupling agent to functionalize carbon fibers in conventional and supercritical methods. The microstructure and mechanical properties of carbon fibers before and after modification were investigated. Polyethyleneimine could increase the polarity, wettability and roughness of the carbon fiber surface, and supercritical methanol was also able to improve the reaction efficiency. The interfacial shear strength and impact toughness improved significantly when using the two methods, especially in supercritical methanol. Reinforcing and toughening mechanisms have also been discussed. Functionalization does not decrease fiber tensile strength.

1. Introduction

Carbon fibers (CFs) have become ideal reinforcements for polymer matrix composites. The mechanical properties of composites are influenced not only by the intrinsic characteristics of CF and epoxy resin, but also by their interfacial adhesion [1]. The interfacial adhesion depends largely on molecular interfacial structure and interactions. However, the non-polar, highly stable and smooth graphitic surface of CF makes it difficult to provide desired interactions without CF surface modification [2].

Grafting of micro-molecules or polymers onto the CF surface can yield a controlled, ordered and active structure, which has proven to be an effective synthesis method [3,4]. Amine groups can react with epoxy groups, and the grafting of CF with amine-containing polymers should result in good bridge formation between the CF and epoxy matrix. Branched polyethyleneimine (PEI), a polymer with three-dimensional elliptic spherical stereo structure and rich in amine and imine groups, can react with acyl chloride and epoxy [5,6]. Some researchers [7] have grafted PEI onto CF after polydopamine pre-deposition, and improved mechanical and thermal properties in CF/epoxy composites. Therefore, PEI is a good candidate to functionalize CF and improve interfacial properties in the CF/epoxy composites.

Supercritical fluids offer a promising technology to functionalize CF since they are environmentally friendly and relatively easy to handle [8–10]. They also possess an interesting combination of properties such as low viscosity, high diffusivity and solvation power, which enables the coupling agent in supercritical fluids to be transported more efficiently and distributed more homogeneously. Some papers report on the investigation of supercritical fluid treatment of the CF surface, mainly CF cleaning and oxidation, however, CF grafting in supercritical fluids has not yet been reported on.

In this work, we develop a high-efficiency supercritical fluid as a reaction medium to functionalize CF with PEI, and compare the results obtained with the traditional method. Because the PEI decomposition temperature is low (543 K), methanol is selected as the supercritical fluid. A microstructure and mechanical property evaluation indicates that PEI is able to form "cross-bridges" to connect the CF and epoxy matrix, and supercritical methanol is an available medium to improve efficiency, which indicates that our strategy holds promise in the functional material field.

2. Experimental

2.1. Materials

Polyacrylonitrile-based CFs, with an average diameter of 7 mm, and density of 1.76 g cm^{-3} were purchased from Sino Steel Jilin

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Carbon Co., China. Branched PEI [molecular mass *Mn* of 600] was purchased from Aladdin Co., Shanghai, China. Potassium persulfate ($K_2S_2O_8$) and silver nitrate ($AgNO_3$) were purchased from Sigma Aldrich Chemicals, China. All other chemicals, such as acetone, methanol, ethanol and thionyl chloride ($SOCl_2$) were from Tianjin Bodi Organic Chemicals Co. Ltd., China and were of reagent grade.

2.2. Functionalization of PEI onto CF

Preliminary experiments were used to determine the optimal parameters of every reaction step. The formation of PEI grafted onto CF was by two methods as illustrated in Fig. 1.

2.2.1. CF cleaning, oxidizing, and acyl chloride treatment

The CFs were desized in supercritical acetone/water at 633 K for 20 min [11], and were denoted as untreated CF. The extracted CF was treated in 0.01 mol/L $AgNO_3$/0.1 mol/L $K_2S_2O_8$ solution at 343 K for 1 h to introduce carboxylic acid groups (CF-COOH) [12]. To form a covalent bond with PEI, the carboxyl groups on CF needed to convert to carbonyl chloride groups [13]. The CF-COOH was reacted with a mixture solution of 100 mL $SOCl_2$/5 mL dimethylformamide (20:1 v/v) at 349 K for 48 h to yield acyl chloride-functionalized CF (CF-COCl).

2.2.2. Conventional grafting of PEI onto CF

PEI (1 mL) was dissolved in 10 mL 1-methyl-2-pyrrolidinone by 10 min sonication. CF-COCl (0.5 g) was added to this solution and dipped at room temperature for 36 h in argon. PEI (2 mL) in 20 mL 1-methyl-2-pyrrolidinone was added to the reaction mixture, which was maintained at room temperature for 24 h. PEI (2 mL) in 20 mL 1-methyl- 2-pyrrolidinone was added to the solution and the reaction mixture was refluxed for 24 h [14]. The grafted CF was removed, washed thoroughly and sequentially with water and methanol three times, dried at 353 K for 24 h, and was denoted CF-g-PEI.

2.2.3. Grafting of PEI onto CF in supercritical methanol

PEI (5 mL) was dissolved in 50 mL anhydrous methanol. CF-COCl (0.5 g) was spread lengthwise on a glass frame. The solution mentioned above and the CF-COCl were transferred into a stainless steel autoclave (95 mL) with a high pressure valve, and the glass frame was immersed into the anhydrous methanol solution. An autoclave was heated to 518 K and greater than 6 MPa, and maintained for 10 min. The autoclave was removed and cooled to room temperature, and the supercritical methanol dropped slowly to atmospheric pressure. The frame was then removed and the cleaning of grafted CF was as described previously. The product was denoted CF-g-s-PEI.

2.3. Characterization techniques

X-ray photoelectron spectroscopy (XPS, ESCALAB 220i-XL, VG, UK) was carried out to detect the presence of surface elements and determine the chemical composition of CFs. XPS Peak version 4.1 was used for data analysis.

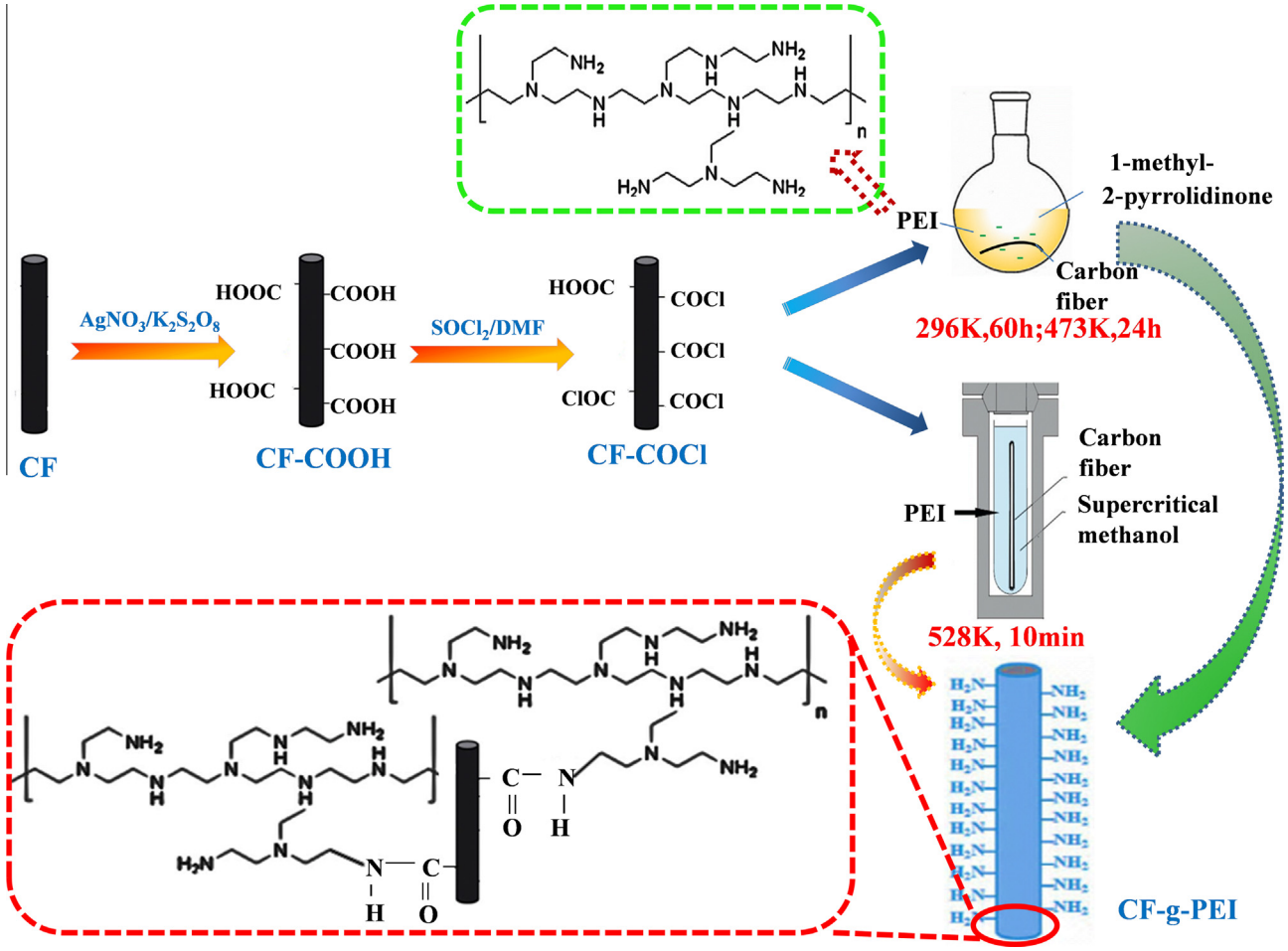

Fig. 1. Schematic illustration of PEI grafted to CF surface in conventional and supercritical methanol method.