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Covalent modification of Aramid fibers' surface via direct fluorination to enhance composite interfacial properties

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ABSTRACT

Covalently introducing amine and epoxy groups on the surface of inert fiber will make a great contribution to the interfacial properties of fiber/epoxy composite. In this study, direct fluorination was utilized to introduce aromatic C—F bonds on the surface of Aramid fiber. The F atom was proved to be linked with phenyl based on the analysis of fluorinated model compounds of the fiber. Those C—F bonds were used as the active sites for further functionalization of Si—OH by the nucleophilic substitution of these active C—F bonds with 3-aminopropyltriethoxysilane (APTES). On the basis of the reactive Si—OH groups, these traditional coupling agents, APTES and 3-glycidoxypropylthrimethoxysilane (GPTES) were respectively grafted on the fiber surface and thus successfully realized the introduction of amine and epoxy groups. Compared to that of untreated fiber, the interfacial shear strength of the fiber with amine/epoxy modified had a dramatical increase of 46.7% and 40.0%, respectively. It is considered that the formation of chemical bond between epoxy resin and amine/epoxy group on fiber surface plays a determining role in improving the interfacial adhesion.

1. Introduction

It is well-known that high-performance organic fibers, such as Aramid fiber, exhibit excellent mechanical and thermal properties, and have been used as ideal reinforcement in fiber/resin composites in the application of marine, aerospace and automobile industry [1–3]. However, those fibers usually possess smooth and chemically inert surface, which obstructs chemical bonding and mechanical interlocking with polymer matrix, thus bringing about poor adhesion between fiber/matrix interfaces [4,5]. As described in many reports, the fiber/matrix interface is a vital intermediate to transfer the stress from matrix to fiber, and can greatly affect the composites properties. Therefore, surface modification of Aramid fiber becomes an area of current interest.

Numerous efforts have been utilized in order to enhance the interfacial interaction between fiber and resin systems, including plasma irradiation, surface coating and acid/alkali treatment, etc [6,7]. All those treatments aim at increasing the surface energy, inducing chemically active functional groups, or changing the microstructure of the fiber surface. Among them, chemical grafting, as an effective route to make substrates meet different requirements in applications, has caught researchers' eyes by its versatile superiority, offering an efficient approach to modify surface chemical component and physical morphology of fiber [8,9].

Generally, polar groups perform as active sites for chemical grafting on account of their chemical activity in reaction. Taking glass fiber for example, active Si—OH groups on their surface are easy to be modified by effective coupling agents, including 3-aminopropyltriethoxysilane (APTES) and 3-glycidoxypropylthrimethoxysilane (GPTES), thus introducing of amine and epoxy groups on glass fiber surface. Those amine and epoxy groups would greatly improve the adhesion of fiber/epoxy composite by forming covalent bond on the composite interfaces. However, introducing those traditional effective coupling agents onto high performance fiber with chemical inert surface is a big challenge.

Chemical oxidation appears to be a popular method among researchers to solve the problem [10–12]. Tang et al. [8] reported that low contents of branched polyethylenimine (PEI) were grafted on carbon fibers (CFs) through chemical oxidation. The interfacial shear strength (IFSS) of PEI modified CFs with epoxy resin can reach a maximum of 107.2 ± 14.3 MPa, compared with that of unmodified CFs (78.1 ± 11.6 MPa). Huang et al. [13] investigated the grafting of silane and graphene oxide (GO) onto Poly-p-phenylene ben-zobisthiazole (PBO) fibers through acid oxidation. The results showed the IFSS of PBO fiber with GO modified had a remarkable increase compared to that of untreated-PBO composite. All the grafting methods above involve acid oxidation treatment. In this way, carboxyl and hydroxyl groups are introduced to the fiber surface and act as active spots in further modification. However, acid oxidation can only generate low contents of function groups, which will undoubtedly limit the grafting density on fiber surface. Also, the diversity of the oxygen-containing groups from acid oxidation makes the grafting process uncontrollable and complicated. Moreover, a sequence of tedious post-process after oxidation is required for the elimination of chemical residuals, making oxidation method time-consuming and laborious.

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One way to circumvent those drawbacks is direct fluorination. It is a new efficient method to generate active functional groups and has been widely utilized in the modification of chemical inert materials [14–16]. In our previous study [17,18], direct fluorination of Aramid fiber will undoubtedly improve the IFSS of fiber/epoxy composite, due to the generation of polar groups like C—F bond to increase the surface energy. It is worth pondering whether the C—F bond on fluorinated fiber can perform as active sites for the introducing of amine and epoxy groups on fiber surface.

Many literatures reported the derivative reactions based on C—F bonds in fluorine-contained aromatics, fluorinated grapheme (FG) and fluorinated carbon nanotube (FCNT) [19–22]. All those C—F bonds are aromatic with high polarity and steric hindrance, so that they are capable of forming substitution reaction with various nucleophiles, including amine and thiol compounds. Zbor˘il et al. [23] reported that fluorine atom was substituted by nucleophilic sulfhydryl groups in FG and this new graphene derivative was used as a low cost biosensor for impedimetric detection of DNA hybridization. Wang et al. [24] prepared the hydrophilic urea-modified FG through the substitution reaction of FG, and the water antiwear ability of functionalized graphene can be largely improved. Therefore, C—F bonds may have the ability to act as intermediate for further modification of Aramid fiber.

Guided by the facts stated above, we attempted to graft APTES and GPTES via the nucleophilic substitution of aromatic C—F bond on Aramid fiber surface to enhance its adhesion with epoxy resin.

PBIA (poly-p-phenylene-benzimidazole-terephthalamide) fiber, as a kind of Aramid fiber, is modified from poly(p-phenyleneterephthalamide) (PPTA) fiber by the introducing of 2-(4-Aminophenyl)-1H-benzimidazol-5-amine (PABZ) as the third monomer by copolycondensation [25]. Due to the introducing of PABZ, PBIA fibers have superior tensile strength which is 25% higher than PPTA, and the IFSS of the fiber/epoxy resin composites also increases by 20%. Therefore PBIA fiber has shown remarkable superiority in producing fiber reinforced advanced composites [26]. The chemical structure of PBIA fiber is presented in Fig. 1.

In this study, PBIA fibers were chosen as substrates to be modified in three steps in order to enhance the interfacial adhesion of fiber/epoxy resin composites. The whole process of modification was illustrated in Fig. 2. In step 1, direct fluorination was used to generate aromatic C—F bonds on PBIA fiber surface. In step 2, using the nucleophilic substitution reaction between the C—F bonds on fiber surface and NH_2 of APTES, $Si—OCH_2CH_3$ of APTES was linked as end group on PBIA structure. Then after hydrolysis, the $Si—OCH_2CH_3$ was transformed to Si—OH, forming the active surface similar to glass fiber. Finally in step 3, the fiber again reacted with APTES and GPTES by the condensation reaction between Si—OH on fiber surface and siloxane from those silane couple agents to obtain separately amine-functionalized and epoxy-functionalized fiber surfaces, thus introducing the traditional effective coupling agent of glass fiber onto Aramid fiber and improving the interfacial adhesive property of PBIA fiber/epoxy matrix.

2. Experiments

2.1. Chemicals

The PBIA fibers were supplied by Chengrand Research Institute of Chemical Industry Co., Ltd. The F_2/N_2 (10 vol% for F_2) with purity up to 99.99% was obtained from Chengdu Kemeite Fluorine Industry Plastic Co., Ltd. Benzoyl chloride (KeLong Chemical, 99%), P-Phenylenediamine (KeLong Chemical, 98%), HCl (KeLong Chemical, 36.5%), APTES(Shin-Etsu Silicone, 99.0%) and GPTES (Shin-Etsu Silicone, 99.0%) were used without further purification.

2.2. Step 1: direct fluorination of PBIA fiber surface

5 g PBIA fiber was put in a closed stainless steel chamber equipped with a vacuum line. The air in closed chamber was removed and replaced by nitrogen gas for three cycles to remove residual oxygen and moisture in the chamber. 20 KPa F_2/N_2 mixed gas was introduced to the chamber at 100 °C for 30 min. Then residual F_2 and byproducts in the chamber were removed by vacuum and absorbed by alkali aqueous solution at once. Afterwards, fluorinated PBIA fiber was taken out and washed by ethanol for further modification. The fluorinated PBIA fiber was denoted as PBIA-F.

2.3. Step 2: grafting Si—OH as end groups on PBIA fiber surface

APTES was diluted to 1 wt.% by ethanol in a glass vial. Then PBAI-F fiber was added in. The vial was placed in oil bath and maintained at 70 °C for 1 h. After that, the fiber was taken out and washed using soxhlet extractor for 12 h to eliminate residual APTES. The siloxane group of APTES was hydrolyzed to Si—OH by putting the APTES-modified PBIA-F fiber into dilute HCl aqueous solution (PH = 4) for 1 h at room temperature. The obtained fiber were denoted as PBIA-A.

2.4. Step 3: amine and epoxy functionalization of PBIA fiber surface

Two parts of obtained PBIA-A fiber were separately immersed in APTES solution and GPTES solution, and active amine and epoxy group were respectively attached on the fiber surface by the reaction between siloxane group from those two silane coupling agents and Si—OH from PBIA-A. Then, those two kinds of functionalized fibers were washed with soxhlet extractor for 12 h to eliminate residual silane coupling agents. These obtained fibers were denoted as PBIA-A-A and PBIA-A-G.

2.5. The preparation and measurement of PBIA fiber/epoxy composites

The composite specimens are prepared using PBIA fiber and Epoxy resin, and the adhesive property of the composite is measured using multi-fiber pull-out strength. Detail process of the preparation is shown in Supporting Information (Fig. 1s).

2.6. Synthesis and direct fluorination of N,N′-Diphenylterephthaldiamide

N,N′-Diphenylterephthaldiamide (NDPD) was synthesized from one part of P-Phenylenediamine and two parts of benzoyl chloride. After synthesized, the products were characterized and fluorinated. The fluorination of NDPD was carried out in the same procedure as the fluorination of PBIA fiber. The chemical structure of NDPD is presented in Fig. 3 and the molecules after fluorination was denoted as F-NDPD.

2.7. Characterization

2.7.1. Characterization of the chemical structure change of NDPD

H^1NMR spectroscopy was performed using Bruker AV II-400 MHz. Electro spray ionization Mass spectrum (ESI-MS) (TSQ Quantum

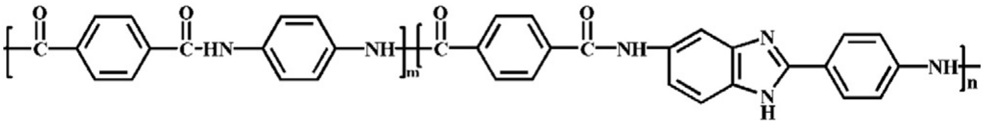

Fig. 1. Chemical structure of PBIA fiber.