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Full Length Article

Nondestructive grafting of PEI on aramid fiber surface through the coordination of Fe (III) to enhance composite interfacial properties

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ABSTRACT

The nondestructive functionalization of aramid fiber is an important research direction. In this study, a kind of benzimidazole-contained aramid fiber, Poly-*p*-phenylene-benzimidazole-terephthalamide (PBIA) fiber, was modified by the coordination of benzimidazole unit in fiber structure with Fe^{3+}. Further, the coordinatively unsaturated sites of Fe^{3+} endow the modified fiber with active sites for the grafting of PEI. Model compound of PBIA unit, PBA, was utilized to confirm the whole process of modification. In comparison with that of the untreated fiber, the IFSS value of fiber with PEI grafted has an increase by 47%, owing to the chemical bond formed on the fiber/epoxy interface and the better wettability of resin to fiber. In all, the study presents a nondestructive functionalization of aramid fiber and can be employed in the modification of other benzimidazole-contained substrates.

1. Introduction

As an important type of high performance fibers, aramid fiber possesses superior performances including high thermal stability, good chemical resistance and mechanical strength due to its rigid structure, and it has been widely adopted in the application of aviation, aerospace, automotive, sports and military [1–3]. However, aramid fiber does not fulfill its potential as the reinforcement in composites materials, owing to the weak adhesion of fiber/matrix interface [4,5]. It is well known that the fiber-matrix interface governs the load transfer efficiency, and can be seen as a crucial factor to achieve the ideal performance of the composites. Therefore, many approaches have been reported to enhance fiber/matrix interfacial properties. In polymeric composites, the presence of reactive functional groups on fiber surface is expected to greatly enhance the mechanical strength of the fiber-matrix interface. Since aramid fiber possesses a chemical inert surface, chemical functionalization is commonly used for the introducing those active groups, and it generally involves chemical oxidation [6] and plasma irradiation [7], which has shown promising results for interface improvements. However, the fiber's mechanical properties are often significantly degraded by the cleavage of macromolecular main chain, resulting in a composite with reduced properties. So the nondestructive chemical functionalization of aramid fiber is an important research direction.

PBIA (Poly-*p*-phenylene-benzimidazole-terephthalamide) fiber is a kind of benzimidazole-contained aramid fiber. it is modified from poly(*p*-phenyleneterephthalamide) (PPTA) fiber by introducing the diamine monomer 2-(4-aminophenyl)-5-aminobenzimidazole (PABZ) into the main chain by copolymerizationis [8]. Due to the introducing of PABZ, PBIA fiber has better 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 (Fig. 1).

The introduced benzimidazole groups not only endow the fiber with a higher tensile strength, but also can be regarded as active sites for further modification to meet industrial requirements with a high specification. As reported by many researchers, benzimidazole exhibits strong chemical reactivity derived from those functional groups, including NH, C=N and the big conjugated system [9–14]. Among them, the C=N bond, which can bond with transition metal ion and hydrogen proton by complexation, has been widely investigated by many researchers. He et al. [15] prepared the N-substituted polybenzimidazole (PBI), with benzimidazole introduced onto the PBI backbones as pendent group. The C=N bond on benzimidazole provided additional basic sites for the H^+ complexation, which resulted in a higher acid doping level and conductivity of the membranes. Fu et al. [16] reported the grafting of benzimidazole on b-cyclodextrins, and the

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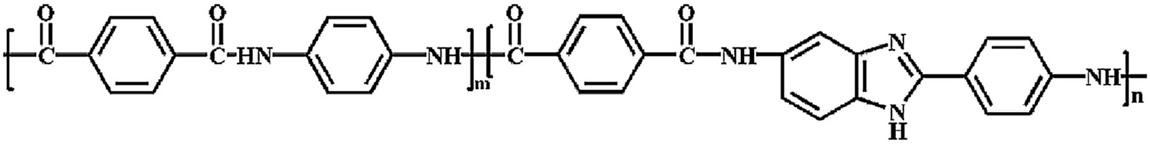

Fig. 1. Chemical structure of PBIA fiber.

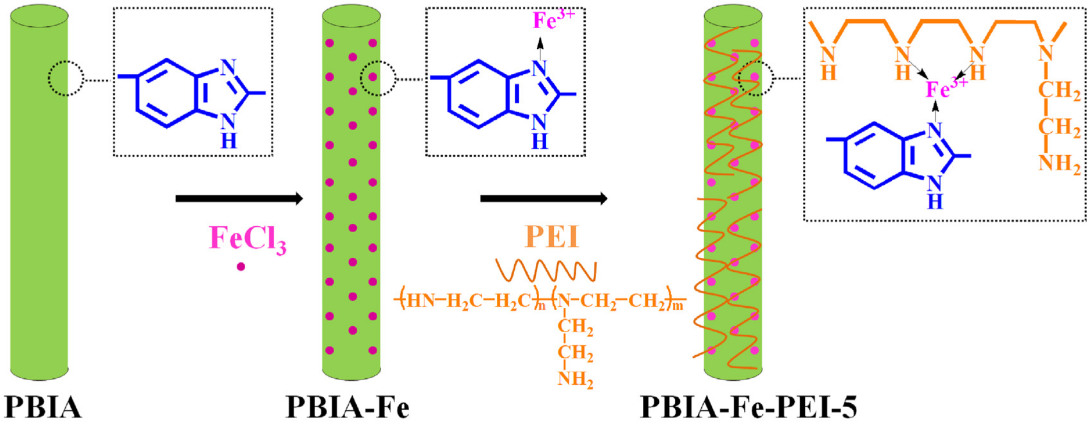

Fig. 2. Scheme of the modification process.

self-complexation behavior of mono-benzimidazole functionalized b-cyclodextrins was investigated. The unique molecular structure showed pH-triggered release property and could be employed as supramolecular nanovalves on the external surface of mesoporous silica. Ma et al. [17] reported that a new pyrene-based probe, 2-(1-pyrenyl) benzimidazole, was synthesized by a one-step process. In aqueous buffer solution, it showed a highly selective and sensitive ratiometric probe for Fe^{3+} based on monomer–excimer conversion. All the aforementioned studies involve the complexation of C=N bond on benzimidazole unit and shows high activity, so it is also available for the modification of PBIA fiber.

The transition metal ions, including Cu^{2+} and Fe^{3+}, usually have several coordination sites [18]. Considering the fact that the benzimidazole unit is immobile on the rigid macromolecular main chain and there exists great hinderance derived from the high crystallinity and orientation of the PBIA structure, the multiple coordination sites of transition metal ion can't be fully consumed if excessive transition metal ions were introduced in the PBIA structure [19,20]. Furthermore, the existence of coordinatively unsaturated metal sites is very beneficial to the introducing of functional groups [21–24]. Jong-San Chang et al. [25] prepared the MOFs with amine grafting on coordinatively unsaturated metal centers. It was found that amine grafted MOFs exhibiting the remarkably high activities in the Knoevenagel condensation. Since the role of amine modifiers on the properties of the interface has been well documented in the literature, it is feasible to introduce amine groups on PBIA fiber surface through the coordinatively unsaturated metal centers.

Polyethyleneimine (PEI), a branched polymer with plentiful amine groups on its molecular chains, has the potential to meet our requirement [26,27]. First, amine group is typically the hard acid in the hard-soft acid-basic principle, they can be easily bonded with those coordinatively unsaturated metal centers, including Fe^{3+} and Cu^{2+}. Then, the chemical reactivity and physical flexibility of PEI backbone could facilitate itself to occupy the unsaturated coordination sites within the framework. Meanwhile, the introducing of PEI on fiber surface could increase surface polarity of fiber and form chemical linkage with epoxy matrix during the curing process. So PEI is a good candidate to functionalize PBIA fiber and improve interfacial properties in the fiber/epoxy composites.

In this study, Fe^{3+}, as a kind of hard acid with six coordination sites, was unsaturatedly coordinated to PBIA fiber by the excessive loading of Fe^{3+} and the regular arrangement of the PBIA structure. Further these coordinatively unsaturated Fe^{3+} acts as active sites for the grafting of PEI in order to enhance the interfacial adhesion of fiber/epoxy resin composites. The whole process of modification was illustrated in Fig. 2. The study raises a nondestructive method for the modification of aramid fiber, which also has a wide application in the activation of benzimidazole-contained polymers.

2. Experiments

2.1. Chemicals

PBIA fibers (diameter 16um) were purchased by Chengrand Research Institute of Chemical Industry Co. $FeCl_3{\cdot}7H_2O$ and PEI (molecular weight 70000) were received from Aladdin Co. All other chemicals (ethanol, water, isopropanol, dimethylacetamide, hydrochloric acid, sulfosalicylic acid and ammonia) obtained from KeLong Chemicals Co. Ltd. were reagent-grade.

2.2. The coordination of Fe^{3+} onto PBIA fiber

1 g $FeCl_3{\cdot}7H_2O$ was dissolved in 40 ml water. 1 ml of the Fe^{3+} solution was diluted to various kinds of 100 ml mixed solution in glass vial with different organic solvents (DMAc, ethanol, isopropanol and water) respectively. Then 1.78 g PBIA fiber was added in. These vials were placed in oil bath and maintained at 50 °C for 6 h. Upon the completion of the reaction, the fibers were taken out from the solution, followed by a two-step washing with ethanol and water. Among all the obtained products, the fiber with the highest Fe^{3+} content was denoted as PBIA-Fe.

2.3. Grafting PEI on fiber surface via coordination bond

PEI was dissolved to 1 mg/ml in water. With the addition of ethanol, different volumes (1 ml, 3 ml, 5 ml, 7 ml, 9 ml, 10 ml and