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# ACCEPTED MANUSCRIPT

## Grafting degradable coordination polymer on aramid fiber surface to

### improve its interfacial properties

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**Abstract:** Surface modification of aramid fiber to improve its interfacial adhesion with epoxy resin is always a meaningful topic. Herein, a layer of coordination polymer (CP) was introduced on aramid fiber surface via chemical grafting, and the thickness of CP layer could be controlled by reaction time. The experimental results showed that CP layer with a thickness of 40nm to 60nm is optimal for fiber's interfacial properties. Also, it is found that this CP layer could be degraded by HCl, making the fiber recyclable in fiber/resin composite with typical fabrication techniques.

Keywords: polymer composites; interfaces; adhesion; interfacial properties

#### Introduction

In order to improve the adhesion with epoxy matrix, surface modification of aramid fiber has long been studied. It is believed that there are three kinds of interactions at the fiber/epoxy interphase that determine the adhesion. They are (1) mechanical interlocking; (2) polarity matching[1]; (3) chemical bonding[2]. Strategies reported for the aramid fiber's surface modification all aim to increase those interactions, and much progress has been presented [3-8]. However, another factor of interphase, interphase thickness, also affects composite interfacial performance, and it is usually neglected[9].

In this paper, chemical grafting was proposed for aramid fiber to improve its interfacial adhesion with epoxy resin. There are three steps for the chemical grafting strategy (see in Figure 1a). Firstly, direct fluorination was applied to generate C-F bonds on fiber surface. Secondly, using C-F bonds as the active sites, polyethyleneimine (PEI) was introduced on fiber surface by a substitution reaction. Thirdly, a layer of coordination polymer structure, made of  $Fe^{3+}$  and PEI, was self-assembled on fiber surface, using PEI as the linking sites. By controlling the self-assembly time, CP layer with different thickness is obtained. It is found that a CP layer of 40-60nm on fiber surface is optimal for fiber's interfacial adhesion with epoxy resin. Also, this CP layer could be degradable by the treatment of HCl, making the fiber recyclable in fiber/resin composite with typical fabrication techniques.

#### 2 Experiments procedure

First, direct fluorination of 5g aramid fiber was performed at 25 °C in a steel reactor. The fluorinated fiber was denoted as AF-F. Second, 2g AF-F was put in a flask containing 1g PEI, and pyridine was used as the catalyst for the reaction. After the reaction, the obtained fiber was washed by soxhlet extractor, and it was denoted as AF-PEI. Third, PEI (30mmol/L for NH/NH<sub>2</sub> in its structure) and FeCl<sub>3</sub>·6H<sub>2</sub>O (5mmol/L) were put in a 100mL beaker. At the same time, 2g AF-PEI fiber was added in to participate in the self-assembly process of the Fe<sup>3+</sup>-PEI CP structure. Controlling the self-assembly time for 24h, 48h,

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