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Enhanced interfacial properties of domestic aramid fiber-12 via high energy gamma ray irradiation

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ABSTRACT

The high energy irradiation was used to modify domestic aramid fiber-12 (DAF12) in epoxy chloropropane. The properties of the interphase between DAF12 and epoxy matrix systems were optimized. Scanning electron microscopy was employed to characterize the surface morphology of DAF12 and high energy irradiated fibers (HEI-DAF12) and composites de-bonding section. Atomic force microscopy showed the original smooth surface disappeared. Single fiber pull-out tests revealed that the interfacial shear strength of HEI-DAF12/epoxy composite was substantially improved by 45.17% after irradiation in 400 kGy dose. Dynamic contact angle analysis indicated the increased total surface free energy. The changes of elemental composition investigated via X-ray Photoelectron Spectrometer verified the increase polar groups on fiber surface caused by high energy irradiation.

1. Introduction

Aramid fiber, with outstanding mechanical properties was successfully used as reinforcements of high-performance composites. Its low density, high tenacity, and high modulus, make aramid fiber fabrics ideal reinforcing materials in the advanced composites fields, such as aviation, aerospace, automobile and shipbuilding application [1–5]. All these excellent properties depend largely on the interfacial adhesion which finally affects the overall properties of the resulting composites. However, inert characteristics of aramid fiber surface usually lead to poor wettability and lack of interfacial covalent bonds [6]. Aramid fiber shows a unique "skin–core" structure. Hydrogen bonding among the molecular chains is weak due to its inert and rigidity and the binding force between the cortex and core is weaker than that between molecular chains. As a result, the fiber transverse strength is only about 20% of the longitudinal strength. In addition, the surface of aramid is smooth and shows poor interfacial performances in the aramid fiber reinforced polymer composite. These two factors significantly influence the strength of aramid fiber composites.

These shortcomings can be improved by the introduction of more polar components and an increase in the fiber surface roughness [7,8]. Extensive researches have been carried out for the surface treatment of aramid fibers, such as oxidation treatment [9,10], electrochemical method [11–13], plasma treatment [14–18], ultrasonic processing [19,20] and coating treatment [21]. But, almost all these methods are only suitable for the aramid fiber filaments, which is due to the compact structures of fabrics. In addition, with the wide application of large tow aramid fibers, these surface modification methods, do not satisfy the needs of large tow fiber surface treatment because of the difficulty in treating interior fibers in bundles. Therefore, it is still a big challenge for relevant scientists and engineers to functionalize the high density fiber fabrics in a much more facile, uniform and economical method.

Recently, high energy irradiation grafting has been extensively applied as a competitive methodology to develop new functional materials [22–26]. The irradiation of polymeric materials with ionizing radiation (g-rays, X-rays, accelerated electrons, ion beams) leads to the formation of very reactive intermediates, free radicals, ions, and excited states. These intermediates can follow several reaction paths that result in disproportion, hydrogen abstraction, arrangements, and/or the formation of new bonds. These grafting reactions can be induced at any temperature in gaseous, liquid, or even solid phases without any catalysts. In addition, high energy irradiation has high penetration depth to various objects and can lead to a uniform distribution of radical initiating sites through the thickness of the irradiated samples without considering the shape and volume [27,28]. In previous study, our research group has used ^{60}Co gamma-ray to modify the surface of Armos fiber,

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carbon fiber and PBO fiber, and finally obtained the significant improved interfacial properties of fiber reinforced polymer composites. For example, Yanhua Zhang has reported the Armos fiber surface modification method by gamma ray in 1.5 wt% phenol–formaldehyde in ethanol [29]. The result showed the interlaminar shear strength of the Armos/epoxy resin composite was improved by 25.4% after treated by 500 kGy radiation. The author also pointed out the irradiation process should be carried under inert gas protection due to the negative effect of oxygen radical in air [30]. Meanwhile, some irradiation methods on high density carbon fiber fabric were studied, which indicated gamma ray can effectively increase the polarity, wettability and roughness of the carbon fiber surface [31–34]. Besides, to improve the interfacial performance between poly[p-phenylene benzobisoxazole] (PBO) fiber and epoxy resin, a modified multi-walled carbon nanotubes (MWCNTs-ECP) were used to achieve this purpose through grafting onto PBO fiber surface using a gamma ray radiation method by Chunhua Zhang [35]. However, all those publications research mainly focus on the imported materials with expensive cost, which limited their actual application. Thus, choosing a kind of reinforcement with relative low cost is significant in industrialized production.

In this paper, domestic aramid fiber-12 (DAF12) was chosen as the reinforcement because of its high strength, high module, high temperature resistance and good flame retardancy. DAF12 (polyheteroarylene-co-p-phenyleneterephthalamide) is electrically insulated and spun from aromatic polyamides and copolyamides with heterocycles in the chain, which makes it possible to bear high tensile strength (4.35–4.67 GPa) that is 1.69 times higher than that of Kevlar-49 [36,37]. Its strength and toughness is 8–10 times and 3 times respectively than those of same-diameter steel wire while the weight is only about 1/5 of steel wire. Moreover, DAF12 can resist temperature as high as 560 °C without degradation and melt. Therefore, DAF12 and their composites are widely used in aerospace and military applications, for ballistic rated body armor fabric and ballistic composites, in bicycle tires, and as an asbestos substitute. Yet it is still limited by its inert surface and poor interfacial adhesion with matrix. Thus, the improvement of interfacial adhesion between DAF12 and matrix may enhance the overall mechanical performance of the resulted composites significantly.

Here, we utilized the high energy irradiation to modify the DAF12 in order to expend the application of the modified aramid fiber fabrics in the functional material fields. The effect of irradiation on the surface aramid fiber and interfacial property of DAF12/epoxy resin composites was investigated.

2. Materials and methods

2.1. Materials

DAF12, tawny and metallic color, was supplied by China Aerospace Science and Industry Corporation. The average filament diameter is about 18.8 μm. The measured tensile strength and modulus are about 4.75 and 158 GPa, respectively. Epoxy chloropropane (ECP), which has the following structure (Fig. 1), used as graft liquid, was purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used as received.

E-51 epoxy resin used as matrix material and 4,4′-methylenebis (2-ethylaniline) (H-256) as curing agent were supplied by Shanghai Research Institute of Synthetic Resins (China), used at a weight ratio of 100:32. Acetone was obtained from the First Factory of Chemical Agents, Tianjin (China).

2.2. High energy irradiation treatment

Cobalt-60 was selected as the high energy irradiation source in this research. The irradiation field was provided by Technical Physics Institute of Heilongjiang Academy of Science. Mutual irradiation grafting was introduced in this paper.

DAF12 was firstly washed in Soxhlet extractor with acetone continuously for 24 h, in order to remove contaminants or surface sizing. Then fibers were dried at 100 °C for 3 h in vacuum drying oven before being used. These obtained fibers were known as untreated fibers. Afterwards, the 15 cm length (~20 g) untreated fiber bundles were placed in each airtight glass container which was filled with epoxy chloropropane under nitrogen atmosphere. The airtight glass container has two vent holes, one for vacuuming and the other for inflating nitrogen. After sealing tightly, seven container samples were deposited into a Co point-source radiator to a total dose of 30, 100, 200, 400, 600, 800 and 1000 kGy respectively with a dose rate of 6 kGy/h at room temperature, as shown schematically in Fig. 2.

2.3. Characterizations

Surface morphologies of aramid fibers were observed by scanning electron microscopy (SEM) (Hitachi S-4700, Japan) after spray-gold treatment, and atomic force microscopy (AFM) (Solver-P47H, NT-MDT, Russia) using a taping mode, respectively.

Single fiber pull-out tests were performed to evaluate the interfacial shear strength (IFSS) between the aramid fibers and matrix (Fig. 3a). An aramid filament was chosen randomly from fiber lacertus and pasted in arched metal framework. The matrix, the mixture of epoxy resin and curing agent, was dropped on the surface of DAF12 and then the prepared samples were placed in an oven heated without any shielding gas by the curing system of references 29, which is 90 °C for 2 h, 120 °C for 2 h and 150 °C for 3 h.

After curing, shown as Fig. 3b, an epoxy droplet was blocked and loaded by two metal blades at a cross-head speed of 0.06 mm/min, which was carried out on an interfacial strength evaluation instrument (Tohei Sanyon Corporation, Japan). The value of IFSS was calculated according to Eq. (1).

$$\mathrm{IFSS} = \frac{F}{\pi D L} \tag{1}$$

where F is the value of maximum load; D is the average diameter of aramid fiber; L is the embedded length of fiber sample in matrix (Fig. 3c). In order to reduce the high scatter of data, at least 60 specimens were tested for each fiber type, and then the average value was considered as the tested value.

Dynamic contact angle tests were measured at room temperature by using a dynamic contact angle meter and tensiometer (DCAT-21, Data-Physics Instruments, Germany). Deionized water (γ^d = 21.8 mN m^{-1}, γ = 72.8 mN m^{-1}) and diiodomethane (γ^d = 50.8 mN m^{-1}, γ = 50.8 mN m^{-1}, 99% purity, Alfa Aesar, USA)

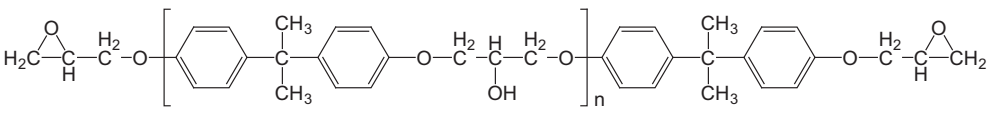

Fig. 1. Epoxy resin structural formula.