

# Electron-beam-induced post-grafting polymerization of acrylic acid onto the surface of Kevlar fibers

Lu Xu, Jiangtao Hu, Hongjuan Ma, Guozhong Wu\*

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

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## ABSTRACT

The surface of Kevlar fibers was successfully modified by electron beam (EB)-induced post-grafting of acrylic acid (AA). The generation of radicals in the fibers was confirmed by electron spin resonance (ESR) measurements, and the concentration of radicals was shown to increase as the absorbed dose increased, but decrease with increasing temperature. The influence of the synthesis conditions on the degree of grafting was also investigated. The surface microstructure and chemical composition of the modified Kevlar fibers were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The SEM images revealed that the surface of the grafted fibers was rougher than those of the pristine and irradiated fibers. XPS analysis confirmed an increase in C(O)OH groups on the surface of the Kevlar fibers, suggesting successful grafting of AA. These results indicate that EB-induced post-grafting polymerization is effective for modifying the surface properties of Kevlar fibers.

## 1. Introduction

Poly(p-phenylene terephthalamide) (PPTA) fibers, often known as Kevlar fibers, are constructed of phenylene rings and amide bonds and are one of the most important para-aramid fibers (Hirogaki et al., 2012; Chae and Kumar, 2006). Because of the rigid aromatic structures, high crystallinity, and strong H-bonding between polymer chains, PPTA fibers show excellent chemical and physical properties, such as high chemical resistance, exceptional tensile strength, high melting point, and excellent flame resistance (Wang et al., 2016; Gies et al., 2006; Yan et al., 2016). PPTA fibers have been intensively studied, attracting considerable interest in many fields, including military and defense, automobiles, space exploration, and civil construction (Shi et al., 2017; Wang et al., 2016; Pan et al., 2017; Zhang et al., 2006; Peng et al., 2012; Lin et al., 2000). As one of the most effective reinforcing fibers, PPTA fibers have frequently been applied in advanced composite materials (Lin et al., 2000; Tamargo-Martínez et al., 2011). For fiber-reinforced materials, it is well known that the interfacial strength between fibers and the polymer matrix plays a very important role in determining the mechanical properties of the composite (Lin et al., 2000; Hughes, 2012; Mathur and Netravali, 1996). Although PPTA fibers have many attractive advantages for the fabrication of polymer composites, the interfacial strength between PPTA fibers and most polymer matrices is poor owing to the chemical inertness and smooth surface of PPTA fibers resulting from their high crystallinity (Lin et al.,

2000; Leal et al., 2009; Wu and Cheng, 2006; Lin, 2002; Yatvin et al., 2015). Thus, surface modification of PPTA fibers is necessary to overcome these disadvantages and fully exploit their application in composite materials. Recently, various techniques have been developed to modify the surface of PPTA fibers. Among these techniques, chemical modification (Lin et al., 1999; Hwang et al., 2015; Castro-Muñoz et al., 2011), plasma treatment (Su et al., 2011; Sun et al., 2014; Shaker et al., 1996; Salehi-Mobarakeh et al., 2007; Wu, 2004), ultrasound treatment (Liu et al., 2006, 2001), and high energy radiation (Zhang et al., 2011, 2008) are known to be the efficient methods for modifying the surface of aramid fibers.

Although irradiation-induced post-grafting polymerization is one of most efficient methods for modifying polymer fibers by anchoring functional groups onto the surface, its application to the modification of PPTA fibers has been rarely reported (Poncinpaillard et al., 1994). High crystallinity, high transition temperatures, and strong interactions between molecules can significantly constrain the migration of radicals to the surface. Thus, the diffusion of monomers to the radicals is very difficult, resulting in inhibition of the grafting reaction (Hirogaki et al., 2012). In this study, surface modification of PPTA fibers was conducted via electron beam (EB)-induced post-grafting polymerization and acrylic acid (AA) was introduced onto the surface of PPTA fibers. The effects of radiation dose, concentration of Mohr's salt, and concentration of monomer on the degree of grafting were investigated. The surface properties of the modified PPTA fibers were evaluated by X-ray

\* Corresponding author. Mailing address: P.O. Box 800-204, Shanghai 201800, China.  
E-mail address: [wuguozhong@sinap.ac.cn](mailto:wuguozhong@sinap.ac.cn) (G. Wu).



Fig. 1. Modification of Kevlar fibers by EB-induced post-grafting polymerization.

photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

## 2. Experimental section

### 2.1. Materials

PPTA fibers with a diameter of 10  $\mu\text{m}$  were kindly supplied by DuPont Company under the commercial name of Kevlar-49. Prior to grafting, the fibers were cleaned to remove contaminants or surface sizing. First, the Kevlar fibers were extracted with methanol in a Soxhlet extraction apparatus for 24 h. Then, the fibers were washed with deionized water several times and dried in an oven at 60  $^{\circ}\text{C}$  for 12 h. AA, Mohr's salt, and other chemical agents were all of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used without further purification.

### 2.2. Post-grafting polymerization

Kevlar fibers were modified by EB-induced post-grafting polymerization, as shown in Fig. 1. First, Kevlar fibers were preirradiated in an air atmosphere using the EB accelerator at Shanghai Institute of Applied Physics with an EB energy of 1.2 MeV, a beam current of 4 mA, and a dose rate of 40  $\text{kGy h}^{-1}$ . To inhibit the decay of radicals, all irradiated samples were stored at a temperature of about  $-18^{\circ}\text{C}$  in air for no more than 2 h. Aqueous solutions with different concentrations of AA and Mohr's salt were prepared in a flask. Then, the irradiated fibers were immersed in these solution, which were then deaerated with nitrogen for about 30 min. Subsequently, grafting of AA onto the irradiated Kevlar fibers was performed at 60  $^{\circ}\text{C}$  for 17 h. After completion of the reaction, the grafted fibers were extracted with deionized water in a Soxhlet apparatus for 24 h, and then dried under vacuum at 60  $^{\circ}\text{C}$  for 24 h. The degree of grafting was calculated using the following equation:

$$DG(\%) = \left( \frac{W_1 - W_0}{W_0} \right) \times 100$$

where  $W_0$  and  $W_1$  are the weights of Kevlar fibers before and after grafting, respectively.

### 2.3. Characterization

Electron spin resonance (ESR) measurements were performed using a JES-FA200 ESR spectrometer (JEOL Ltd., Japan) at a frequency of 9.1 GHz with 1 mW power and 100 kHz field modulation frequency at room temperature. Variable-temperature ESR experiments were performed from 20 to 80  $^{\circ}\text{C}$  with a step of 10  $^{\circ}\text{C}$ . The sample was held at each point for 5 min before collecting data. All experiments were conducted with the samples exposed to air.

XPS measurements were performed on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA) using Al K $\alpha$  radiation with a cathode voltage of 15 kV, a current intensity of 10 mA, and a pressure of  $2 \times 10^{-9}$  mbar. The survey scans were recorded from 0 to 1350 eV with a step of 1 eV.

SEM images were collected using a JSM-6500F microscope (JEOL Ltd., Japan) with an acceleration voltage of 5 kV. All samples were coated with gold before imaging.

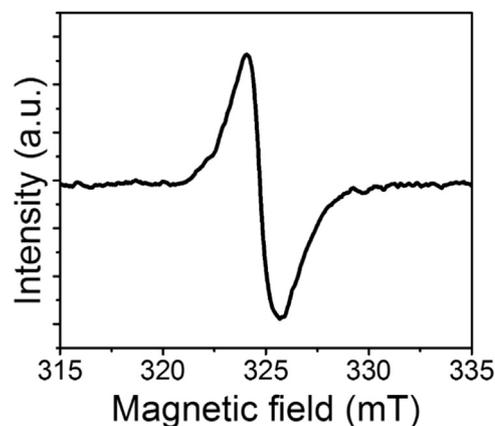


Fig. 2. ESR spectrum of Kevlar fibers irradiated by an EB at a dose of 200 kGy.

## 3. Results and discussion

### 3.1. Generation of radicals

The radicals generated in the Kevlar fibers during EB irradiation were analyzed by ESR, as shown in Fig. 2. The hyperfine structure observed in the spectrum indicates the generation of radicals in the molecular chains of the Kevlar fibers. The variations in the concentration of radicals with dose and temperature were also determined by ESR, as plotted in Fig. 3. With increases in the absorbed dose, the concentration of radicals increased, as shown in Fig. 3a. Increasing the accelerator current allowed more energy to be absorbed by the Kevlar fibers, leading to the formation of a large amount of radicals. As high temperatures can promote recombination or transformation of radicals, the radicals generated during irradiation can be eliminated by heating. Therefore, the concentration of radicals decreased with increasing temperature. At 60  $^{\circ}\text{C}$ , almost half of the radicals were eliminated. However, further increasing the temperature above 60  $^{\circ}\text{C}$  only decreased the amount of radicals very slightly. As the residual radicals were trapped in crystalline regions of the fibers, the migration of radicals was remarkably restricted. Consequently, interactions between the radicals were limited.

### 3.2. Post-grafting of AA

The effects of different parameters on the degree of grafting of AA were investigated. The influence of absorbed dose on the grafting yield was analyzed, as plotted in Fig. 4. The degree of grafting increased with increasing absorbed dose up to 150 kGy, then, at higher doses, a decrease was observed. Typically, an increase in grafting yield with absorbed dose can be attributed to an increase in the number of active sites. When the fibers were irradiated in air, trapped radicals and peroxides were formed. The thermal decomposition of hydroperoxides during the reaction resulted in the formation of mobile  $\cdot\text{OH}$  radicals, which can initiate undesirable homopolymerization of AA. This process can be suppressed by Mohr's salt as follows:



However, at higher doses, more  $\cdot\text{OH}$  radicals were generated and the low amount of Mohr's salt did not effectively inhibit the homopolymerization of AA. In this case, AA homopolymerized to form a viscous reaction system that restricted the diffusion of monomers, resulting in a decrease in the grafting yield. The maximum degree of grafting is approximately 1.63%. Such a low degree of grafting can be attributed to the special chemical structures of Kevlar fibers. As the main chains of aramid fibers are constructed from phenylene rings and amide bonds, the aromatic content is relatively high, leading to high energy dissipation of the EB. The stabilization effect of resonance

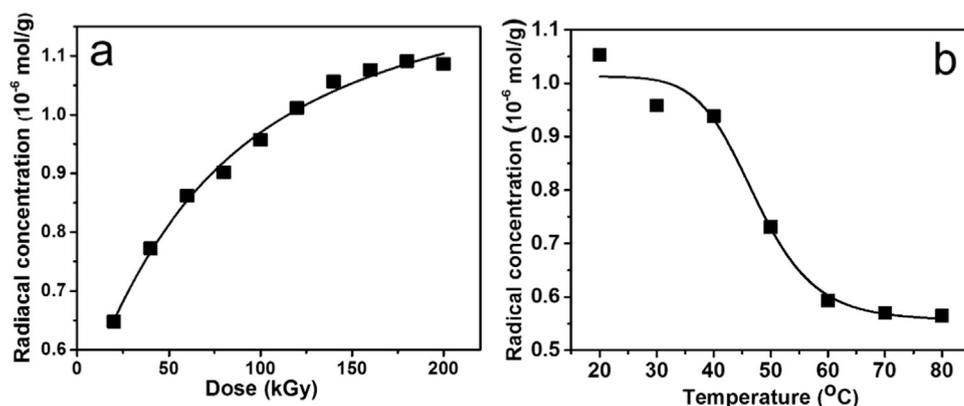


Fig. 3. Radical concentration as a function of dose (a) and temperature at a dose of 200 kGy (b).

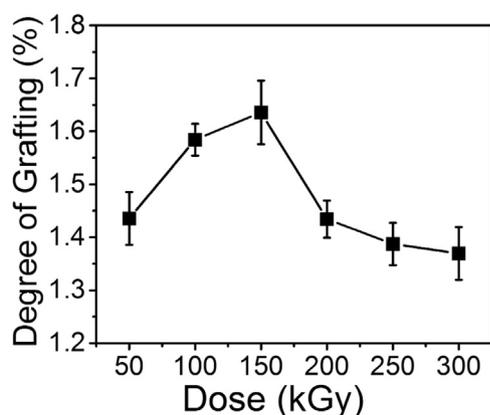


Fig. 4. Effect of absorbed dose on degree of grafting (40 wt% AA, 0.4 wt% Mohr's salt, 60 wt% DI water, temperature: 60  $^{\circ}$ C, reaction time: 17 h).

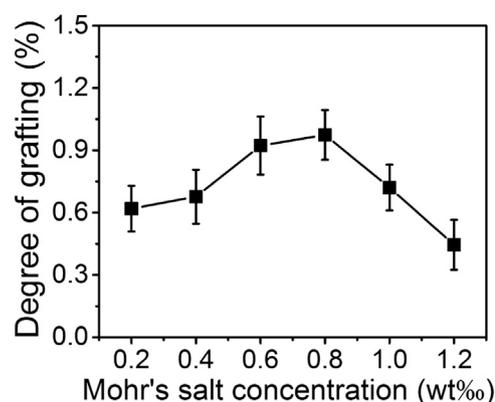


Fig. 5. Effect of Mohr's salt concentration on degree of grafting (absorbed dose: 300 kGy, 40 wt% AA 40, 60 wt% DI water, temperature: 60  $^{\circ}$ C, reaction time: 17 h).

between carbonyl groups and the radicals on the nitrogen atom could further reduce the activity of radicals, resulting in a very low grafting yield (AbdelBary et al., 1997). Furthermore, owing to the rigid aromatic structures, high crystallinity, and strong H-bonding between polymer chains, the motion of free radicals and the diffusion of monomers into the fibers were extremely restricted, which hindered the grafting polymerization process.

The optimal condition of grafting was obtained at adsorbed dose of 150 kGy, AA concentration of 40 wt%, and Mohr's salt concentration of 0.4 wt%. However, for the conditions with low monomer concentrations or high Mohr's salt concentrations, the measured degree of grafting was extremely low. Consequently, a higher absorbed dose (300 kGy) was adopted to investigate the influences of Mohr's salt concentrations and AA concentrations on the degree of grafting.

During irradiation-induced grafting polymerization, undesirable homopolymerization can occur from the beginning of the grafting reaction. Homopolymerization of the monomers can be initiated at active sites formed by chain transfer reactions of the growing polymer radicals or by decomposition of hydroperoxides. This process may result in a highly viscous reaction system and limit the diffusion of monomers, leading to a low grafting yield (Gupta et al., 2000; Ishigaki et al., 1982). The addition of a reducing agent, such as Mohr's salt, is an effective method for suppressing homopolymerization. In the presence of  $\text{Fe}^{2+}$ , the generated active sites, such as monomer radicals and  $\text{OH}$  radicals, can be deactivated by redox reactions as per Eq. (1). Fig. 5 shows the influence of Mohr's salt on the degree of grafting. At low concentrations, the degree of grafting increased as the concentration of Mohr's salt increased because homopolymerization of AA was suppressed. In fact, the presence of Mohr's salt not only inhibited homopolymerization, but also influenced the grafting reaction. The reactive sites on the main fiber chains generated by thermal decomposition of peroxides and

trapped radicals can also be deactivated by the addition of Mohr's salt. Above 0.8 wt% Mohr's salt, the degree of grafting decreased gradually, suggesting that some of the growing chain radicals were terminated by the following mechanism:



Fig. 6 shows the effect of monomer concentration on the degree of grafting. The degree of grafting increased as the concentration of monomer increased until 40 wt%. Further increases in the AA concentration led to severe decrease in the degree of grafting. At low monomer concentrations, homopolymerization of AA was hindered and the monomer could easily diffuse to the surface of the aramid fibers, resulting in a relatively high degree of grafting. As the monomer concentration increased, more active sites were generated by chain transfer of the growing chain radicals to monomers or  $\text{OH}$  radicals. However,

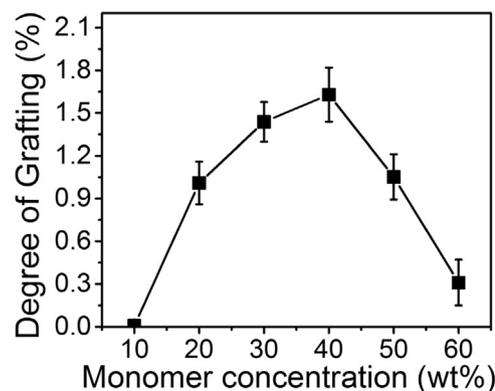


Fig. 6. Effect of monomer concentration on the degree of grafting (absorbed dose: 300 kGy, 0.4 wt% Mohr's salt, temperature: 60  $^{\circ}$ C, reaction time: 17 h).

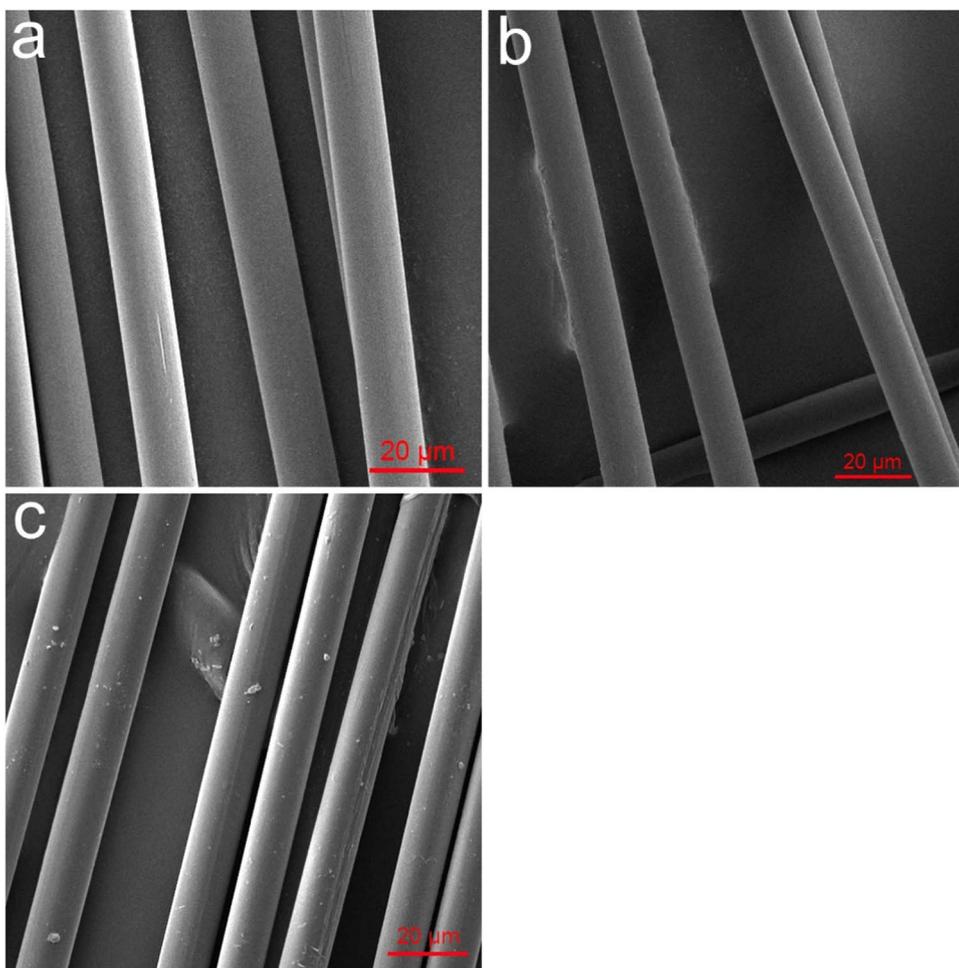


Fig. 7. SEM images of pristine fibers (a), EB-irradiated fibers (300 kGy) (b), and AA-grafted fibers (2.3%) (c).

owing to the low concentration of Mohr's salt, inhibition of homopolymerization was not effective. Consequently, a gelatinous homopolymer was formed and the solution became viscous, which restricted diffusion of AA to the surface of the aramid fibers, leading to a decrease in the degree of grafting.

### 3.3. SEM and XPS analyses

SEM images of the surface morphologies of pristine and modified fibers are shown in Fig. 7. The surface of the pristine fibers is very smooth (Fig. 7a), and the EB-irradiated fiber surface shows no obvious changes as compared with the pristine fiber surface (Fig. 7b). After grafting, the surface of the modified fibers is rough and some dots are observed on the surface, which were attributed to grafted poly(acrylic acid) (PAA) polymerized from the surface of the fibers. These common features of grafting-modified fibers have been reported in many previous studies (Gupta et al., 2008; Grover et al., 2010; Wang et al., 2015).

The elemental composition on the surface of the Kevlar fibers was characterized by XPS. Spectra corresponding to the pristine Kevlar fibers, EB-irradiated fibers, and AA-grafted fibers are shown in Fig. 8. The intensity of the O1s peak increased obviously after grafting, whereas the intensity of the N1s peak decreased. The changes in the elements on the surface of the Kevlar fibers were quantitatively analyzed, as summarized in Table 1. The pristine fibers had the lowest O/C ratio and the highest N/C ratio on the surface. After irradiation with a dose of 300 kGy in air, the O/C ratio increased from 0.25 for pristine fibers to 0.30, whereas the N/C ratio decreased slightly from 0.14 to 0.13. As the fibers were irradiated by an EB in air, the generated radicals may react

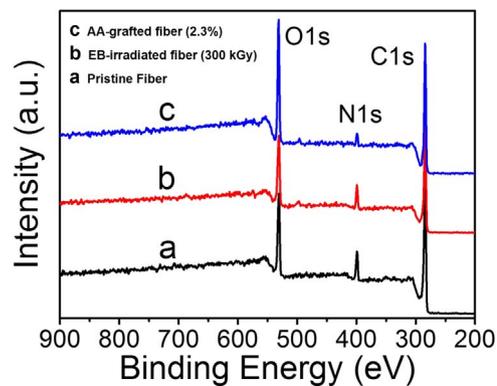


Fig. 8. XPS spectra of pristine Kevlar fibers (a), EB-irradiated fibers (b), and AA-grafted fibers (c).

Table 1  
Elemental composition on the surface of the Kevlar fibers before and after modification.

Sample	C / at%	O / at%	N / at%	O/C	N/C
Pristine fibers	72.15	18.03	9.82	0.25	0.14
EB-irradiated fibers (300 kGy)	70.20	20.85	8.95	0.30	0.13
AA-grafted fibers (2.3%)	67.80	28.43	3.77	0.42	0.06

with oxygen, which would increase the number of oxygen-containing polar groups on the surface of the Kevlar fibers. After treatment in AA aqueous solution, carboxyl groups were introduced onto the fiber surface, leading to a further increase in the O/C ratio. Notably, the N/C

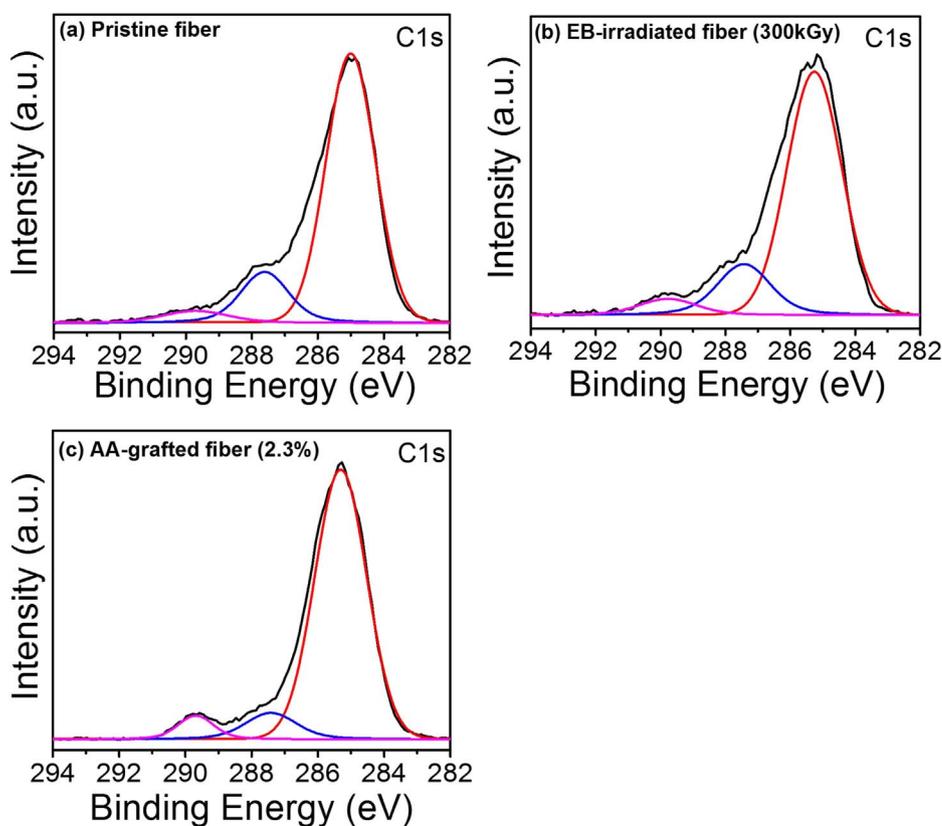


Fig. 9. C1s spectra of pristine fibers (a), EB-irradiated fibers (300 kGy) (b), and AA-grafted fibers (2.3%) (c).

Table 2  
C1s components of the Kevlar fibers before and after modification.

Sample	C1s components (%)		
	C–C	C–O O=C–N	C(O)OH
Pristine fibers	74.50	22.20	3.30
EB-irradiated fibers (300 kGy)	71.21	23.93	4.86
AA-grafted fibers (2.3%)	68.49	16.59	14.92

ratio decreased from 0.14 to 0.06 after treatment, which suggests successful grafting of AA onto the fiber surface.

The C1s spectra of the pristine fibers, EB-irradiated fibers, and AA-grafted fibers were further analyzed, as shown in Fig. 9. The C1s peak of each of the samples could be deconvoluted into three components: C–C bonds at 285.2 eV, C–O and O=C–N groups at approximately 287.5 eV, and C(O)OH groups at 289.8 eV. (Wang et al., 2015; Inagaki et al., 1997; Zhang et al., 2007) The relative concentrations of the three components are summarized in Table 2. There are obvious differences between the C1s components of the pristine and modified fibers. After irradiation with the EB at a dose of 300 kGy, the content of C–C bonds decreased, whereas the contents of C–O and C(O)OH groups increased. This phenomenon can be attributed to the formation of oxygen functionalities on the surface of the Kevlar fibers after EB treatment in air. After AA grafting, the fiber surface was covered by PAA, leading to a further decrease in the contents of C–C and C–O groups but an increase in the content of C(O)OH groups.

#### 4. Conclusions

The surface of Kevlar fibers was modified by EB-induced post-grafting polymerization. The generation of radicals in Kevlar fibers was confirmed, and the concentration of radicals increased as the absorbed dose increased, but decreased as the temperature increased. The

influence of synthesis conditions (absorbed dose, monomer concentration, and Mohr's salt concentration) on the degree of grafting was investigated. The degree of grafting was greatly affected by homopolymerization of AA. High adsorbed doses, high monomer concentrations, and low inhibitor concentrations made the monomer more prone to homopolymerization, leading to a decrease in the degree of grafting. The effect of grafted AA on the surface properties of the Kevlar fibers was analyzed by SEM and XPS. The SEM images showed that the surface of the AA-grafted fiber was rougher than that of the pristine and irradiated fibers. The XPS result indicated that C(O)OH groups were introduced onto the surface of the Kevlar fibers, suggesting the successful grafting of AA. While the degree of grafting achieved by EB preirradiation is low relative to those realized with other surface grafting methods, such as UV or plasma, it is sufficient for modification of the surface properties of Kevlar fibers. In conclusion, EB-induced post-grafting polymerization is an effective method to modify the surface of Kevlar fibers for application in fiber-reinforced composites.

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