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Surface Modification of Aramid Fibers by Bio-Inspired Poly(dopamine) and Epoxy Functionalized Silane Grafting

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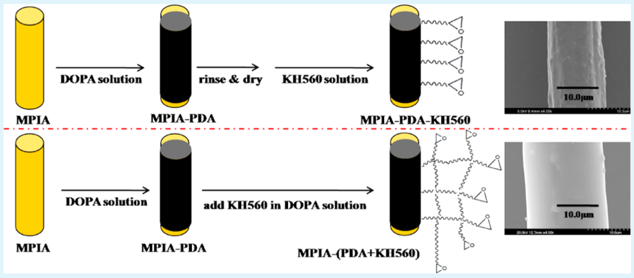
Ⓢ *Supporting Information*

ABSTRACT: A novel biomimetic surface modification method for meta-aramid (MPIA) fibers and the improvement on adhesion with rubber matrix was demonstrated. Inspired by the composition of adhesive proteins in mussels, we used dopamine (DOPA) self-polymerization to form thin, surface-adherent poly(dopamine) (PDA) films onto the surface of MPIA fibers simply by immersing MPIA fibers in a dopamine solution at room temperature. An epoxy functionalized silane (KH560) grafting was then carried out on the surface of the poly(dopamine)-coated MPIA, either by a "one-step" or "two-step" method, to introduce an epoxy group onto the MPIA fiber surface. The surface composition and microstructure of the modified MPIA was characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The results indicated successful grafting of KH560 on the PDA-coated MPIA surface. A single-fiber pull-out test was applied to evaluate the adhesion of MPIA fibers with the rubber matrix. Compared with the untreated MPIA fibers, the adhesion strength between the modified MPIA fibers by "one step" method with rubber matrix has an increase of 62.5%.



KEYWORDS: *aramid fiber, dopamine, silane, surface modification, aramid/rubber composite, interfacial adhesion*

1. INTRODUCTION

As one of the high performance fibers, aramid fibers combine high mechanical properties and thermal and chemical stability with low density,[1,2] becoming one of the ideal reinforcements in various high performance composites used in space and aviation, electronics, tanks, bullet- or cut-proof products, and so on.

However, the aramid application was limited by poor adhesion properties due to its smooth and chemically inert surface. Extensive studies have been performed and a variety of techniques have been utilized to enhance the interfacial adhesion strength of aramid/polymer composites. These studies and techniques mainly focused on chemical etching and grafting,[3−9] plasma treatment,[10−12] ultrasonic treatment,[13] γ-ray irradiation,[14] and ultraviolet radiation.[15] The chemical etching or grafting generally modifies the surface by introducing active functional groups like amino, hydroxyl, and carbonyl through etching, nitrification, reduction, or chlorosulfonation. Tarantili et al. carried out surface treatment of aramid fibers by immersion in a solution of methacryloyl chloride in carbon tetrachloride, and chloride-treated aramids displayed better flexural properties, whereas their tensile strength was drastically reduced.[4] In Wu's research, Kevlar 49 fibers were surface-modified by NH_3-, O_2-, and H_2O-plasma etching and chlorosulfonation and subsequent reaction with some reagents (glycine, deionized water, ethylendeiamine, and 1-butanol) to improve the adhesion to epoxy resin.[10] However, these approaches were limited in practical industrial use due to multistep procedures, high cost instruments, stringent reaction conditions, toxic materials, and decrease of fiber strength and so on.

Recently, Lee et al. reported a surface chemistry for functional coatings inspired by the adhesive proteins secreted by mussels.[16] Mussels display universal adhesive property of the ability to attach to almost any substrates of organic and inorganic, depending on dopamine (3,4-dihydroxy-phenylalanine) and other catechol compounds. Inspired by this motif, researchers have used small molecules with catechol-amine moiety, such as dopamine, as an adhesive agent to mimic the mussel's adhesion. Thin layers are formed on the substrates through oxidative self-polymerization of dopamine during a simple deposition process. This versatile surface modification method has significant advantages such as simple ingredients, mild reaction conditions, and applicability to various materials regardless of types, sizes, and shapes.[17−21] Furthermore, the poly(dopamine) layer could act as a versatile platform for

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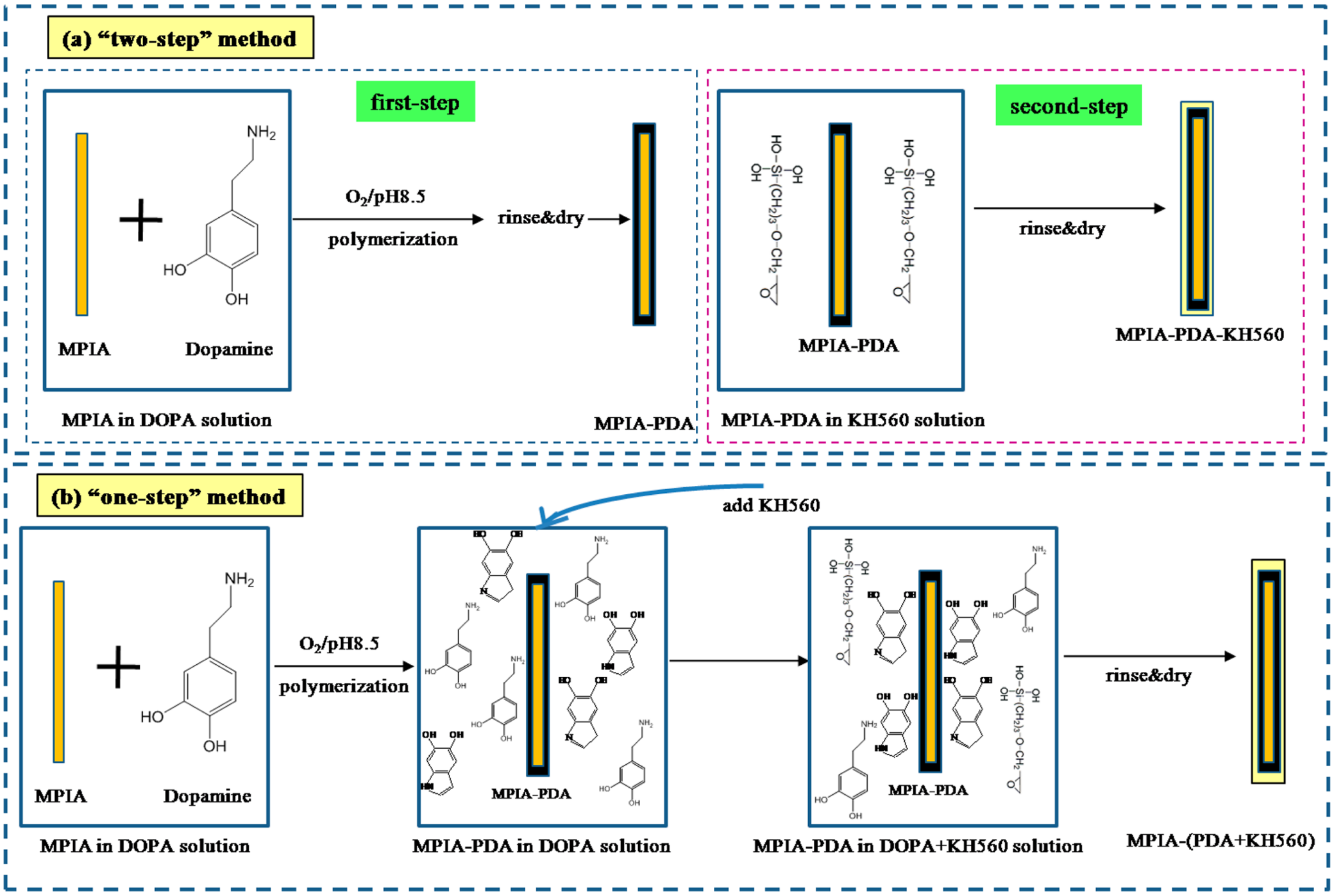
Scheme 1. Illustration of Procedures for Preparing MPIA-PDA-KH560 Fibers (a) and MPIA-(PDA+KH560) Fibers (b)



secondary reactions for further increase of surface activity or functionality.[22−27] In Chawla's study, lubrication properties of poly(dimethylsiloxane) (PDMS) was improved by modification of L-3,4-dihydroxyphenylalanine and lysine and grafting of polyethylene glycol(PEG).[28] In a former study reported, filtration, rinse, and dry were always followed after PDA coating on organic or inorganic substrate. Thereafter, the PDA deposited substrates were put into the solution of second functionalization monomers for further grafting. In this process, the secondary monomers reacted with −NH and −OH groups of PDA surface and the steric hindrance of PDA affects the efficiency of grafting. However, to the best of our knowledge, the surface modification of fibers by poly(dopamine) for improving the interfacial adhesion has rarely been reported and there is no sign that anybody has discussed co-grafting of secondary functionalization monomer and dopamine and/or its derivatives. The target of our research was to make some progress on the challenging topic.

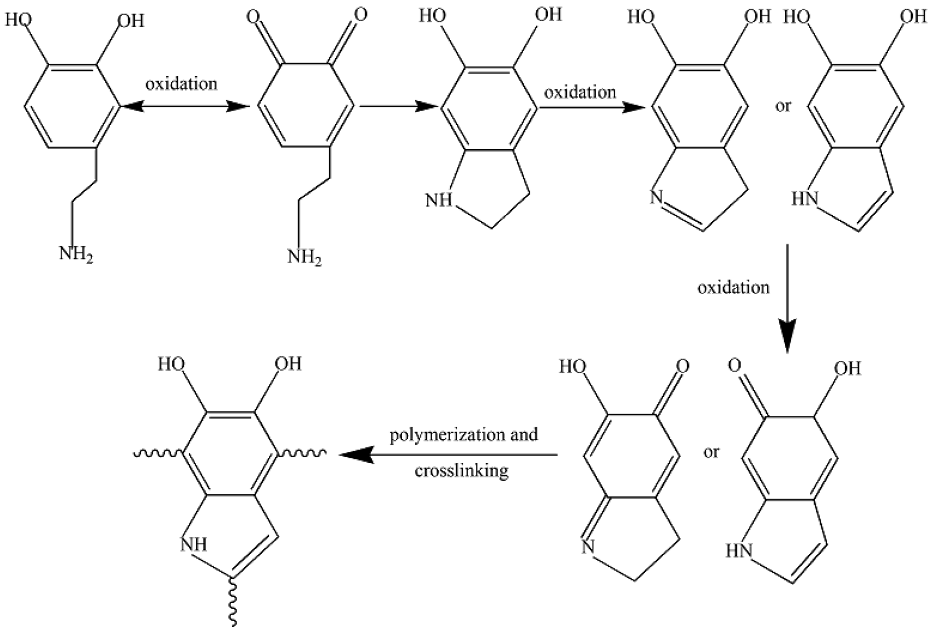
The modification method used in our study displayed a low cost, effective, nontoxic process that is most importantly harmless to mechanical properties of fibers and it is a milestone in the fiber surface modification. To discover the grafting mechanism of KH560 on the PDA layer, and to discuss the reactivity of PDA, dopamine, and its derivatives with secondary functionalization monomers, we established the two kinds of grafting processes: the "two-step" method and the "one-step" method. The chemical composition and microstructure of original and modified MPIA was investigated by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and thermogravimetric analysis (TGA). The morphology of the fibers was investigated by scanning electron microscopy (SEM). The interfacial adhesive performance of MPIA fibers with rubber matrix was characterized by single-fiber pull-out test on a tensile tester and the diameter increase of fibers after modification was neglected when calculating the interfacial shear strength. Furthermore, the combination of bioinspired dopamine oxidative self-polymerization and epoxy functionalized silane grafting will lead to the feasible application of the high-performance fibers (carbon fiber, aramid fiber, and ultrahigh molecular weight polyethylene fiber) in composites.

Hypothetically that can be one interface between the post-treated fibers and the rubber matrix due to very limited interfacial thickness. At the interface, it is considered that either secondary hydrogen bonding or covalent primary bonding can exist between the fiber surface and rubber matrix. This primary or secondary bonding may contribute to improving the interfacial adhesion of composite by chemical bonding.[29]

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(*m*-phenyleneisophthalamide) (MPIA) fibers with diameter of 15 μm and length of 1 mm were purchased from Heilongjiang Hongyu Short Fibers and Novel Materials Co., Ltd., China. The fibers were cleaned by ultrasound in acetone for 30 min and dried in a vacuum oven at 50 °C for 6 h before use. Dopamine (DOPA) and tris(hydroxymethyl aminomethane) (Tris) were purchased from Alfa Aesar Company, USA. The epoxy fuctionalized silane γ-(2,3-epoxypropoxy)propytrimethoxysilane (KH560) was obtained from Beijing Chemical Works, China. All chemicals were of analytical reagent grade and used without further purification.

Scheme 2. Possible Polymerization Mechanism of Dopamine



2.2. Surface Modification of MPIA Fibers by Poly(dopamine) and Silane Grafting. Dopamine solution with a concentration of 2.0 g/L was prepared by dissolving dopamine in distilled water. Tris was added into the dopamine solution to adjust pH to a predetermined value of 8.5. Generally, a solution of 2.0 g/L of dopamine and 1.2 g/L Tris will get to pH of 8.5.

To discuss the grafting mechanism of KH560 on PDA layer, we established two kinds of grafting process. In this work, so-called "two-step" and "one-step" methods were used for comparison. The process of both the "two-step" and the "one-step" methods is schematically shown in Scheme 1a and b.

In a typical "two-step" method, MPIA fibers were immersed in dopamine solution under mild stirring at room temperature for 4 h in the first step, and MPIA fibers obtained were filtered and rinsed thoroughly with distilled water and dried to constant weight under reduced pressure. The obtained MPIA fibers were denoted as MPIA-PDA in this article. The MPIA-PDA fibers were then added to aqueous solutions of KH560 with different concentration (1.0, 1.5, 2.0, 2.5, and 3.0 wt %) at different temperature (20 °C, 40 °C, 60 °C, and 80 °C) for another 5 h in the second step. After the reaction, the samples were washed three times by acetone, rinsed in distilled water, and dried by pumping under reduced pressure for subsequent characterization. The obtained MPIA fibers were referred to as "MPIA-PDA-KH560" in this article.

In the "one-step" method, after 4 h of deposition of poly(dopamine) on MPIA fibers surface at room temperature, KH560 was added into the dopamine solution. The grafting reaction was allowed to proceed under mild stirring for 5 h with different concentration (1.0, 1.5, 2.0, 2.5, and 3.0 wt %) at different temperature (20 °C, 40 °C, 60 °C, and 80 °C). After that the fibers were washed three times with acetone, rinsed in distilled water, and dried by pumping under reduced pressure for subsequent characterization. The MPIA fibers modified with this method were referred to as MPIA-(PDA+KH560).

2.3. Preparation of Samples for Single-Fiber Pull Out Test. The ingredients of the rubber formula for the adhesion test were weighed and mixed in an internal mixer, and rolled into rubber sheets with 5 mm thickness on a roll mill. The rubber sheets were placed in the channel of a stainless steel mold, and then MPIA samples were embedded in rubber and covered with rubber sheets in the mold. These prepared composites were vulcanized at 150 °C for 45 min under a pressure of 3.5 MPa. Then, the vulcanizates were cut for single-fiber pull-out test.

2.4. Characterization. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 (Thermo Electron Corporation, USA) with an Al Kα X-ray source (1486.6 eV photons) run at a reduced power of 150 W to determine the surface chemical composition of MPIA samples. The core-level signals were obtained at a photoelectron take off angle of 45° (with respect to the sample surface). During each measurement, the MPIA samples were mounted on standard sample studs under the pressure of 10^{-8} Torr or lower. All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV to compensate for surface charging effects. In peak synthesis, the line width (full width at half-maximum or fwhm) of Gaussian peaks was kept constant for all components in a particular spectrum.

Scanning electron microscopy (SEM, Hitachi S-4700, Japan) was employed to observe the surface morphology of the MPIA samples and the measurements were performed at an accelerating voltage of 20 kV. The surface of the samples was sputtered by a thin layer of gold prior to each measurement.

Fourier transform infrared spectroscopy (ATR-FTIR) (Tensor 27, System 2000, Thermo Fisher Scientific, USA) was used to characterize the chemical structural changes before and after modification of MPIA fibers by attenuated total reflectance in the mid infrared region (4000–500 cm^{-1}).

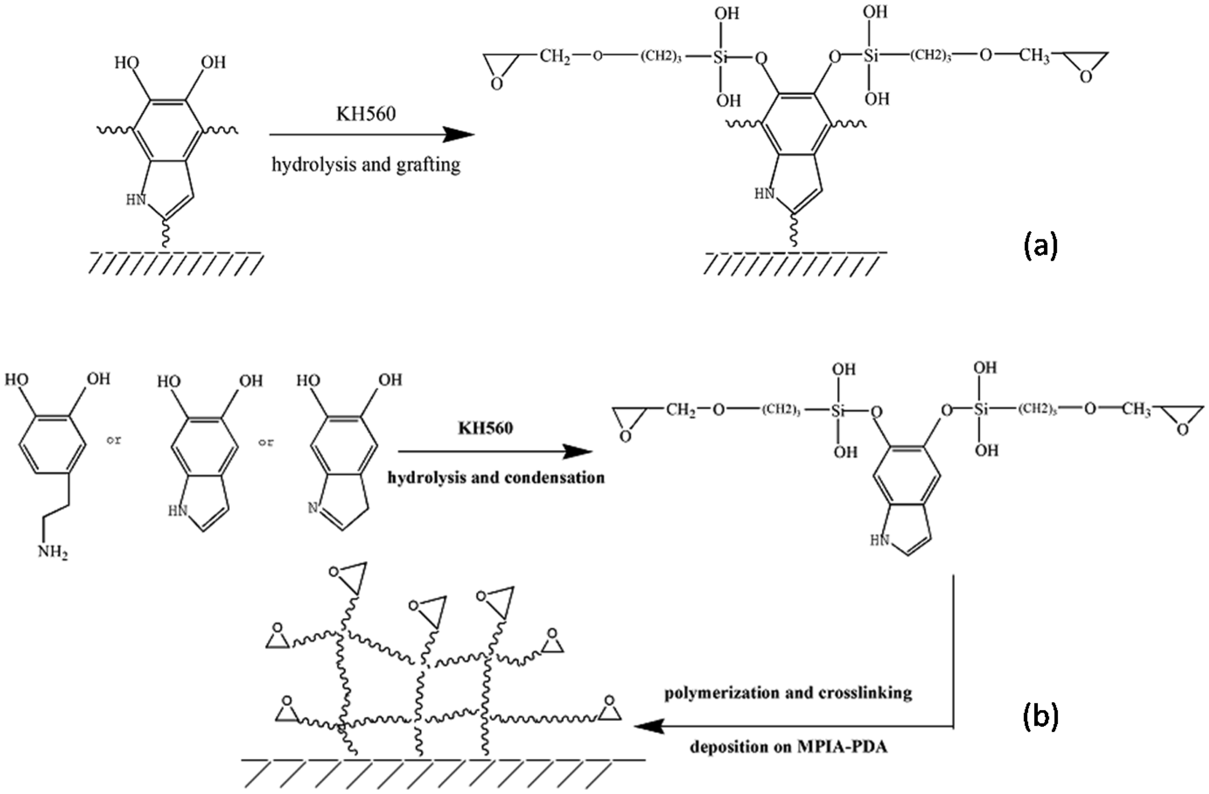
Thermogravimetric analysis (TGA) was performed by using a METTLER-TOLEDO thermogravimetric analyzer, Switzerland. The system was operated in the dynamic mode in the temperature range of 30 to 800 °C at a heating rate of 10 °C/min. All the experiments were carried out under a nitrogen atmosphere.

The interfacial adhesion of MPIA fibers/rubber composites was evaluated by single-fiber pull-out tests performed on a tensile tester at a crosshead speed of 100 mm/min. Every measurement was repeated at least 10 times and the average was taken. The interfacial shear strength (IFSS), τ, was calculated using the following relationship:

$$\tau = \frac{F}{\pi d l}$$

where F is the pull-out force, d is the diameter of the fiber, and l is the embedded length of the fiber. Each reported interfacial shear strength (IFSS) value is the average of 10 successful measurements.

Scheme 3. Possible Chemical Reactions in "Two-Step" Method (a) and "One-Step" Method (b) on the Surface of MPIA-PDA Fibers



3. RESULTS AND DISCUSSION

The procedures of surface modification of MPIA fibers are described in Scheme 1. Two methods denoted as "two-step" and "one-step" both began with dopamine oxidative self-polymerization on the surface of MPIA. A possible reaction mechamism for self-polymerization of dopamine is presented in Scheme 2.[30,31] Catechol was oxidized to benzoquinone, followed by a reaction in a manner of melanin formation, resulting in the formation of poly(dopamine) (PDA) with high-strength irreversible covalent bonds on matrix. From the mechanism point of view, the poly(dopamine) network is presumably formed by Schiff base formation and/or by Michael type addition involving quinone groups of oxidized dopamine with its primary amino group. Catechol was oxidized to benzoquinone, including the oxidation of dopamine to dopamine-quinone, its intramolecular cyclization, oxidation to leucodopaminechrome, formation of 5,6-dihydroxyindole, and further oxidation to 5.6-indolequinone. The last two monomers are able to undergo branching reactions, leading to oligomers and self-assembly to form particles in 100 nm scale.[32] Color transfer from transparent to light pink and to deep dark was observed in the poly(dopamine) deposition process.

Epoxy functionalized silane γ-(2,3-epoxypropoxy)-propytrimethoxysilane (KH560) was chosen as grafting agent, ascribed to the high reactivity of epoxy group. KH560 is easily hydrolyzed in water and alkyl siloxane hydrolysis into silanol. Possible chemical reactions in the two methods are described in Scheme 3a and b. In the "two-step" method, γ-(2,3-epoxypropoxy)propytrimethoxysilane hydrolyzed into silanol which directly reacted with hydroxyl groups on the surface of PDA deposited MPIA fibers and the epoxy groups were left outside of the surface of modified MPIA fibers to participate in vulcanization of diene rubber (see Scheme 3a). Sulfur is chosen as the curing agent in the adhesion rubber used for the single-fiber pull-out test. Sulfur radicals, which were produced by sulfur homolysis reaction at high temperature, reacted with a double bond of diene rubber to produce mercapto groups. Thereafter, the ring opening reaction was conducted between the mercapto groups and epoxy groups,[33,34] while in the "one-step" method, with the addition of EP669 into the dopamine solution, KH560 monomers, residue dopamine, and indole monomers as well as PDA coated MPIA coexist in solution. In this condition, KH560 would prefer to react with the hydroxyl groups of dopamine and indole monomers, which are much more active than the hydroxyl groups obtained from PDA. Thereafter, epoxide-dopamine is obtained to conduct the self-polymerization process on the surface of MPIA-PDA (see Scheme 3b).

3.1. Surface Chemical Composition of the Aramid Fibers.

The success of surface modification of MPIA fibers was ascertained by comparing the XPS spectra of fiber surface. Figure 1 shows the XPS wide scan and C 1s core-level spectra of pristine MPIA (Figure 1a), MPIA-PDA (Figure 1b), MPIA-PDA-KH560 (Figure 1c), and MPIA-(PDA+KH560) (Figure 1d), respectively. The wide scan spectra of pristine MPIA and PDA-MPIA shows the same peak components of C 1s, N 1s, and O 1s ascribed to the existence of C, N, and O elements in both MPIA and PDA. The C 1s core-level spectrum of the pristine MPIA could be curve-fitted with five peak components, having binding energies (BE's) at 284.6 eV for $\underline{C}$−C species, at 285.5 eV for the $\underline{C}$−N species, at 287.5 eV for the $\underline{C}$=O species, at 288.5 eV for the O−$\underline{C}$=O species, and at 282.6 eV for $\underline{C}$−Si species introduced by the MPIA synthesis process. Poly(*m*-phenyleneisophthalamide) (MPIA) is a polymer of *m*-

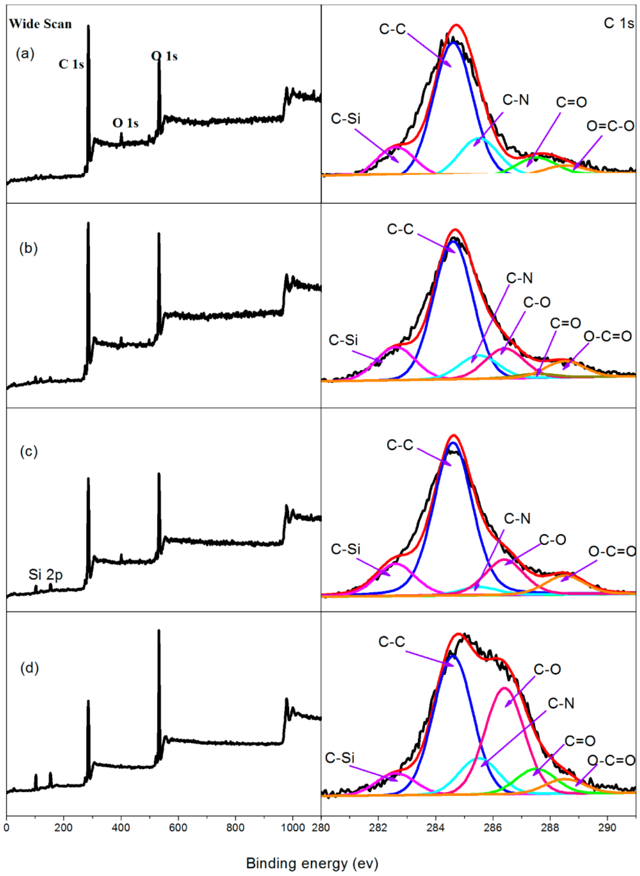


Figure 1. XPS wide-scan and C 1s core-level spectra of (a) untreated MPIA fibers, (b) MPIA-PDA fibers, (c) MPIA-(PDA+KH560) fibers treated with 2.5 wt % of KH560 at 60 °C, and (d) MPIA-PDA-KH560 fibers treated with 2.5 wt % of KH560 at 60 °C.

phthalic acid and *m*-phenylenediamine. From the perspective of molecular structure, there are few C—O bonds in pristine MPIA fibers. From Scheme 2, we can find that there are two C—O bonds in one repeating unit of PDA. Therefore, the additional peak of C—O species appears at Figure 1b, indicating the presence of PDA layer on the surface of MPIA fibers. While there are ten C—O bonds in one repeating unit of KH560 grafted PDA as shown in Scheme 3, which lead to increase in area of C—O peak in MPIA-PDA-KH560 (Figure 1c) and MPIA-(PDA+KH560) (Figure 1d). This increase suggests that KH560 was successfully introduced onto the MPIA fibers surface. Higher increase in C—O peak area indicates that the "one-step" method has higher KH560 grafting and more efficiency than the "two-step" method.

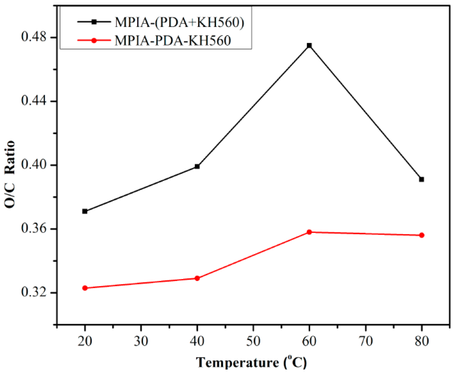


Figure 2. O/C ratios of MPIA-PDA-KH560 fibers and MPIA-(PDA +KH560) fibers (treated at temperatures of 20 °C, 40 °C, 60 °C, and 80 °C) (at concentration of 2.5 wt %).

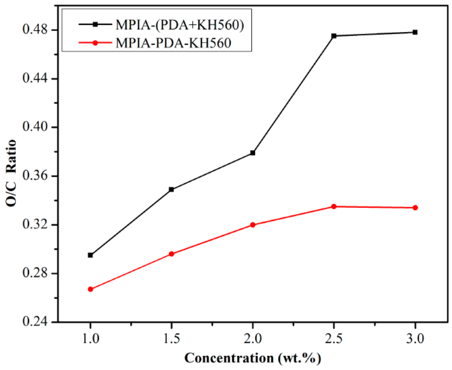


Figure 3. O/C atomic ratios of MPIA-PDA-KH560 fibers and MPIA-(PDA+KH560) fibers (at concentrations of 1, 1.5, 2, 2.5, and 3 wt %) (at temperature of 60 °C).

Determined by XPS, the carbon, nitrogen, and oxygen concentration on the surface of pristine MIPA is 79.5%, 9.9%, and 10.6%, respectively. After deposition of poly(dopamine) on MPIA, the O/C ratio is increased from 0.21 to 0.23, due to the higher O/C ratio of PDA than MPIA. A further increase in O/C ratio was achieved after grafting with KH560, due to higher oxygen content in epoxy group, C—O, and Si—O bonds in KH560. Figure 2 shows the O/C ratio on the surface of MPIA-PDA-KH560 and MPIA-(PDA+KH560) reacted in different grafting temperature. The O/C ratio increases with respect to temperature increase and the maximum value occurs at 60 °C in both methods. This is mainly due to the fact that the higher the grafting temperature, the higher reaction activity between dopamine and KH560, but excessively high temperature may cause self-polycondensation rather than grafting. The changes of O/C ratio regarding to concentration of KH560 is displayed in Figure 3. An increase of O/C ratio was also obtained as the concentration of KH560 increases, and the maximum value occurs at a KH560 concentration of 2.5 wt % in both methods. When the KH560 concentration is higher than the optimal value, hydroxyl groups of PDA, dopamine, and indole monomers were all involved in the chemical reaction with KH560, and the extra KH560 could not be grafted with the absence of reactive groups on the surface of fibers. These results indicate that the optimum temperature and KH560 concentration for treating MPIA is 60 °C and 2.5 wt %, respectively. The higher O/C ratio of MPIA-(PDA+KH560) compared to that of MPIA-PDA-KH560 indicates higher grafting yield in the "one-step" method due to the fact that KH560 grafting was confined by the steric hindrace and limited amounts of hydroxyl groups of PDA in the "two-step" method.

The chemical structure of MPIA fibers before and after treatment was investigated further by ATR-FTIR measurements in the mid infrared region (4000—500 cm^{-1}). Figure 4 illustrates the ATR-FTIR spectra of the pristine MPIA fibers (a), the MPIA-PDA fibers (b), the MPIA-PDA-KH560 fibers (c), the MPIA-(PDA+KH560) fibers (d), and pristine KH560 (e). For the MPIA fibers, the C═O stretching peak at 1642 cm^{-1}, N—H bending peak at 1543 cm^{-1}, and C—N stretching peak at 1319 $\text{cm}^{-1}$and 3325 cm^{-1} can be observed. After the oxidative self- polymerization and grafting treatment, these peaks either diminish or disappear. The absorption peaks at

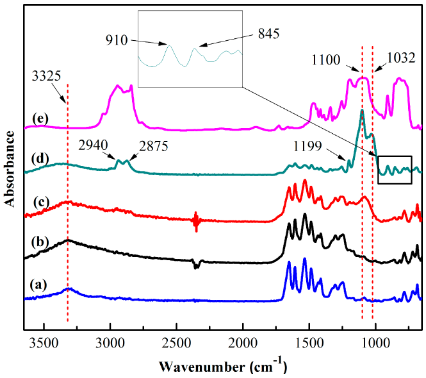


Figure 4. ATR-FTIR spectra of (a) the untreated MPIA fibers, (b) MPIA-PDA fibers, (c) MPIA-PDA-KH560 fibers, (d) MPIA-(PDA+KH560) fibers, and (e) epoxy functionalized silane KH560.

2940 and 2875 cm^{-1} are attributed to methylene nonsymmetric stretch vibration and methylene symmetric stretch vibration, respectively, and the absorption peaks at 1199 cm^{-1}, 1100 cm^{-1}, and 1032 cm^{-1} are attributed to Si−CH$_2$-R stretch vibration, Si−O stretch vibration, and Si−O−C stretch vibration. These above peaks ought to derive from the grafting of the epoxy functionalized silane KH560. The absorption peak at 1032 cm^{-1}, attributed to Si−O−C stretch vibration, proves that KH560 is introduced onto MPIA surface by the chemical reaction between poly(dopamine) and KH560. The absorption peaks at 910 and 845 cm^{-1} are attributed to the nonsymmetric stretch vibration of the epoxy group. Figure 4d shows that the characteristic peaks of MPIA fibers almost disappear after the treatment of MPIA fibers with 2.5 wt % concentration of KH560 at 60 °C by the "one-step" method. Meanwhile, the strong and distinct characteristic peaks at 910 and 845 cm^{-1} of KH560 appear. These changes are well consistent with XPS results, indicating that the oxidative self-polymerization and grafting reaction did take place on the surface of MPIA fibers.

3.2. Surface Morphology of the Aramid Fibers. The surface morphology of MPIA fibers before and after treatment was observed by SEM. It can be seen from Figure 5a that the pristine MPIA fibers display an uneven surface with micropits and grooves resulted from processing. After dopamine oxidative

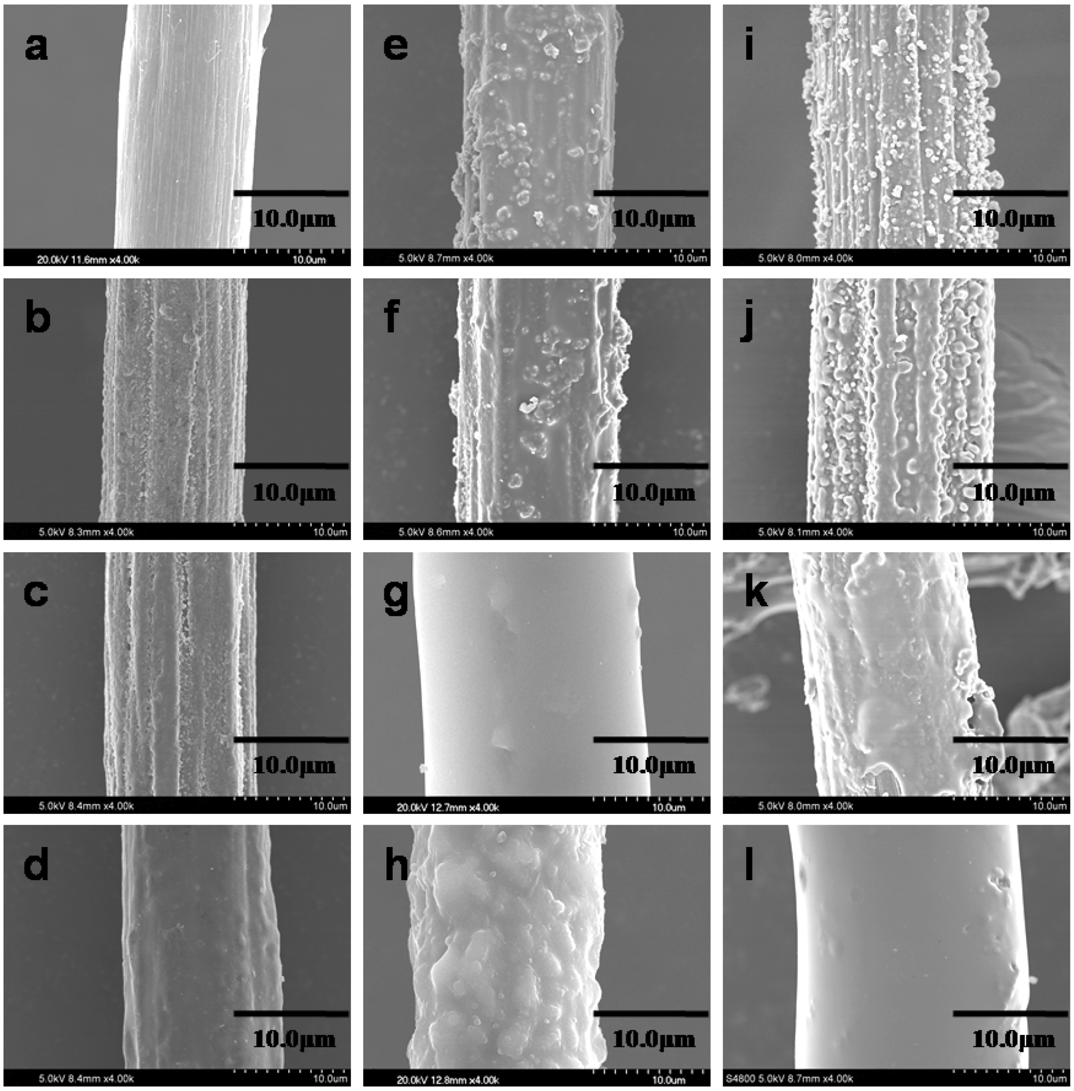


Figure 5. SEM images of (a) the untreated MPIA fibers; (b) MPIA-PDA fibers; MPIA-PDA-KH560 fibers treated at different temperatures: (c) 20 °C and (d) 60 °C; MPIA-(PDA+KH560) fibers treated at different temperatures: (e) 20 °C, (f) 40 °C, (g) 60 °C, and (h) 80 °C; and MPIA-(PDA+KH560) fibers treated with KH560 at different concentrations: (i) 1 wt %, (j) 1.5 wt %, (k) 2 wt %, and (l) 2.5 wt %.

self-polymerization, the poly(dopamine) deposits a distinct rough layer on the surface of MPIA fibers, as shown in Figure 5b. Figure 5c,d shows the KH560 layer on the surface of MPIA-PDA-KH560 fibers. A thin grafted layer of KH560 is formed on the surface of MPIA fibers, and the diameter increases a little bit with an increase of the grafting temperature. However, the MPIA-(PDA+KH560) obtained from the "one-step" method displays much difference with 0.5−1-μm-scale microdots at the beginning. The 0.5−1-μm-scale microdots should be attributed to the copolymer of KH560 and dopamine and/or its derivatives, as introduced in the mechanism of the "one-step" method. It can be seen in Figure 5e−h that, the higher the reaction temperature, the denser and thicker the grafted layer. The diameter of MPIA fibers also increased with the increase of KH560 concentration (see Figure 5i−l). The fact that the diameter of MPIA-(PDA+KH560) is much thicker compared with that of MPIA-PDA-KH560 fibers treated under same temperature and KH560 concentration also proved a higher effectiveness of the "one-step" method.

3.3. Thermogravimetric Analysis. The thermal decomposition of the pristine PDA, pristine MPIA fibers, the MPIA-PDA fibers, the MPIA-PDA-KH560 fibers, and the MPIA-(PDA+KH560) fibers in nitrogen atmosphere is shown in Figure 6a,b,c,d,e, respectively. Thermodegradation data of PDA and MPIA fibers are listed in Table 1. It can be seen from curve b that the weight loss of the pristine MPIA fibers is a two-stage process: the weight loss of 8.0% between 30 and 420 °C corresponds to the elimination of water and residual solvent resulted from processing; the weight loss of 43.2% between 420 and 800 °C corresponds to partial dehydroxylation and alkoxide decomposition of MPIA fibers. A comparison of Figure 6c to b shows decreased weight loss at the temperature range of 420−800 °C, indicating the deposition of PDA layer. It can be seen from Figure 6d that the MPIA-PDA-KH560 fibers begin to decompose at around 310 °C due to the grafting of KH560, and the weight loss between 420 and 800 °C decreased to 30.1%. The slight difference of the weight loss in the 420−800 °C temperature range of MPIA-PDA-KH560 fibers and that of MPIA-PDA indicates a small amount of KH560 grafting in the "two-step" method, consistent with the XPS, FTIR, and SEM results. The MPIA-(PDA+KH560) fibers also begin to decompose at 310 °C as shown in curve e. However, the weight loss of 23.7% between 310 and 420 °C corresponds to the decomposition of grafted epoxide-dopamine. The weight loss of 22.2% between 420 and 800 °C is due to the decomposition of MPIA fibers and PDA, similar to the results shown in Figure 6c. The weight loss between 420 and 800 °C further decreased to 26.4%, indicating the decrease of mass percentage of MPIA component.

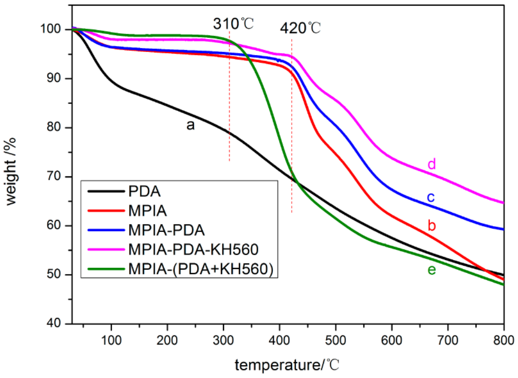


Figure 6. Thermogravimetric analysis results of (a) pristine PDA, (b) untreated MPIA fibers, (c) MPIA-PDA fibers, (d) MPIA-PDA-KH560 fibers, and (e) MPIA-(PDA+KH560) fibers.

Table 1. Thermodegradation Data of PDA and MPIA Fibers under N_2 Atmosphere

temperature range	30−310 °C	310−420 °C	420−800 °C	>800 °C
PDA	21.1%	8.2%	20.7%	50.0%
MPIA	5.7%	2.3%	43.2%	48.8%
MPIA-PDA	4.1%	2.6%	34.0%	59.3%
MPIA-PDA-KH560	2.8%	2.4%	30.1%	64.7%
MPIA-(PDA+KH560)	2.3%	23.7%	26.4%	47.6%

3.4. Interfacial Adhesion of Aramid Fibers/Rubber Composites. The single-fiber pull-out test was conducted to investigate the interfacial adhesion of MPIA fibers/rubber composites. The MPIA-PDA-KH560 and MPIA-(PDA+KH560) fibers were both prepared with a KH560 concentration of 2.5 wt % at 60 °C. As shown in Table 2, the pull-out force of MPIA-PDA/rubber composite is only 22.7 N and 9.1% higher than that of MPIA/rubber composite, indicating a slight increase in adhesion after dopamine treatment. Although the PDA deposition is usually considered a universal adhesive layer, the limited quantities of hydrogen bonds on the surface cannot contribute much to the adhesion with the rubber matrix. Direct KH560-treatment also shows little improvement in adhesion properties of MPIA to rubber matrix, due to the lack of chemical or physical bonding between KH560 with MPIA fibers. For the MPIA-PDA-KH560 fibers prepared by the "two-step" method, a pull-out force of 24.6 N was achieved. However, a pull-out force of 33.8 N which is 62.5% higher than that of pristine MPIA fibers was achieved in MPIA-(PDA+KH560) fibers. The successful introduction of epoxy groups is the major contributor to the adhesion improvement between fibers and rubber matrix. According to the results of XPS and FTIR, more epoxy groups are introduced to the surface of MPIA fibers through the "one-step" method, enhancing the surface reactivity and polarity. The MPIA fibers are coated with a thick grafted layer of KH560 as shown in SEM pictures, and the grafted layer improved the roughness of the MPIA fiber surface. During the vulcanization process of MPIA fiber/rubber composites, the epoxy groups left outside the MPIA fibers participated in the vulcanization, and the adhesion property was improved both chemically and physically.

Table 2. Adhesion Strength of MPIA Fibers/Rubber Composites

sample	pull-out force (N)	interfacial shear strength (IFSS) (MPa)
MPIA/rubber	20.8 ± 1.2	1.3 ± 0.1
MPIA-PDA/rubber	22.7 ± 1.9	1.4 ± 0.1
MPIA-KH560/rubber	21.4 ± 2.0	1.3 ± 0.1
MPIA-PDA-KH560/rubber	24.6 ± 1.4	1.5 ± 0.1
MPIA-(PDA+KH560)/rubber	33.8 ± 2.7	2.1 ± 0.2

SEM micrographs of fiber surfaces after the pull-out test are shown in Figure 7. It can be seen from Figure 7a that little rubber is left on the surface of the untreated MPIA fibers, indicating a poor interfacial adhesion between fibers and rubber. On the other hand, however, significant amounts of rubber matrix was adhered to the MPIA-PDA-KH560 and MPIA-(PDA+KH560) fibers surface, as shown in Figure 7c and d, which resulted from epoxy groups introduced by KH560. More rubber adherence on the surface and gaps of MPIA-(PDA+KH560) as well as the remarkable increase in interfacial adhesion between the MPIA-(PDA+KH560) fibers and rubber attested to the efficiency of the "one-step" method.

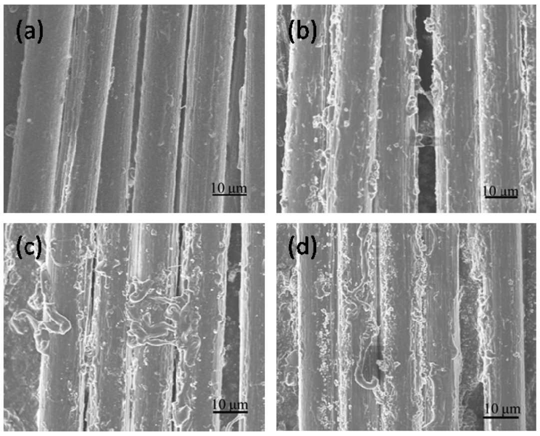


Figure 7. SEM images of interlamellar fracture surfaces of MPIA fibers/rubber composites after the pull-out test: (a) MPIA/rubber, (b) MPIA-PDA/rubber, (c) MPIA-PDA-KH560/rubber, and (d) MPIA-(PDA+KH560)/rubber.

4. CONCLUSION

Surface modification of MPIA fibers was successfully developed by the combination of bioinspired dopamine self-oxidative polymerization and epoxy functionalized silane KH560 grafting. The experimental results showed that the surface of MPIA fibers was surrounded by a KH560 layer after the grafting. The epoxy functionalized silane KH560 introduces epoxy groups to the surface of MPIA fibers, which can react with the rubber matrix. As a result, the interfacial adhesion of MPIA fibers/rubber was significantly improved by 62.5%.

This study also provides a universal method for the surface modification of chemically inert high-performance fiber, such as carbon fiber, aramid fiber, and ultrahigh molecular weight polyethylene (UHMWPE) fiber. Furthermore, the combination of bioinspired dopamine self-oxidative polymerization and epoxy functionalized silane grafting will lead to the feasible application of these high-performance fibers in the rubber industry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Rubber formula for adhesion measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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