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Journal Name

ARTICLE

Improved Adhesion Properties of Poly-p-phenyleneterephthamide Fibers with Rubber Matrix via UV-Initiated Grafting Modification

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In this research, ultraviolet (UV) irradiation induced graft polymerization of glycidyl methacrylate (GMA) was performed to modify the surface properties of poly-p-phenyleneterephthamide (PPTA) fibers. The improvement on adhesion with rubber matrix was achieved due to the introduction of epoxy groups. The successful grafting of GMA on the PPTA fiber surface was ascertained by characterization of X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning electron microscopy (SEM). The tensile properties of PPTA fibers after each stage of surface modification were determined by tensile testing of single-filament. Single-fiber pull-out test was applied to evaluate the adhesion of PPTA fibers with rubber matrix. The pull-out force of grafted PPTA fibers exceeded that of the pristine fibers by 53.7%. Resorcinol-formaldehyde-latex (RFL) dipping was applied to further improve the adhesion properties. As a result, the fibers with GMA grafting followed by RFL dipping exhibited a 80.8% improvement compared with the pristine fibers and achieved much higher adhesion strength with rubber matrix, rather than the PPTA fibers modified with conventional industrial method of isocyanate (NCO) and RFL two bath dipping.

1. Introduction

Currently, high-performance fibers such as aramid fibers, ultra-high molecular weight polyethylene (UHMWPE) fibers and carbon fibers are ideal reinforcement materials in polymer-based composites ascribed to the light weight in addition to their high stiffness and strength.¹ Among these, aramid fibers exhibit comprehensive properties of high modulus and strength, high fracture strain, high heat and flame resistance, and low density. The availability of aramid fibers has advanced in materials science.²⁻⁴ Aramid fibers are particularly used as reinforcement in rubber industries such as tires, belts, and hoses instead of polyester, nylon and steel cords for high performance, long service life and energy saving.

However, the poor interfacial adhesion properties resulted from the high crystallinity of the surface layer and the steric hindrance of benzene rings in the aramid molecular chain limited the application of aramid in composites. Extensive researches had been performed and a variety of

techniques had been utilized to overcome the shortcomings. Functional groups like amino, hydroxyl and carbonyl were introduced on the fiber surface through nitrification, reduction, chlorosulfonation, and etching treatment.⁵⁻⁸ Ultrasonic,⁹ γ -ray radiation¹⁰ and plasma treatment¹¹⁻¹³ are typical physical methods used for surface modification of aramid fibers, which are commonly recognized as "grafting from" techniques. However, these approaches often require sophisticated equipment, low security and multistep operations with high cost, substantial deterioration to the bulk properties of aramid fibers.

UV-induced surface graft polymerization^{14,15} has been widely applied to achieve materials with designed surface properties for specific applications. Compared with above-mentioned methods, UV-induced graft polymerization exhibits advantages of fast reaction rate, low cost of operation, simple equipment, continuous process, easy industrialization and maybe the most important, ability to tune and manipulate surface properties without damaging the bulk material. UV-induced surface grafting method was performed for graft polymerization of acrylamide (AAM) or acrylic acid (AAC) onto the surface of polyethylene (PE), polystyrene (PS),¹⁶ polypropylene (PP) film,¹⁷ polyester (PET) fiber¹⁸ and PP fiber,¹⁹ as well as electroless plating of copper on fluorinated polyimide films.^{20,21} Wang et al. studied the surface modification of UHMWPE fibers via UV initiated grafting, and acrylamide (AAM) groups were grafted onto UHMWPE chains.

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As a result, the single-fiber pull-out strength of the epoxy based composite was improved by 43.8% at the maximum.²² Meta-aramid fabrics were photo-oxidized by ultraviolet/ozone irradiation and the modified aramid fabrics showed higher affinity to cationic dyes.²³ Mori et al. modified aramid fibers with pretreatment of argon plasma, followed by ultraviolet irradiation and AAm and GMA was successfully performed onto the surface of Kevlar 49 fibers,²⁴ in-depth investigation of the influence of as-mentioned surface modification to the adhesion properties of aramid fibers was not discussed. In general, the surface modification of aramid fibers via UV initiated grafting to improve adhesion properties with rubber matrix has not been reported.

In this research, the surface modification of PPTA fibers by UV irradiation induced glycidyl methacrylate (GMA) grafting was studied. The surface composition and microstructure of the PPTA fibers were characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning electron microscopy (SEM). The grafting degree was investigated on dependence of monomer concentration and UV irradiation time. The modified fibers were then dipped in resorcinol-formaldehyde-latex (RFL) to further enhance adhesion with rubber matrix. The tensile properties of PPTA fibers after each stage of surface modification were determined by tensile testing of single-filament. Single-fiber pull-out test was applied to evaluate the adhesion of PPTA fibers with rubber matrix. The adhesion properties of the PPTA fibers modified by UV-initiated grafting and RFL dipping were compared with PPTA fibers modified via industrial method of isocyanate (NCO) and RFL two bath dipping.²⁵⁻²⁷ The adhesion properties with aging resistance were further discussed.

2. Experimental

2.1 Materials

Table 1 The properties of pristine PPTA fibers

| Trade mark | Linear Density dtex | Tensile strength cN/dtex | CV of tensile strength % | Elongation at break % | CV of elongation at break % |
|----------------------------|---------------------|--------------------------|--------------------------|-----------------------|-----------------------------|
| Taparan® para-aramid 1000D | 1100 | 20.60 | 3.69 | 2.85 | 3.60 |

Note: CV means coefficient of variation.

Poly-p-phenyleneterephthamide (PPTA) fibers used in this study were manufactured by Yantai Tayho Advanced Materials

Co. Ltd., China. The molecular structure of PPTA fibers is illustrated in Fig. 1. The mechanical properties of the PPTA fibers are detailed in Table 1. The fibers were cleaned by ultrasound in ethanol for 30 min and dried in a vacuum oven at 50 °C for 6h before use. Glycidyl methacrylate (GMA) was purchased from Aladdin Industrial Corporation, USA. The photo-initiator benzophenone (BP) was purchased from Tianjin Fu Chen Chemical Reagents Factory, China. Acetone was obtained from Beijing Chemical Works, China. All chemicals were of analytical reagent grade and used without further purification.

Epoxy used in dipping is Ethylene glycol diglycidyl ether (EGDE) (EP669), which was obtained from Beijing Chemical Works, China. Isocyanate (CBI50) was purchased from Maanshan Koin Synthetic Materials Pty. Ltd., China. Resorcinol-formaldehyde-latex (RFL) dipping solution was prepared according to the formula shown in Table 2. Vinylpyridine latex was purchased from Zibo Zeyang Chemical Works, China. Other chemicals listed in Table 2 were supplied by Beijing Chemical Works, China.

Table 2 The formula of resorcinol-formaldehyde-latex (RFL) dipping solution

| Component | Dry weight (g) | Wet weight (g) |
|----------------------------|----------------|----------------|
| resorcinol | 11.0 | 11.0 |
| formaldehyde | 6.0 | 16.2 |
| sodium hydroxide | 0.3 | 3.0 |
| deionized water | - | 235.8 |
| vinyl-pyridine latex (41%) | 100 | 250.0 |
| ammonia water (28%) | - | 11.3 |
| deionized water | - | 59.2 |

The rubber formula for adhesion measurement is given in Table 3. Natural rubber (standard 10 Malaysian rubber) was supplied by Malaysia Lee rubber industry, Malaysia. Styrene butadiene rubber (SBR1502) was purchased from Sinopec Yangzi petrochemical company Ltd., China. All ingredients used in the formula were of industrial grade.

Table 3 Rubber formulation used in adhesion measurement

| Component | Phr |
|--|-----|
| NR (standard 10 Malaysian rubber) | 30 |
| SBR 1502 | 70 |
| Zinc oxide | 5 |
| Stearic acid | 2 |
| Carbon black N330 | 25 |
| Antioxidant (4010NA) | 1.5 |
| Aromatic oil 840 | 10 |
| Silica (VN3) | 10 |
| Coumarone indene | 10 |
| 2,4,6-tri[double (methoxy methyl) amino] 1,3,5-triazine (RA) | 1 |

| | |
|--|--------------|
| Compound of resorcinol and stearic acid (RS) | 1 |
| N-cyclohexyl-2-truxene thiazole sulfonamide (CZ) | 4 |
| Sulfur | 1 |
| Total | 168.5 |

2.2 Surface modification of PPTA fibers by UV-induced GMA grafting

The photo-initiator BP with a 2.5 wt.% concentration was firstly prepared by using acetone as solvent. GMA with a predetermined concentration (2.5 wt.% to 20 wt.%) was then added to the solutions. PPTA fibers were immersed into the above solutions and transferred into glass tubes. The solutions were purged with nitrogen for 5 min to eliminate oxygen. After that, the glass tubes were subjected to 5 to 30 min of UV irradiation in a photochemical reactor (manufactured in Beijing Institute of Electric Light Source, China), with wavelength of 300–400 nm under 500 W high pressure Hg lamp at room temperature. Thereafter, the UV irradiated PPTA fibers were taken out and washed with ethanol and distilled water for 3 times to remove physically absorbed monomers and homopolymers. Finally, the fibers were dried by an oven at 50 °C for 12 hours. The as-modified PPTA fibers are referred as PPTA-g-PGMA in this article.

2.3 Impregnation of PPTA fibers by RFL

Preparation of RFL: Resorcinol, sodium hydroxide and formaldehyde were dissolved in distilled water, and pre-polymerization of resorcinol-formaldehyde (RF) resin was carried out by stirring at room temperature for 6 h. Vinylpyridine latex was diluted in distilled water and added into the RF resin solution. RFL dipping solution was then obtained after 20 h of stirring at room temperature.

Impregnation of PPTA fibers by RFL: Impregnation of the PPTA fibers was conducted by immersing the pristine and grafted PPTA fibers in RFL dipping solution. After 2 minutes, the fibers were taken out from the solution and put in 160 °C oven for another 5 min. The obtained fibers were noted as PPTA/RFL and PPTA-g-PGMA/RFL.

Impregnation of PPTA fibers by two bath dipping of industrial method: In industrial market, aramid fibers are usually pre-dipped in solution of epoxy and isocyanate (NCO) with proportion of 1:6, and then dipped in RFL solution. The PPTA fibers prepared in as-mentioned two bath process are noted as PPTA/NCO-RFL in this article.

2.4 Preparation of PPTA fibers/rubber composites

The ingredients of rubber formula shown in Table 3 were weighed and mixed in an internal mixer, and rolled into rubber sheets with 5 mm thickness in a roll mill. The rubber sheets were placed in the channel of a stainless steel mold and then

PPTA samples were embedded in rubber and covered with rubber sheets in mold. These prepared composites were vulcanized at 150 °C for 45 min under a pressure of 3.5 MPa. Then the vulcanizates were cut according to ISO 4647 for single-fiber pull-out test.

2.5 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

The changes of surface chemical structure on the PPTA fibers were characterized by infrared spectrometer (Tensor 27, System 2000, Bruker, Germany) in the attenuated total reflectance (ATR) method.

2.6 X-ray photoelectron spectroscopy (XPS)

The surface composition of the PPTA fibers was determined by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo Electron Corporation, USA) with monochromatized Al K α X-ray source (1486.6 eV photons). The X-ray source was run at a reduced power of 150 W. The PPTA samples were mounted on standard sample studs by means of double-sided adhesive tapes. The pressure in the analysis chamber was maintained at 8–10 Torr or lower during each measurement.

The O/C ratio means the atomic molar ratio of two elements. Extract the experimental details of all interested regions from VG XPS files and **NO. of scan** can be obtained directly from the files. Area information of interested peaks from XPSPEAK is collected thereafter. The sample charge effect is calibrated with C 1s peak of the carbon contamination to a value of 284.6 eV. **Expt Area** of each element is displayed in XPSPEAK. **Atomic Sensitivity Factor (ASF)** can be obtained from "Handbook of X-ray Photoelectron Spectroscopy", Appendix F, Physical Electronic Inc., c1992. The calculation of **O/C atomic ratio** is as Equation 1-5.

$$\text{Atomic area} = \text{Expt Area} / \text{NO. of scan.} \quad \text{Eqn. 1}$$

$$\text{Real Area} = \text{Atomic area} / \text{ASF.} \quad \text{Eqn. 2}$$

$$\text{Total Area} = \sum \text{Real Area.} \quad \text{Eqn. 3}$$

$$\text{Elemental atomic \%} = \text{Real Area} / \text{Total Area.} \quad \text{Eqn. 4}$$

$$\text{O/C atomic ratio} = \text{O atomic \%} / \text{C atomic \%}. \quad \text{Eqn. 5}$$

2.7 Scanning electron microscopy (SEM)

The morphology of the fibers and the fracture surface of composites after single-fiber pull-out tests were observed under a scanning electron microscope (Hitachi S-4700, Japan). The samples were gold-coated to give electronic conductivity before each measurement. The SEM measurements were performed at an accelerating voltage of 20 kV.

2.8 The grafting degree of GMA

The grafting degree (GD) for the PPTA fibers was determined gravimetrically and the weight of the fibers was measured in the dry state. The grafting degree was defined by the Equation 6:

$$GD (\%) = (w_2 - w_1) / w_1 * 100 (\%) \quad \text{Eqn. 6}$$

where w_1 and w_2 are the weight of PPTA fibers before and after UV grafting.²⁸

2.9 Tensile testing of single filament

The tensile properties of PPTA fibers after each stage of surface modification were determined by tensile testing of single-filament specimens according to ISO 11566:1996 using an electronic tensile tester of single filament (YM-06B, Shaoxing Yuanmao Electrical and Mechanical Co. Ltd., China) at the speed of 10 mm/min. Prepare at least 20 test specimens from each elementary unit, to enable the average of 20 measurements to be made for each result.

2.10 The interfacial adhesion of PPTA fibers/rubber composites

The interfacial adhesion of PPTA 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.

3. Results and Discussion

Scheme 1 depicts the process of UV-induced GMA grafting with PPTA fibers using benzophenone (BP) as initiator. BP is the most frequently used Norrish type II photoinitiator due to the high grafting efficiency.¹⁴ In this study, under UV irradiation, BP is excited to a single state and then to a triplet state, which can undergo hydrogen abstract reaction from PPTA fibers substrate. Consequently, the radicals on the surface of PPTA fibers were utilized to initiate graft polymerization of GMA.

3.1 Surface chemical composition of the modified PPTA fibers

The changes of surface chemical composition and chemical bonds can dramatically affect the wettability and adhesive performance of the fibers. The chemical structure of PPTA fibers was investigated by ATR-FTIR measurements in the mid infrared region (4000-500 cm^{-1}). Fig. 2 illustrates the respective ATR-FTIR spectra of (a) pristine PPTA fibers, (b) PPTA-g-PGMA fibers, (c) GMA monomer and (d) differential spectra of b and a (the peak at 1543 cm^{-1} as internal standard). For the pristine PPTA fibers, four characteristic absorption bands at 3325 cm^{-1} for hydrogen bonded N-H band, at 1642 cm^{-1} for the amide group, at 1543 cm^{-1} for combination of N-H

bending and C-N stretching and at 1319 cm^{-1} for combination of N-H bending and C-N stretching can be observed.²⁹ Comparing with Fig. 2a, new absorption bands of methylene group at 2935 cm^{-1} and 2854 cm^{-1} and carbonyl group of GMA at 1725 cm^{-1} ^{24,30,31} are discernible in the spectrum of PPTA-g-PGMA. Note that, the absence of the C=C bending absorptions at 1170 cm^{-1} and 946 cm^{-1} and stretching absorption at 3000 and 2954 cm^{-1} indicates that the UV-initiated graft polymerization of GMA was proceeded mainly through the vinyl group of GMA.²¹ Most importantly, appearance of new absorption peak at 910 cm^{-1} and enhance of absorption peak at 828 cm^{-1} shown in Fig. 2b and d confirmed the introduction of epoxy groups on the surface of PPTA-g-PGMA which can improve the adhesion to rubber matrix.^{24,30,31}

The surface chemical compositions of the pristine PPTA fibers and PPTA-g-PGMA fibers were determined by XPS. Fig. 3 shows the XPS wide scan and C 1s core-level spectra of (a) pristine PPTA fibers and (b) PPTA-g-PGMA fibers. Determined by XPS, the carbon, nitrogen, and oxygen atomic % on the surface of pristine PPTA is 79.5%, 3.9% and 16.6%, respectively. After UV induced GMA grafting on PPTA, the N peak is dramatically decreased, what's more, the C peak decreased and O peak increased in wide scan curve due to higher oxygen content in epoxy and ester group in GMA. The C 1s core level spectrum of the pristine PPTA fibers can be curve fitted with five peak components, having binding energies (BE's) at 284.6 eV for C-C species, at 285.5 eV for the C-N species, at 287.5 eV for the C=O species, at 288.5 eV for the O-C=O species due to carboxyl end groups of PPTA and at 282.6 eV for C-Si species introduced by the synthesis process (see Fig. 3a). The successful grafting of polymerize GMA (PGMA) on the surface of PPTA fibers can be deduced from the appearance of new peak component at 286.4eV for C-O species attributed to the epoxy groups and the enhance of the peak at 288.5 eV for the O-C=O species ascribed to the ester group in GMA molecular structure. The content of corresponding functional groups was calculated by the area of peak. The peak content of C-O group is up to 12.4%, and that of O-C=O species increases from 5.4% in PPTA fibers to 8.0% in PPTA-g-PGMA fibers. The original species of C-N and C=O of pristine PPTA fibers are still discernible in Fig. 3b, indicating that the thickness of grafted layer is within the depth of XPS probe.

3.2 Effect of the UV irradiation time on the O/C atomic ratio and grafting degree

Fig. 4 shows the grafting degree and the surface oxygen to carbon (O/C) atomic ratio of modified fibers treated at different UV irradiation time (5, 10, 15, 20, 30 min) with GMA concentration of 5 wt.%. Determined by XPS, the surface O/C ratio of PPTA fibers is 0.133. After UV-induced GMA grafting, the O/C ratio increases to 0.200–0.300 due to higher oxygen content in epoxy and ester groups in GMA, another potent

indication that PGMA was successfully grafted onto the surface of PPTA fibers. Both the O/C ratio and the grafting degree increase linearly with increase of UV irradiation time, due to the fact that the extension of irradiation time would supply more amounts of radicals on the surface of PPTA fibers reactive to GMA. The grafting degree reaches the peak at 15 min and decreases after that resulted from the depletion of GMA monomers in solution. These results are consistent with the results of O/C ratio of XPS analysis. It can be deduced that the prolonged irradiation time would attribute little to the grafting degree and could cause deterioration to PPTA fibers.^{29,31,32}

The surface graft polymerization caused remarkable changes in the surface topography of PPTA fibers and the changes were observed by SEM. The extremely smooth surface of the pristine PPTA fibers can be seen from Fig. 5a. After UV-induced grafting, the original featureless topography of the pristine fibers is substituted with growing granules, which can be observed from Fig. 5b–f. The PGMA granules formed on fiber surface become denser and larger with increase of the UV irradiation time from 5 to 15 min. Note that, the height of the granules increases almost linearly with the diameter of the granules.³³ It can be inferred that the polymer chains extended with increase of the irradiation time. The SEM evidence indicates that the graft polymerization of GMA is restricted to the fiber surface and therefore the mechanical properties of fiber substrate are retained.

3.3 Effect of the GMA concentration on the O/C atomic ratio and grafting degree

The dependence of the surface oxygen to carbon (O/C) atomic ratio and grafting degree of the modified fibers on the monomer concentration is illustrated in Fig. 6. The O/C ratio on the surface of PPTA-g-PGMA fibers increases linearly to the maximum at 10 wt.% of monomer concentration, and then decreases as further increase of monomer concentration. It is mainly due to the formation of GMA homopolymers, which is inevitable in the process of ordinary UV-induced graft polymerization. Meanwhile, it can be seen that the grafting degree displays the same tendency with the O/C ratio. It may be appropriate to point out that the amount of radicals is constant under a given irradiation time, excessive monomer may not be contributive to higher grafting degree.

The surface morphology of fibers also influences the anchoring or tethering effects on the interface of fibers and matrix. And the presence of an adhesive interface with physicochemical effects can promote the adhesion of the components in composites. Thus the surface morphology of PPTA fibers was further studied. Compared to the extremely smooth surface of the pristine fibers shown in Fig. 7a, rough layer with grafted granules can be observed in Fig. 7b–f. At a constant UV irradiation time, sufficient amount of GMA supply

enough grafting for the fibers with the constant amount of radicals. With increase of the monomer concentration, the PGMA granules formed on fiber surface become denser and thicker with increased roughness. The results of SEM analysis confirm to the results of O/C atomic ratio and grafting degree.

In summary, the grafting degree can be manipulated with control of monomer concentration and UV irradiation time. In this work, 10 wt.% of monomer concentration and 15 min of UV irradiation time is the optimum condition for the GMA grafting of PPTA in acetone solution.

3.4 Tensile properties of PPTA fibers after UV irradiation and RFL dipping

Fig. 8 shows the changes of single-filament tensile strength of PPTA fibers before and after different surface treatment. For pristine PPTA fibers, the single-filament tensile strength is 4.47 GPa. As we all know, UV irradiation would deteriorate the structure of aramid fibers and their tensile properties resulting from the breakage of amide bonds.^{31,34–36} Fig. 8a demonstrates the changes of tensile strength of PPTA-g-PGMA fibers with regard to GMA concentration irradiated for 15 min. After UV irradiation with different GMA concentration, the fiber strength decreased dramatically to 2.89–2.82 GPa. Apparently, the decrease of tensile strength was not affected by the changes of GMA concentration. However, the changes of tensile strength with respect of the UV irradiation time present declining trend, as shown in Fig. 8b. Tensile strength of PPTA-g-PGMA fibers drops to 3.35 GPa (75% retention of the tensile strength of original PPTA fibers) after 5 min of irradiation, and the drop decelerated with increase of irradiation time. Extension of irradiation time results to breakage of more amide bonds of PPTA, and the minimum value appears at 30 min of irradiation, which is only 2.80 GPa (63% retention of the tensile strength of original PPTA fibers).

RFL dipping was conducted under 160 °C for 5 min, therefore single-filament tensile testing was also used to evaluate the effect of RFL dipping process on the tensile properties of PPTA fibers. The results are shown in Fig. 8c. The PPTA-g-PGMA fibers exhibit 2.89 GPa of tensile strength, 65% retention of the tensile strength of original PPTA fibers. However, PPTA-g-PGMA/RFL fibers exhibit 2.87 GPa of tensile strength, only 0.02% decrease of the tensile strength of PPTA-g-PGMA fibers. It is mainly due to the excellent heat resistance of PPTA fibers.

3.5 Interfacial adhesion of PPTA fibers/rubber composites

The single-fiber pull-out tests were conducted to investigate the interfacial adhesion of PPTA fibers/rubber composites. Fig. 9 and 10 illustrate the effect of grafting degree on the pull-out force related to UV irradiation time and

GMA concentration. It can be concluded that the pull-out force increases with the increase of the grafting degree. In fiber reinforced composites, the outmost surface of each component material is most prone to interact with its environment both physically and chemically.¹⁴ The higher the grafting degree of PGMA, the more epoxy groups introduced to the fibers surface. The possible interaction in PPTA-g-PGMA and RFL is depicted in Scheme 2. Epoxy groups on the surface of PPTA-g-PGMA fibers react with phenolic hydroxyl groups of RF and then form to three dimensional network with encapsulated latex particles.^{37,38} In the vulcanization process, sulfur homolysis into sulfur radicals at high temperature. The obtained sulfur radicals react with double bonds of rubber matrix and further with double bonds of latex, forming crosslinked network structure. The possible interaction in PPTA-g-PGMA/RFL and rubber matrix is shown in Scheme 3.

Fig. 11 demonstrates the adhesion properties of the PPTA-g-PGMA/RFL and PPTA/NCO-RFL fibers with rubber matrix. The GMA grafted fibers exhibit 80.8% improvement in pull-out force than the pristine PPTA fibers and 53.5% higher pull-out force than PPTA/NCO-RFL fibers. The epoxy groups introduced by GMA in PPTA-g-PGMA/RFL fibers are the main contribution to the improvement due to the formation of strong chemical bonds in the vulcanization of composites with RFL and rubber matrix. In addition, the PPTA-g-PGMA fibers also display higher pull-out force after 72h air aging at 90–150 °C. Pristine PPTA fibers incorporate with NCO and RFL coating with covalent or hydrogen bonds, which is unstable in high temperature. The high heat aging would result in the breakage of these labile bonds and cause decrease in adhesion properties. On the contrast, the epoxy groups of GMA grafted fibers form a desirable three-dimensional network with RFL and the strong chemical bonding would survive in high temperature aging. Therefore, it can be concluded from the data that the UV-induced GMA grafting brought improvement of the interfacial adhesion properties between PPTA fibers and rubber.

The SEM photograph of interlaminar fracture surface reveals more information of the fracture mode of composites and the fracture surface of PPTA fibers/rubber composites after pull-out test is displayed in Fig. 12. Torn filament and rubber can be observed on the surface of PPTA/NCO-RFL fibers after pull-out test, indicating that the fracture occurs at the interface of fiber and rubber matrix. However, the surface of PPTA-g-PGMA/RFL fibers is covered with rubber after pull-out test, suggesting the fracture appears at the composition of rubber matrix. Hence, it is reasonable to conclude that the interfacial bond strength of PPTA-g-PGMA/RFL fibers/rubber composite is greater than the internal strength of rubber matrix. It can be seen from Fig. 12d that little rubber is adhered to the PPTA/NCO-RFL fibers after pull-out test, and it is resulted from the breakage of labile bonds at high

temperature aging. However, thick rubber layer is still adhered to the surface of PPTA-g-PGMA/RFL after high temperature aging. As a result, effective contribution of epoxy groups introduced by GMA in improving anti-aging adhesion properties of PPTA fibers is ascertained.

Conclusions

GMA was successfully introduced to the surface of PPTA fibers via UV-induced graft polymerization, introducing epoxy groups for adhesion enhancement. It was concluded that the grafting degree increased with monomer concentration and UV irradiation time within a certain range. The adhesion properties of PPTA fibers was improved by 53.7% after UV-initiated GMA grafting and further enhanced by 80.8% with RFL dipping. Compared with PPTA fibers modified by industrial isocyanate and RFL two bath dipping, the PPTA fibers modified by UV-initiated grafting and RFL dipping achieved much higher adhesion properties with rubber matrix. What's more, the bonding between grafted fibers and rubber matrix still survived in high temperature aging. In summary, UV-initiated graft polymerization is a feasible way of improving the interfacial adhesion properties of PPTA fibers and rubber matrix with satisfying aging resistance.

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Graphs:

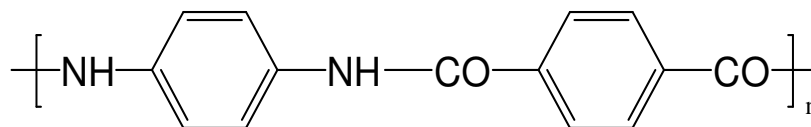
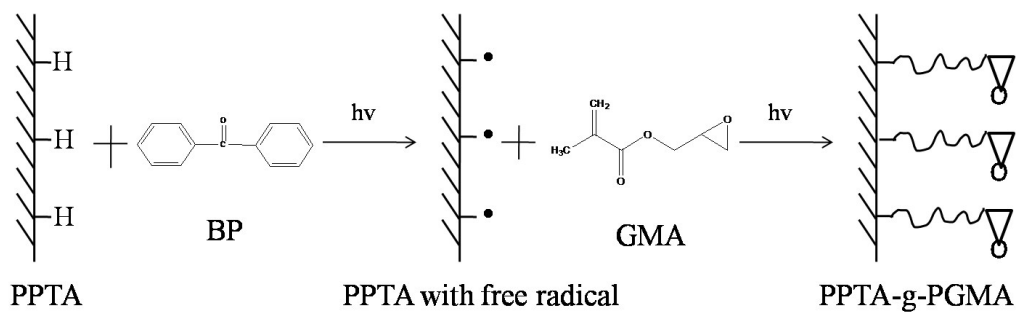


Figure 1 the molecular structure of PPTA fibers



Scheme 1. The process of UV-induced GMA grafting of PPTA fibers

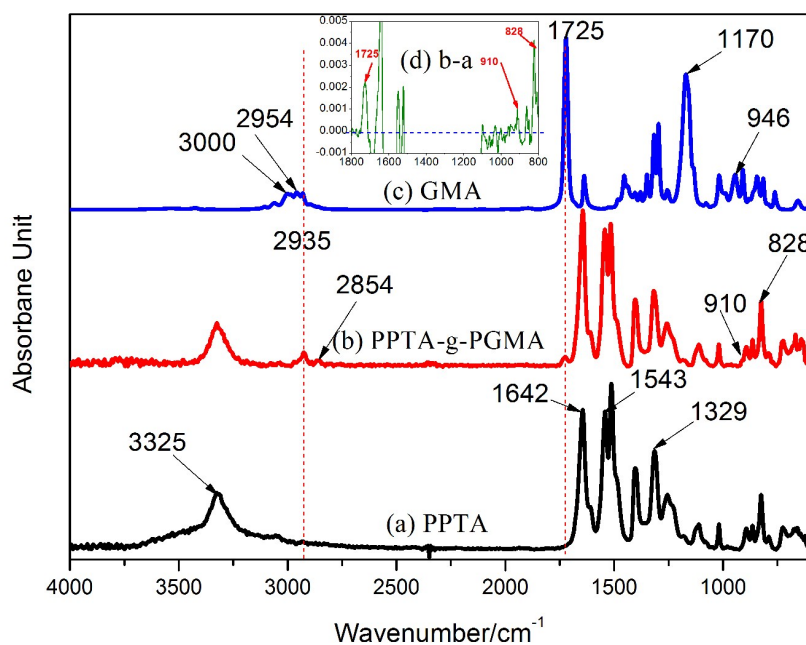


Figure 2. ATR-FTIR spectra of (a) PPTA fibers, (b) PPTA-g-PGMA fibers and, (c) GMA monomer and (d) differential spectra of b and a

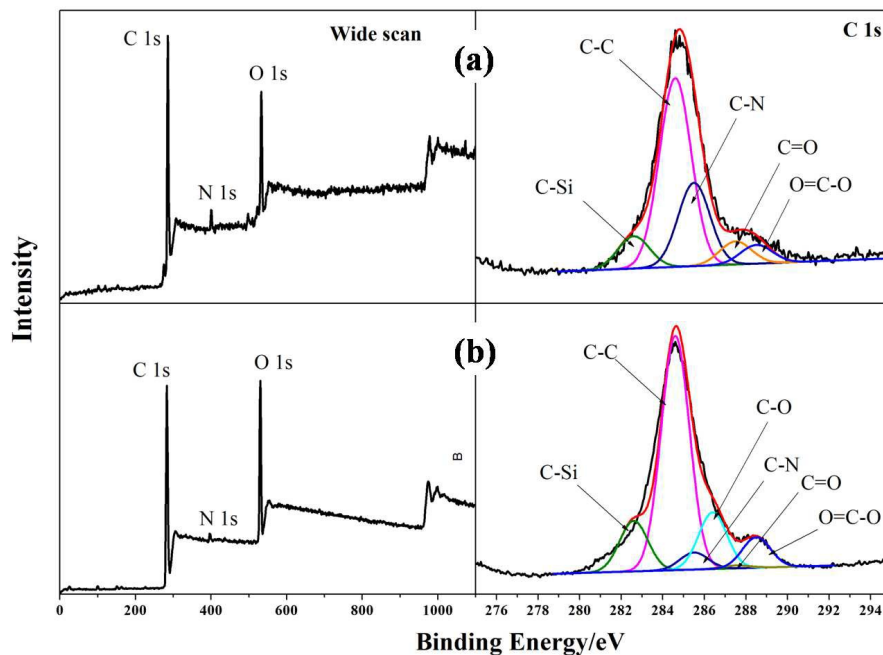


Figure 3. XPS wide scan and C1s core-level spectra of (a) PPTA fibers and (b) PPTA-g-PGMA fibers

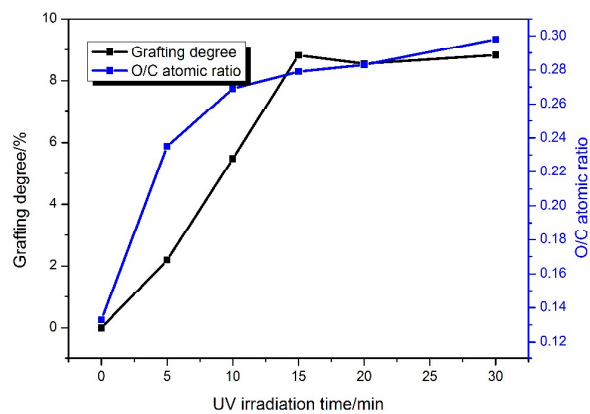


Figure 4. Effect of UV irradiation time on the O/C atomic ratio and the grafting degree of the PPTA fibers (5 wt.% of GMA concentration)

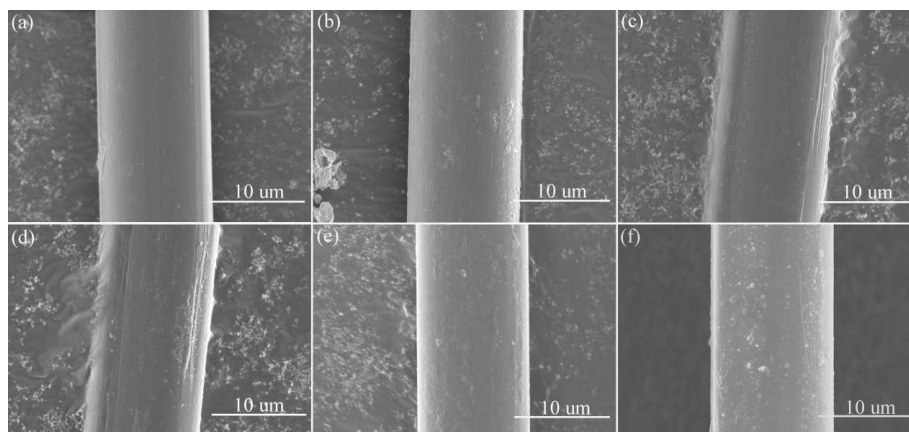


Figure 5. SEM images of (a) pristine PPTA fiber and PPTA-g-PGMA fibers irradiated for: (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, (f) 30 min

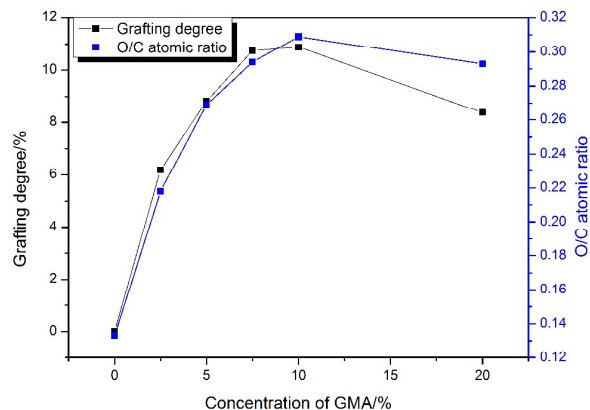


Figure 6. Effect of the GMA concentration on the O/C atomic ratio and the grafting degree of the PPTA fibers (15min of irradiation time)

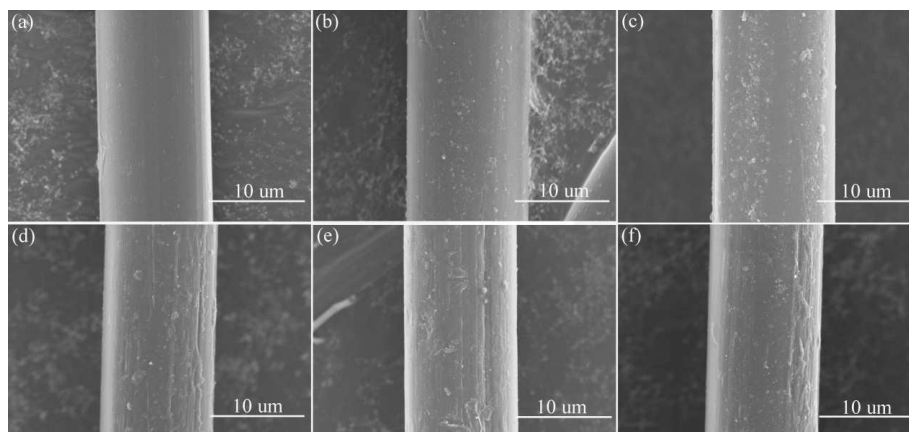


Figure 7. SEM images of (a) pristine fiber and PPTA-g-PGMA fibers grafted with GMA concentration of (b) 2.5 wt.%, (c) 5 wt.%, (d) 7.5 wt.%, (e) 10 wt.% and (f) 20 wt.%

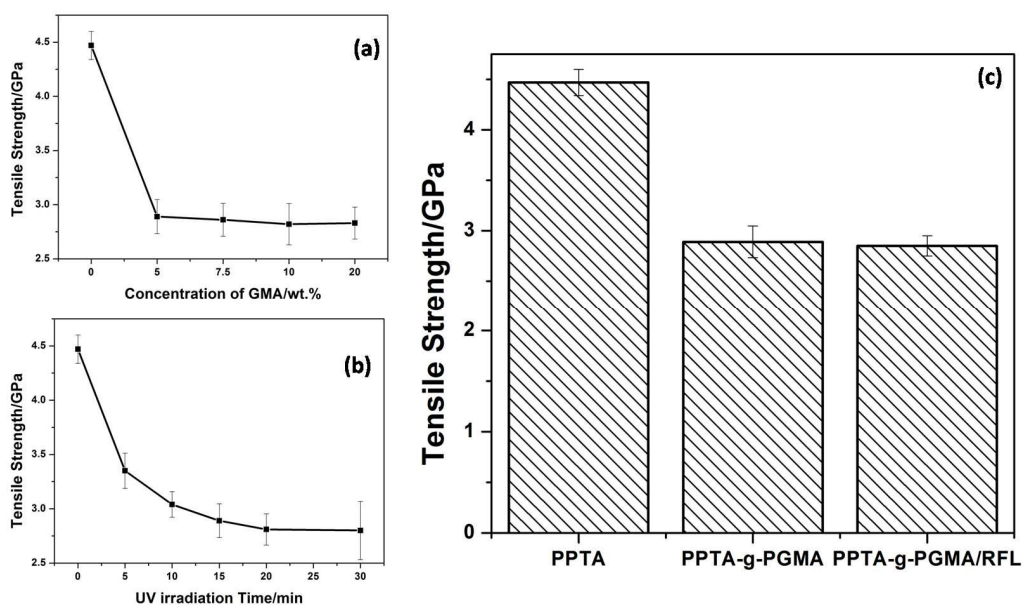


Figure 8. (a) Single-filament tensile strength of pristine PPTA fibers and PPTA-g-PGMA fibers treated with different GMA concentration at irradiation time of 15 min;

(b) Single-filament tensile strength of PPTA and PPTA-g-PGMA fibers treated with different irradiation time at the GMA concentration of 5%;

(c) Single-filament tensile strength of PPTA, PPTA-g-PGMA and PPTA-g-PGMA/RFL fibers

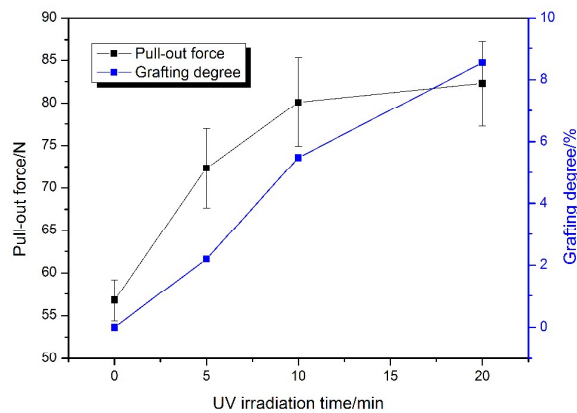


Figure 9. The relation between pull-out force and the grafting degree of PPTA fibers grafted under different irradiation time

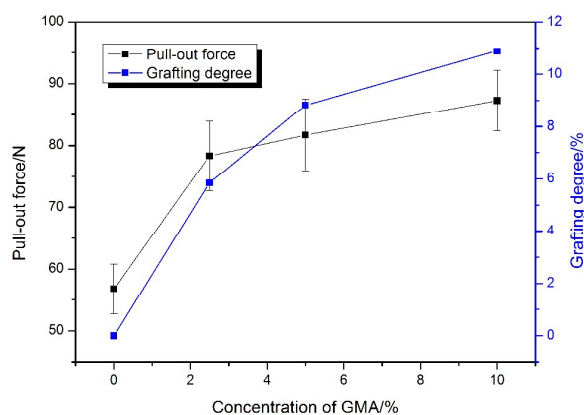
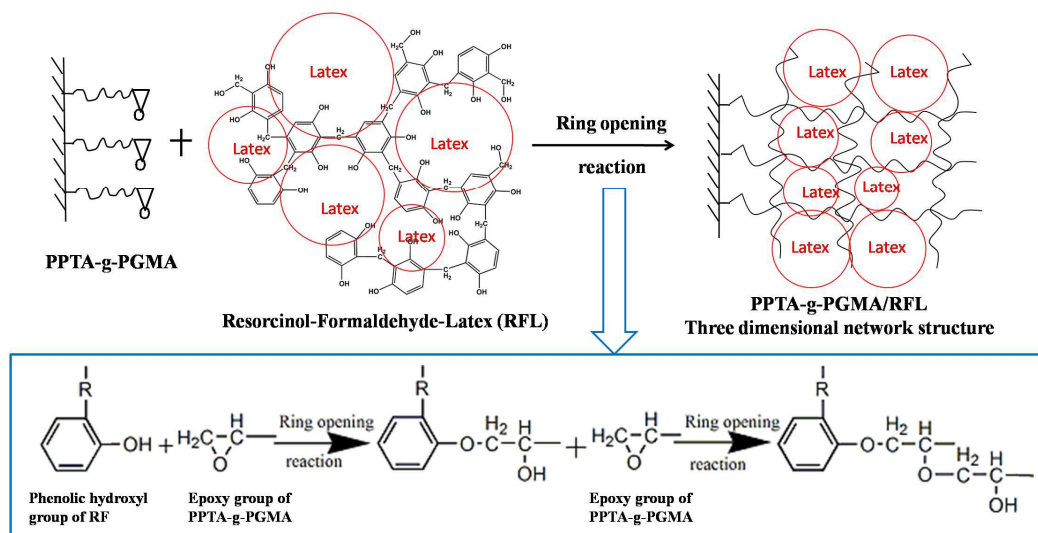
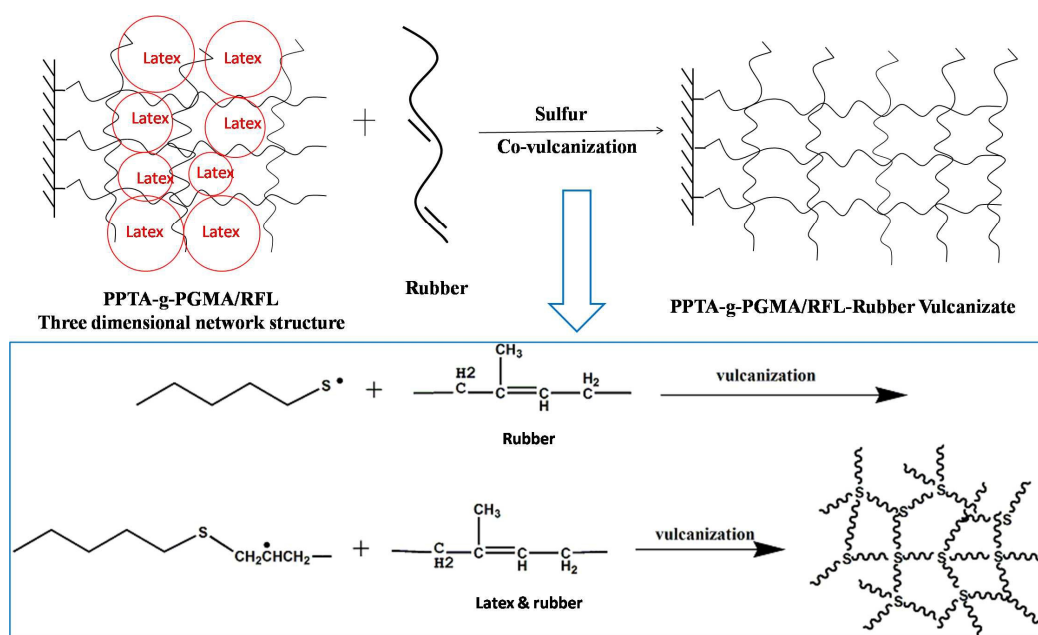


Figure 10. The relation between pull-out force and the grafting degree of PPTA fibers grafted with different GMA concentration



Scheme 2. Illustration of chemical interaction between PPTA-g-PGMA and RFL



Scheme 3. Illustration of chemical interaction between PPTA-g-PGMA/RFL and rubber

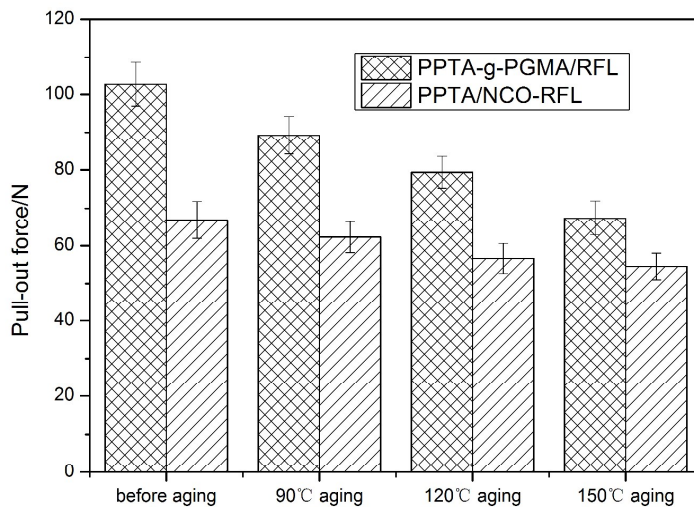


Figure 11. Pull-out force of PPTA fibers/rubber composites before and after hot air aging (72h)

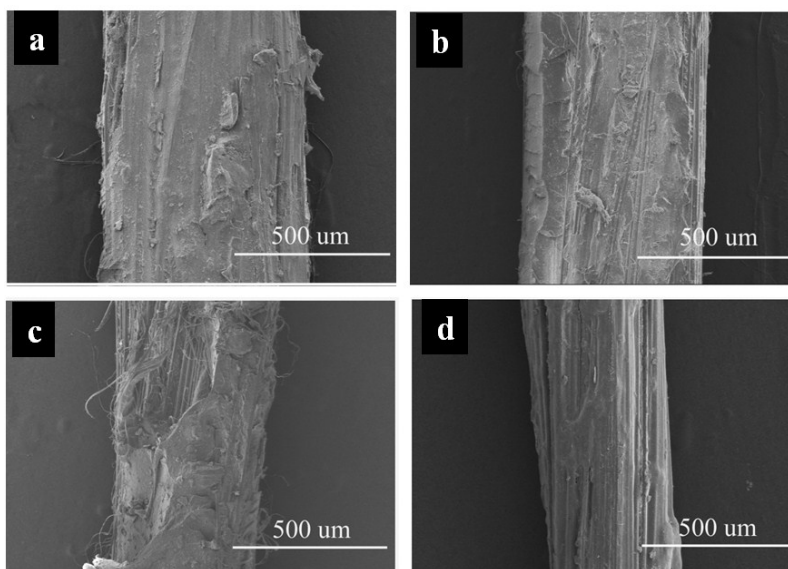


Figure 12. SEM images of interlamellar surfaces after pull-out test:

(a) PPTA-g-PGMA/RFL, (b) PPTA-g-PGMA/RFL after 90 °C*72h air aging, (c) PPTA/NCO-RFL, (d) PPTA/NCO-RFL after 90 °C*72h air aging