

# Bioenzyme-Catalyzed Grafting of Aramid Fibers and Interfacial Properties of Composites Post-print

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## Abstract

Horseradish peroxidase (HRP) was utilized as a bioactive enzyme catalyst to perform grafting reactions on aramid fiber surfaces, generating a coating layer containing active functional groups of allyl glycidyl ether. The effects of the bioenzyme-catalyzed grafting reaction on the comprehensive performance of aramid fibers were investigated. The results demonstrate that the bioenzyme can effectively catalyze grafting reactions on the fibers, with enzyme concentration affecting the monomer grafting ratio on the fibers. As enzyme concentration increases, more monomers are grafted onto the fibers, resulting in substantial enhancements in surface polar functional group content, surface free energy, and surface roughness, which strengthens the interfacial bonding between fibers and resin. Simultaneously, compared with conventional fiber modification methods, the bioenzyme-catalyzed grafting method essentially preserves the excellent thermal and mechanical properties of aramid fibers.

## Full Text

### Surface Modification and Interface Properties of Enzyme-mediated Grafting Kevlar Fibers

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## Abstract

A surface coating with functional groups on poly(p-phenylene terephthalamide) (Kevlar, KF) fibers was prepared through polymerization using

horseradish peroxidase (HRP) as a bioactive catalyst. The effect of this approach on the integrated properties of KF fibers was investigated. The results show that the polymerization can effectively proceed on the fiber surface in the presence of HRP. The HRP content affects the grafting percentage on the fiber surface. More monomer was grafted onto the fiber surface with increasing HRP content, whereby the fiber surface possessed higher amounts of polar groups, higher surface free energy, and higher roughness, which subsequently resulted in enhanced interface adhesion between the fibers and the resin matrix of the composite. Moreover, these HRP-catalytically grafted fibers retained more or less the same thermal and mechanical properties as the original KF fibers.

**Keywords:** organic polymer materials, enzyme-mediated grafting, Kevlar fibers, surface modification, mechanical properties

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## 1. Experimental

### 1.1 Raw Materials

The main raw materials are listed in .

### 1.2 Surface Treatment and Enzymatic Grafting Modification of KF Fibers

KF fibers were first cleaned with acetone, petroleum ether, and deionized water for 4 h to remove surface contaminants, then dried at 110°C and stored in a desiccator for later use. Untreated KF fibers are denoted as KF.

Cetyltrimethylammonium bromide, n-butanol, and isooctane were dissolved in phosphate buffer solution (PBS) and stirred until a clear, transparent solution was obtained. This solution was then poured into a triangular flask containing KF fibers, 1,4-dioxane, HRP, and allyl glycidyl ether monomer. The mixture was degassed at 38°C for 30 min to remove dissolved oxygen. Under continuous stirring, 30 vol% H<sub>2</sub>O<sub>2</sub> was added dropwise to the solution over a period of more than 1 h. After reacting for 20 h, the samples were removed and treated with deionized water and acetone for 3 h each in a Soxhlet extractor. The products were vacuum-dried at 110°C for 12 h and then sealed for storage. In this experiment, samples obtained with different enzyme concentrations were labeled as KF-C (where C represents the enzyme concentration).

### 1.3 Preparation of Composites

**Resin matrix:** Bisphenol A dicyanate was heated in an oil bath to 100°C until melted, then maintained at 150°C with stirring for approximately 2 h until homogeneous and transparent.

A single KF fiber was passed through the center of a polytetrafluoroethylene circular mold with a thickness of 1 mm and fixed in place. The prepared epoxy

resin matrix was poured into the mold, then vacuum-treated at 80°C for 20 min to remove bubbles. Curing and post-treatment were performed at 150°C/2 h + 180°C/2 h + 200°C/2 h + 220°C/2 h and 240°C/4 h, followed by natural cooling to room temperature in the oven.

#### 1.4 Sample Testing and Characterization

Fiber specimens were bundled and cut into powders with lengths less than 20 m for KBr pellet preparation. Fourier transform infrared spectroscopy was performed using a Nicolet 5700 spectrometer.

Fiber samples were adhered to clean copper plates with double-sided tape, sputter-coated with gold under vacuum, and analyzed using low-vacuum scanning electron microscopy (SEM, HITACHI S-4700) to compare surface morphology before and after treatment, with an operating voltage of 15 kV.

X-ray photoelectron spectroscopy (XPS) was used to analyze changes in the surface chemical state of fiber samples before and after treatment. MgK $\alpha$  ( $h = 1486.6$  eV) was used as the excitation source with an X-ray gun power of 250 W, pass energy of 23.50 eV, and spot diameter of 400  $\mu$ m. The analysis chamber vacuum was  $10^{-9}$  Torr during testing, with C1s electron binding energy of 284.6 eV used as an internal standard for both full-spectrum and C1s single-spectrum scans of KF fibers.

Wide-angle X-ray diffraction (XRD) was performed using a MERCURY CCD diffractometer to characterize the crystal structure of KF fibers, with a test range of 5–45° and a scanning rate of 2°/min.

Thermogravimetric analysis (TGA) was conducted on a PE TGA-7 instrument at a heating rate of 10°C/min to measure weight loss of KF fibers from 50–800°C under N<sub>2</sub> atmosphere.

Wettability was tested using a dynamic contact angle measurement instrument (DCAT 21, Germany). A cylindrical container holding 1 g of KF fibers was suspended from an electronic balance. When the container was lowered to be level with the liquid surface, the wetting liquid would wet the KF fibers, and the weight gain versus wetting time curve was measured. The contact angle was obtained using the instrument's software. The wetting liquids used were deionized water ( $\gamma = 72.8$  mN/m,  $\gamma = 21.8$  mN/m,  $\gamma = 51.0$  mN/m) and ethylene glycol ( $\gamma = 48.3$  mN/m,  $\gamma = 29.3$  mN/m,  $\gamma = 19.0$  mN/m).

Using the obtained contact angle data, the non-polar component ( $\gamma^d$ ) and polar component ( $\gamma^p$ ) of the surface free energy of KF fibers were calculated according to the following equation, thereby obtaining the surface free energy:

$$\gamma = \gamma^d + \gamma^p$$

where  $\theta$  is the contact angle of KF fiber with the test liquid,  $\gamma$  is the surface free energy (mN/m),  $\gamma^d$  is the non-polar component of surface free energy (mN/m),

and  $\gamma$  is the polar component of surface free energy (mN/m). The subscript l represents the test liquid, and f represents the fiber.

Single-fiber tensile strength was tested using a YG004N+ electronic single-fiber strength tester (cross-head speed: 1 mm/min, gauge length: 10 mm) according to GB/T 14337-2008 [Figure 1: see original paper], with at least 10 valid specimens.

The interface bonding strength of KF fiber composites was determined by single-fiber pull-out tests. A YG004N+ electronic single-fiber strength tester was used to measure the maximum load required to pull out a single KF fiber from the composite, with 10 parallel tests per sample. The tensile speed was 1 mm/min. According to relevant theory, the interfacial shear strength (IFSS) is calculated as:

$$\text{IFSS} = \frac{F_{\max}}{\pi dl}$$

where IFSS is the interface bonding strength of KF fiber/resin composites (Pa),  $F$  is the maximum load to pull out the KF fiber monofilament from the composite (N),  $d$  is the diameter of the KF fiber monofilament (m), and  $l$  is the embedded depth of the KF fiber monofilament in the epoxy resin (m).

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## 2. Results and Discussion

### 2.1 Surface Morphology of Enzyme-catalyzed Grafted KF Fibers

[Figure 2: see original paper] shows the surface morphology of KF fibers before and after treatment: KF, KF-0.01, KF-0.02, and KF-0.03. The untreated fiber exhibits a smooth surface with minimal adsorption and a cylindrical shape. In contrast, fibers catalytically grafted with monomer by HRP/H<sub>2</sub>O<sub>2</sub> show rougher surfaces with grooves and protrusions, indicating that grafting reactions occurred on the surface.

HRP is a heme enzyme with a structure combining protein and iron porphyrin rings, capable of catalyzing reactions with organic or inorganic substrates [11]. The polymerization of AGE on the fiber surface follows a radical polymerization mechanism (see ESI†(1)). Upon addition to the polymerization system, HRP generates cationic radicals under the action of the oxidant H<sub>2</sub>O<sub>2</sub>, which abstract hydrogen from the benzene rings in the fiber, creating KF fiber radicals. These radicals initiate the radical polymerization of AGE, forming PAGE polymer on the fiber surface. The figure also reveals that surface roughness gradually increases with enzyme concentration, demonstrating that higher enzyme concentrations enhance the degree of catalytic grafting.

The grafting degree can be calculated from mass measurements before and after grafting using the following equation [Figure 3: see original paper]:

$$\text{GY} = \frac{w_g - w_i}{w_i} \times 100\%$$

where GY is the grafting degree,  $w_i$  is the mass of aramid fiber before grafting, and  $w_g$  is the mass of fiber after grafting. [Figure 3: see original paper] shows that the grafting degree increases with enzyme concentration, indicating that monomer concentration determines not only the molecular weight of the formed polymer but also controls the grafting degree on the corresponding fiber. At low AGE monomer concentrations, the polymer molecular weight from each radical initiation point is small, and only a few initiation points form longer-chain polymers. Consequently, only a few “ribbon-like” polymers are observed on the fiber surface (e.g., KF-0.01). As AGE concentration increases, the average molecular weight of surface polymers increases, molecular chains extend, and increasing numbers of “ribbon-like” polymers fuse together, resulting in a “flocculent” polymer morphology on the fiber surface (e.g., KF-0.03), which indicates that more polymer surrounds the carbon fiber surface.

## 2.2 Surface Chemical Composition of Enzyme-catalyzed Grafted KF Fibers

FTIR spectra were obtained for untreated KF fibers and KF fibers grafted under four enzyme concentrations [Figure 4: see original paper]. Compared with untreated KF fibers, the enzyme-grafted polymerized fibers show significantly enhanced carbonyl vibration peaks at  $1650\text{ cm}^{-1}$ , benzene ring vibration peaks at  $1510\text{ cm}^{-1}$ , and epoxy vibration peaks at  $1250\text{ cm}^{-1}$ . Additionally, new peaks appear at  $760\text{ cm}^{-1}$  and  $690\text{ cm}^{-1}$ , corresponding to monosubstituted benzene ring absorptions, indicating successful grafting of PAGE onto the benzene ring positions.

To further analyze changes in surface chemical elements, XPS characterization was performed on KF fibers before and after modification. [Figure 5: see original paper] presents the survey spectra of surface chemical composition before and after grafting. Each curve shows three strong peaks corresponding to the three elements C, N, and O present on the fiber surface. Integrating the peak intensities allows qualitative determination of the relative content of each element, as shown in . The results reveal that after enzyme-mediated grafting polymerization modification, the C content on the fiber surface decreases while O content increases significantly and N content decreases substantially. This occurs because PAGE formation introduces numerous oxygen-containing functional groups, and PAGE itself contains no nitrogen. Initially, at low monomer concentrations, little polymer forms, so elemental content changes are minimal. As monomer concentration increases, high-molecular-weight polymers gradually form on the KF fiber surface, eventually creating a dense coating layer. Since XPS detection depth is only about 10 nm, the N element content decreases significantly.

### 2.3 Crystallinity and Monofilament Tensile Properties of Enzyme-catalyzed Grafted KF Fibers

[Figure 6: see original paper] shows the wide-angle X-ray diffraction patterns of KF fibers, with crystalline parameters listed in . The results demonstrate that KF fibers possess a two-phase crystalline-amorphous structure. Comparison of lattice parameters before and after modification reveals minimal changes, indicating that the enzyme-mediated grafting modification technique does not affect the internal crystal structure of KF fibers and that the overall lattice structure remains unchanged during enzyme grafting [12]. However, the degree of crystallinity decreases after modification, likely because changes in surface functional groups after enzyme grafting alter the overall crystallinity of the carbon fiber.

To directly observe the effect of enzyme grafting on mechanical properties, changes in single-fiber tensile strength before and after modification were examined. As shown in [Figure 7: see original paper], the average breaking strength of KF fiber monofilaments decreases slightly after grafting, confirming that the reduced crystallinity after grafting leads to decreased overall fiber strength.

### 2.4 Thermal Properties of Enzyme-catalyzed Grafted KF Fibers

[Figure 8: see original paper] presents the TG and DTG curves of KF and PAGE-grafted KF fibers, with corresponding thermal parameters including initial decomposition temperature ( $T_{di}$ ), maximum decomposition temperature ( $T_{max}$ ), and char yield ( $Y_c$ ) listed in . Compared with unmodified KF fibers, the enzyme-grafted fibers show a slight decrease in  $T_{di}$ , while  $T_{max}$  decreases from 565.4°C to 560.3°C. This indicates that the thermal properties decrease slightly after grafting, but the overall thermal performance of aramid fibers remains preserved. Additionally, the decrease in thermal temperature correlates with the degree of polymer grafting on the fiber surface. Greater polymer grafting leads to a larger decrease in  $T_{max}$ , resulting in lower  $Y_c$  values for modified fibers.

### 2.5 Wettability of Enzyme-catalyzed Grafted KF Fibers

Contact angle and surface free energy are the most typical evaluation indicators for interfacial wetting performance. The contact angles and surface free energies of KF fibers after enzyme-catalyzed grafting are listed in . Untreated KF fibers exhibit large contact angles with both deionized water and ethylene glycol, indicating poor wettability with both strongly and weakly polar solvents. After enzyme grafting, the contact angles with both solvents decrease significantly, demonstrating improved wettability. The primary reasons for enhanced surface wetting performance are increased surface roughness and introduction of polar functional groups. Additionally, because the introduced functional groups are hydrophilic, the decrease in contact angle with water is more pronounced than that with ethylene glycol.

Surface free energy ( $\gamma$ ) consists of polar ( $\gamma_p$ ) and non-polar ( $\gamma_n$ ) components. The surface free energy data for KF fibers before and after enzyme-mediated grafting modification are shown in . The surface free energy of modified fibers increases significantly compared to KF fibers, with KF-0.03 reaching 29.3 mN/m, approximately 1.3 times that of KF. The main reasons are: first, the introduced PAGE helps overcome the liquid surface tension, enabling easier spreading on the fiber surface. Second, compared with KF, the surface free energy of PAGE-grafted KF shows a significant increase in the polar component ( $\gamma_p$ ) and a decrease in the non-polar component ( $\gamma_n$ ), indicating that the increase in surface free energy primarily originates from contributions of the polar component ( $\gamma_p$ ). The increase in polar component ( $\gamma_p$ ) results from the introduction of numerous polar functional groups onto the fiber surface [13].

### 2.6 Interface Bonding Strength of Enzyme-catalyzed Grafted KF Fibers

As shown in [Figure 9: see original paper], the interfacial bonding strength of the KF/CE system increases with enzyme concentration. When the enzyme concentration reaches 0.03 mg/ml, the IFSS increases by 20.8% compared to unmodified fibers. This enhancement likely results from two factors: first, increased surface roughness and specific surface area increase the pull-out force and pull-out energy; second, chemical reactions strengthen the bonding system, as cyanate ester reacts with AGE epoxy groups to form chemical crosslinks that enhance interfacial strength, with the reaction scheme shown in ESI†(2) [14, 15].

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## 3. Conclusion

Using AGE as monomer and HRP as catalyst in a reverse microemulsion system enables surface modification of aramid fibers. The bioenzyme can effectively catalyze grafting reactions on fibers, with enzyme concentration affecting the monomer grafting degree. As enzyme concentration increases, numerous hydrophilic polar functional groups are introduced onto the fiber surface, leading to increased surface roughness and polar functional group content, decreased contact angles with deionized water and ethylene glycol, and enhanced surface free energy. Simultaneously, the crystal structure remains unchanged after grafting, preserving the original thermal and mechanical properties of the fibers.

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