

Structural Regulation and High-temperature Thermo-oxidative Aging Behavior of Quartz Fiber/Thermoplastic Polyimide Composites

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Electronic Supplementary Information

Abstract Thermoplastic polyimide serves as a promising high-performance polymer matrix for fiber-reinforced composites, yet its high melt viscosity severely impairs fiber wetting and filler dispersion, limiting the high-temperature service performance. In this work, we propose and validate a universal and controllable fabrication strategy using quartz fibers and a pyromellitic dianhydride/4,4'-oxydianiline (PMDA/ODA)-type polyimide as a model system. Our approach involves significantly diluting the poly(amic acid) (PAA) solution to reduce viscosity and improve fiber wetting, combined with the intercalation of PAA films to enhance laminar interlaminar adhesion within prepreg. Cross-sectional scanning electron microscopy (SEM) reveals a dense, defect-free microstructure with no evidence of voids or delamination. Following thermal aging at 300 °C for 504 h, the composite exhibit no macroscopic damage and retain 70%–75% of their initial mechanical properties. To achieve high filler loading, multi-walled carbon nanotube (MWCNT)/Fe₃O₄ (at a weight ratio of polyimide (PI):MWCNT:Fe₃O₄=10:1:5) are pre-dispersed in pure solvent, resulting in excellent microwave absorption ($RL_{\min} = -55.07$ dB, EAB=1.9 GHz at 1.5 mm) alongside high thermal stability. The process method allows precise control over composite thickness and resin distribution by adjusting the number of prepreg layers and the amount and placement of PAA film. This study demonstrates that thermoplastic polyimide can act as a high-performance polymer matrix, enabling advanced fiber-reinforced composites with exceptional long-term thermo-oxidative stability for harsh high-temperature polymer composite applications.

Keywords Thermoplastic polyimide; Fiber-reinforced composite; Process; Microwave absorption; Thermal aging

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INTRODUCTION

Fiber-reinforced polymer composites (FRPC) have drawn extensive attention owing to their low density and superior mechanical performance, which endow them with great potential for advanced high-temperature service scenarios.^[1–5] Nevertheless, severe thermo-oxidative aging and structural failure easily occur in common resin matrices at long-term temperatures above 300 °C, greatly restricting their high-temperature application in harsh thermal environments. Therefore, it is essential to develop high-performance polymer matrices with intrinsic high-tem-

perature resistance and structural stability for next-generation fiber-reinforced composite systems.^[6–8]

Polyimides (PI) are a class of high-performance engineering polymers with rigid molecular chain backbones, excellent thermal stability, and inherent thermo-oxidative resistance.^[9,10] When reinforced with quartz fibers (QF), which offer inherent high-temperature resistance and load-bearing capacity, quartz fiber-reinforced thermosetting PI composites (QFRTSC) have become ubiquitous in critical aerospace structures.^[11–15] A common manufacturing technique is prepreg technology, which involves uniformly impregnating fibers or fabrics with a varnish containing prepolymers dissolved in a solvent, followed by hot pressing.^[16–18] Despite these advances, the aerospace industry, led by giants such as Boeing and Airbus, is accelerating its transition toward thermoplastic composites. This shift is driven by their superior manufacturing efficiency, structural performance, opera-

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tional maintainability, and sustainability compared with traditional thermosets.^[19–22] However, translating these advantages to fiber-reinforced thermoplastic PI composites (FR-TPI) remains challenging due to inherent processing limitations. The rigid chain structure of high-performance thermoplastic polyimides inevitably leads to extremely high melt viscosity and poor solution solubility, creating a fundamental polymer-derived processing dilemma for fabricating high-performance FRPC. Intensive efforts have been devoted to developing novel polyimide materials, including commercial TPIs, such as amorphous LARC-TPI ($T_g \approx 250^\circ\text{C}$), ULTEM® ($T_g \approx 217^\circ\text{C}$), and semi-crystalline Aurum® ($T_g \approx 250^\circ\text{C}$), which are achieved, however, at the expense of the intrinsic high-temperature stability of polyimides.^[23–25] Therefore, the development of fiber-reinforced thermoplastic polyimide composites, particularly a universal processing route suitable for high- T_g thermoplastic polyimides, is urgently required.

The synthesis of thermoplastic polyimides typically follows a two-step process: polymerization of diamine and dianhydride monomers to form a viscous poly(amic acid) (PAA) solution, followed by thermal imidization after solvent removal.^[26–28] Compared with conventional prepreg resin systems that exhibit low viscosity (100–1000 mPa·s), PAA solutions display extremely high viscosity (e.g., 5×10^4 – 8×10^4 mPa·s for commercial grades) because of their ultrahigh molecular weight (typically tens to hundreds of thousands) and rigid molecular chains. This high viscosity presents two critical hurdles for the fabrication of prepreps. First, it impedes uniform resin impregnation into the fiber bed and the homogeneous dispersion of functional fillers, leading to poor batch consistency and compromised performance.^[14] Second, the low solid content of the PAA solution (typically about 15 wt%) results in insufficient resin coverage on the fibers, hindering the direct bonding between the prepreg layers during hot pressing. Consequently, there is an urgent need to develop a novel FR-TPI prepreg and associated fabrication technology that ensures complete fiber impregnation, uniform filler dispersion, precise resin content control, and robust interlaminar bonding.

Herein, we propose an innovative fabrication strategy involving solvent dilution, filler prewetting, and film insertion to address these challenges. Specifically, (1) the viscosity of the PAA solution was significantly reduced by solvent dilution to overcome poor fiber wetting. (2) To reduce the viscosity, functional fillers were pre-wetted with a solvent prior to addition to the PAA solution, ensuring uniform dispersion. (3) To compensate for the reduced solid content (which otherwise hinders bonding) and to control the resin distribution, a neat PAA film was inserted between the prepreg layers. This design enhances the interlaminar adhesion while preventing delamination, as the film and prepreg share identical chemical compositions, ensuring excellent interfacial compatibility after hot pressing. Furthermore, the film insertion approach effectively addresses the problem of extremely high melt viscosity of polyimide.

In this study, QFR-TPI composites were fabricated using a classic Kapton-type PMDA/ODA polyimide matrix, a well-established benchmark in the polyimide family, along with QF and common microwave-absorbing fillers (MWCNT and

Fe_3O_4). A significantly diluted PAA solution was employed for two purposes: thoroughly impregnating QF to produce QF/PI prepreps with uniform resin distribution and casting PAA films. The prepreps and films were alternately stacked and subsequently vacuum hot-pressed to obtain QF/PI composites with a controllable resin content and distribution. The composite materials were thermally aged for 5, 20, 168, or 504 h. After aging, the morphology and mechanical performance of the composites were comprehensively characterized and analyzed at different aging intervals. The same procedure was followed for the QF/PI@MWCNT+ Fe_3O_4 composites; the only difference was the addition of pre-wetted fillers to the diluted PAA solution to form the PAA@MWCNT+ Fe_3O_4 solutions. Similarly, the morphology, mechanical properties, dielectric properties, and microwave absorption characteristics of these composites were systematically evaluated and discussed as a function of thermal aging duration. Notably, this proposed fabrication strategy has also been successfully extended to other polyimide systems, further verifying its versatility and robustness.

EXPERIMENTAL

The experimental details are included in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Preparation of QF/PI Composites

Fig. 1(a) illustrates the preparation process of the QF/PI composite. Initially, a highly viscous PAA solution with a solid content of 20 wt% was prepared to ensure the formation of a high-molecular-weight PI. Gel permeation chromatography (GPC) was employed to verify successful polymerization, revealing a number-average molecular weight (M_n) of approximately 108 kg/mol (Table S1 in ESI) for the resulting PAA. To optimize the processability for fiber impregnation and film casting, the PAA solution was diluted with DMF to achieve a dynamic viscosity (η) of 946.4 cP.^[29] Using the blade coating technique, the diluted PAA solution was cast into a freestanding film. Concurrently, the QF was thoroughly impregnated with the same PAA solution *via* a prepreg preparation process, yielding a QF/PAA prepreg with exceptional uniformity, flexibility, and processability. Notably, the prepreg exhibited self-adhesive properties and could be peeled without damage at room temperature, allowing for error correction during the layup process. In contrast to commercial PAA solutions, which typically possess high viscosity ($\eta \approx 6 \times 10^4$ – 7×10^4 mPa·s), the diluted PAA solution offers lower viscosity and improved flowability, thereby facilitating fiber wetting and impregnation. Furthermore, the residual solvent content was controlled at approximately 3 wt% in the prepreg and 15 wt% in the PAA film, which effectively guaranteed a favorable resin flow during the hot-pressing stage (Fig. S2 in ESI). For the prepreg, an excessively low residual solvent would impair resin fluidity, while an overly high solvent content could not be fully removed during hot pressing and eventually carbonized, deteriorating the mechanical properties of the final composite plate. As for the PAA film, further reduction of the solvent content requires prolonged high-temperature treatment, which makes the film overly brittle and difficult for subsequent pro-

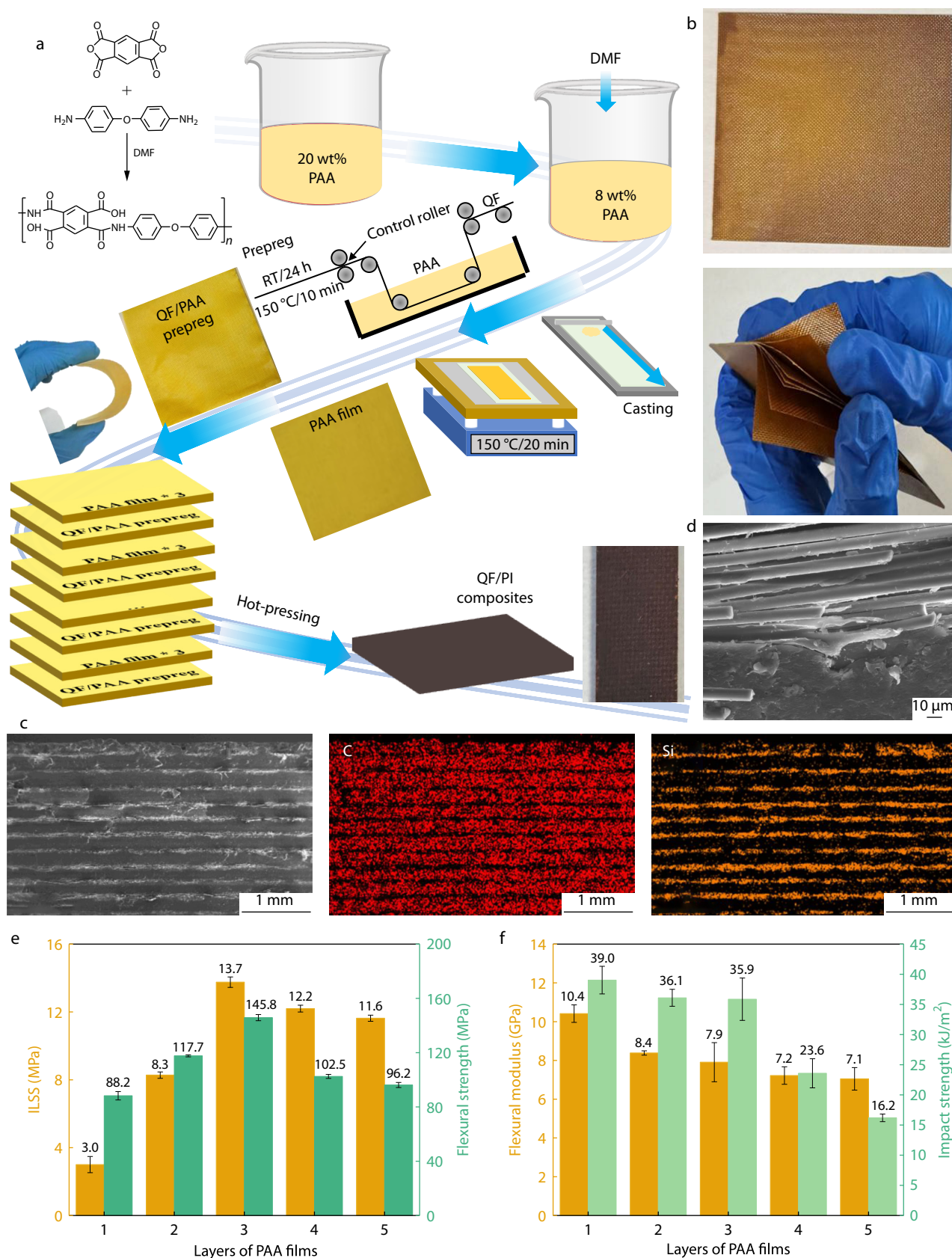


Fig. 1 QP composites: (a) schematic illustration of the preparation process, (b) schematic diagram of conventional processing routes, (c, d) SEM and EDS image, (e, f) mechanical properties.

cessing. Finally, the prepregs and films were stacked and thermally cured under the conditions shown in Fig. 1(a) and Fig. S1 (in ESI) to fabricate composites with controllable resin contents.

The density of the QF/PI composite, measured via the Archimedes method, was approximately 1.49 g/cm^3 , which is comparable to typical values reported for similar high-performance composites.^[14] In contrast, conventional processing routes applied to fiber-reinforced thermoplastic polyimide composites often lead to insufficient densification and poor interlayer adhesion, highlighting the advantages of the present approach (Fig. 1b). The cross-sectional SEM and EDS images (Fig. 1c) revealed a dense, defect-free microstructure with no voids or delamination. High-magnification analysis (Fig. 1d) further indicated that, while the resin fully infiltrated the interstitial spaces between the quartz fiber bundles, minimal resin adhered to the individual fiber surfaces. This phenomenon is primarily attributed to the inherent surface inertia of both the PMDA/ODA matrix and the QF.^[30–34] Consequently, this specific microstructure impedes efficient stress transfer across the fiber-resin-fiber interface, leading to reduced mechanical properties.

QF/PI composites with varying resin content were successfully prepared by inserting different numbers of PAA films, and their mechanical properties were systematically characterized. As shown in the Figs. 1(e), 1(f) and Fig. S3 (in ESI), with a gradual increase in the resin content (RC) within the laminates, the interlaminar shear strength (ILSS) and flexural strength showed a trend of first increased and then decreased. Specifically, when one layer of the PAA film was inserted, the low RC led to the easy formation of pores within the composite, resulting in an ILSS of only 3.0 MPa (Fig. S4 in ESI). As the number of inserted PAA films increased, the resin content of the laminates also increased. When three layers of PAA film were inserted, the internal structure of the composite reached a dense state, and a maximum ILSS of 13.7 MPa was achieved. When the number of inserted PAA films was further increased, the resin content increased and the ILSS became dominated by the PI matrix. Because the shear strength of the PI matrix itself is much lower than that of QF, the excessive resin promotes interlayer sliding, causing a slight decrease in the ILSS. The flexural strength exhibited the same trend as that of ILSS.

The flexural strength followed the same trend as that of the ILSS, and the underlying reasons were consistent. At a low resin content, the QF could not be effectively coated or fixed by the PI matrix, making the fibers prone to dislocation under the applied load, which resulted in low flexural strength. As the resin content increased, the QF was gradually and uniformly coated, the interface bonding improved, and the flexural strength increased accordingly. When the resin content increased, the overall rigidity of the composite material decreased, leading to a slight reduction in the flexural strength. In contrast, the flexural modulus is governed primarily by the fibers, and the modulus of the QF is much higher than that of the PI matrix. Therefore, a higher resin content leads to a lower flexural modulus in the QF/PI composite. In addition, owing to the inherent brittleness of the PI matrix, the impact strength of the composite gradually decreased with increasing resin content. This is likely because the excessive resin

tends to fracture in a brittle manner and cannot dissipate energy efficiently under impact.^[35–37] Taking all these factors into consideration, a sample with three layers of inserted PAA films was selected as the representative case for further experiments.

Thermal Aging of QF/PI Composites

The surface morphology of the composite after thermal aging at 300°C for different time intervals is shown in Fig. 2(a). Even after 504 h of aging, no significant degradation or morphological damage is observed. These results demonstrated the robust thermal stability of the composites at elevated temperatures.

FTIR spectroscopy was used to characterize the chemical structural evolution of the QF/PI composites during thermal aging at 300°C . The successful synthesis of the PI matrix was confirmed by the characteristic absorption bands observed in Fig. 2(b) and Fig. S5 (in ESI), including the imide carbonyl ($\text{C}=\text{O}$) stretching vibrations at 1777 and 1713 cm^{-1} and the $\text{C}-\text{N}$ stretching mode at 1364 cm^{-1} . Additionally, the bands at 1500 and 1245 cm^{-1} were assigned to the benzene ring ($-\text{Ph}$) and ether bond ($\text{C}-\text{O}-\text{C}$) from ODA, respectively.^[38] Notably, the FTIR spectra of the composites remained largely unchanged throughout the aging process, with no new characteristic peaks emerging. This indicates the absence of significant chemical degradation or the formation of new chemical species, demonstrating the exceptional chemical stability of the PI matrix under the investigated thermal conditions. This finding was consistent with the TGA results, in which $T_{d5\%}$ and $T_{d10\%}$ remained essentially unchanged during aging, further confirming the thermal stability of the material (Fig. 2c).

To further elucidate the subtle structural changes, the peak intensities at 1713 , 1500 , 1364 , and 1245 cm^{-1} were selected for quantitative comparative analysis, as summarized in Table 1. First, the $\text{C}-\text{N}$ bond peak intensity in the QP504 sample exhibits an overall upward trend, reaching 1.61 times that of the QP0 sample. This increase was primarily attributed to secondary imidization reactions involving trace residual PAA chains within the PI film. Notably, the DSC analysis (Fig. 2d) corroborates this mechanism, as it demonstrates a gradual increase in the glass transition temperature (T_g) of the composite with prolonged aging time, which is consistent with the enhanced chain rigidity and reduced chain mobility resulting from secondary imidization. Previous studies have shown that even commercially available PI films with a high degree of imidization may retain small amounts of uncyclized PAA because of factors such as the film thickness or rapid thermal processing.^[39,40] Under high-temperature aging conditions (300°C), these residual PAA chains likely undergo further dehydration and cyclization, forming additional imide rings, thereby enhancing the FTIR signals of both $\text{C}-\text{N}$ and $\text{C}=\text{O}$ bonds.^[41]

Interestingly, the $\text{C}=\text{O}$ peak intensity showed a slightly more pronounced increase, reaching 1.65 of that of the QP0 sample. While part of this increase can be explained by the same secondary imidization mechanism, the higher magnitude suggests an additional contribution from the surface oxidation. Specifically, the composite surface may react with oxygen in air, forming new carbonyl-containing groups such as carboxylic acids, ketones, and aldehydes.^[41,42] In contrast, the intensity of the $\text{C}-\text{O}-\text{C}$ peak showed a minimal change

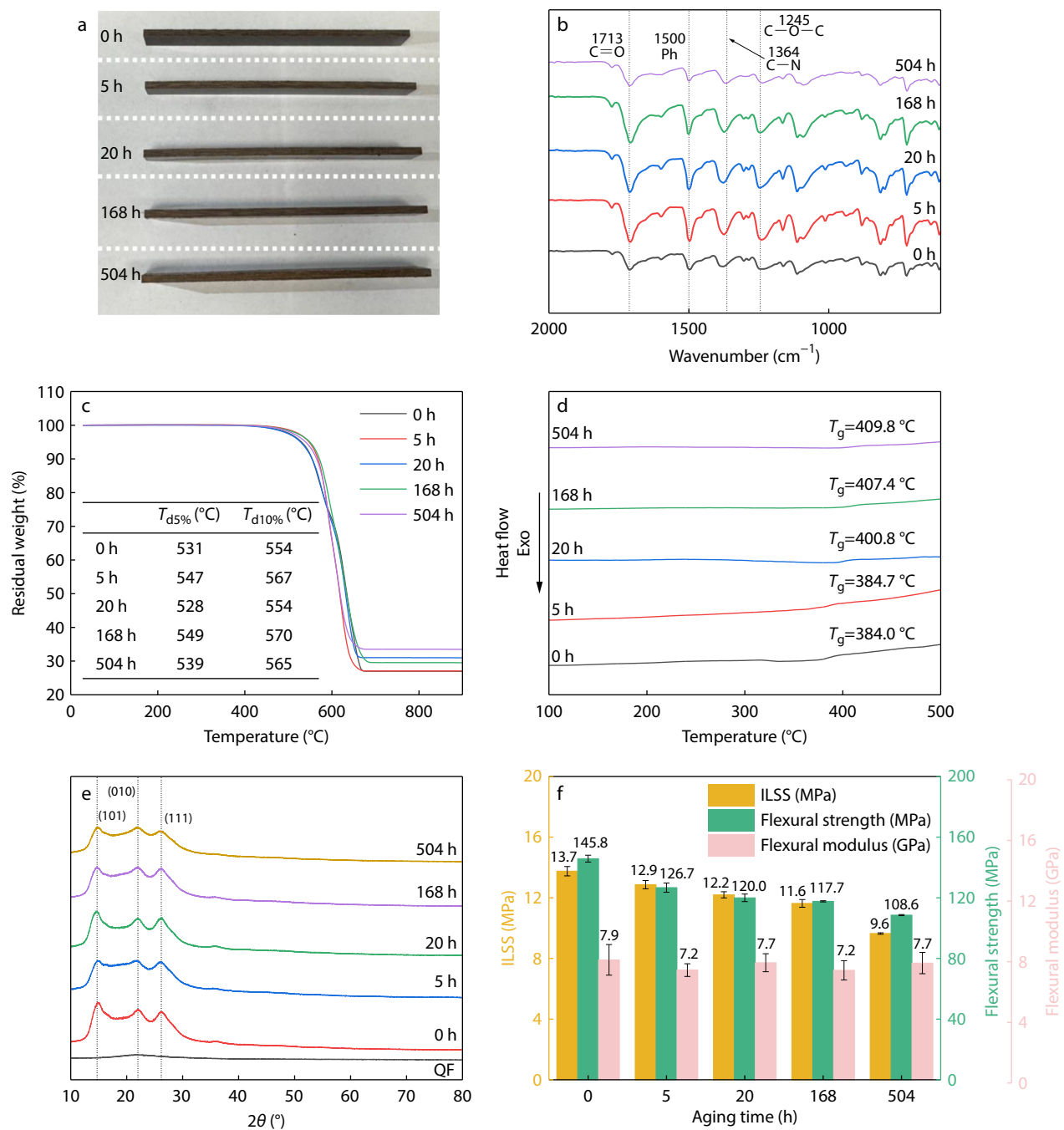


Fig. 2 QP composites after thermal aging: (a) digital photos, (b) FTIR spectra, (c) TGA thermograms, (d) DSC thermograms, (e) XRD patterns, (f) mechanical properties.

Table 1 FTIR peak area and mechanical properties variations of QP composites during thermal aging.

	$A_{1713\text{ cm}^{-1}}$	$A_{1500\text{ cm}^{-1}}$	$A_{1364\text{ cm}^{-1}}$	$A_{1245\text{ cm}^{-1}}$	$A_{1713\text{ cm}^{-1}}/A_{1500\text{ cm}^{-1}}$	$A_{1364\text{ cm}^{-1}}/A_{1500\text{ cm}^{-1}}$	$A_{1245\text{ cm}^{-1}}/A_{1500\text{ cm}^{-1}}$	ILSS (MPa)	Flexural strength (MPa)	Flexural modulus (GPa)
QP0	5.49	4.18	3.02	3.82	1.31	0.72	0.70	13.7	145.8	7.9
QP5	15.02	9.46	8.33	10.59	1.59	0.88	0.70	12.9	126.7	7.2
QP20	12.67	8.33	7.06	8.76	1.52	0.85	0.69	12.2	120.0	7.7
QP168	15.43	7.98	8.49	7.07	1.93	1.06	0.46	11.6	117.7	7.2
QP504	6.23	2.89	3.35	2.72	2.16	1.16	0.44	9.6	108.6	7.7

during the initial 20 h, decreased significantly between 20 and 168 h, and then plateaued. Ultimately, the intensity in the

QP504 sample was only 63% of that in the QP0. This trend indicates that the thermal oxidation of ether bonds was most

active between 20 and 168 h, as the composite surface initially exhibited high reactivity toward oxygen. After 168 h, the formation of a dense surface oxide layer creates a barrier that impedes further oxygen diffusion, thereby stabilizing the concentration of ether bonds.

Fig. S6 (in ESI) shows the XPS spectra of the QP composite after different thermal aging times. The deconvoluted C 1s spectrum revealed four distinct peaks, assigned to the C—C (284.8 eV), C—N (285.9 eV), C—O (286.6 eV), and C=O (288.8 eV) bonds.^[43,44] In good agreement with the ATR-FTIR results, XPS analysis confirmed that no new characteristic peaks emerged during the thermal aging process.

XRD analysis was conducted to further elucidate the microstructural evolution. As shown in Fig. 2(e), annealing the QP composite at 400 °C (near its T_g) induced crystallization, as evidenced by the emergence of three new diffraction peaks at 14°, 22°, and 26°. These peaks correspond to the monoclinic pseudo-orthorhombic PMDA-ODA lattice with (101), (010), and (111) crystal planes, respectively.^[45,46] Throughout the aging process, the positions of these crystalline peaks remained unchanged, indicating the absence of a new phase formation. This finding is consistent with the conclusions drawn from FTIR and XPS analyses.

Fig. 2(f), Fig. S7 (in ESI) and Table 1 present the ILSS and flexural properties of the QP composites after exposure to 300 °C. Before aging, the QP composites exhibited an ILSS of 13.7 MPa, flexural strength of 145.8 MPa, and flexural modulus of 7.9 GPa. These values are relatively low compared to those of other fiber-reinforced thermoset polyimide composites. Because the ILSS and flexural properties are primarily matrix-dependent, they are significantly influenced by the interfacial adhesion between the fibers and matrix. Both QF and the PMDA/ODA matrix possess low surface energy which hinders effective interfacial bonding.^[30–34] This impedes efficient stress transfer at the fiber-matrix interface, leading to diminished mechanical performance and rendering laminates prone to shear failure under relatively low applied loads.

Thermal aging significantly affected the mechanical properties of the composites (Fig. 3a). As shown in Fig. 2(f), the material degradation progressed with an extended aging duration. After 504 h of aging, the ILSS and flexural strength of the QP composites decreased by 29.9% and 25.5%, respectively, whereas the flexural modulus remained nearly unchanged. This indicates that the material retained satisfactory mechanical integrity even after thermal aging at 300 °C for 504 h. During prolonged thermal aging, the matrix underwent oxidative decomposition upon exposure to oxygen (Fig. 3), leading to the formation of voids within the composite. This exacerbates the interfacial defects between the fiber reinforcement and the matrix, compromising the overall performance of the composite and ultimately degrading its mechanical properties.^[47] Concurrently, mechanical stresses accumulate at the interface during thermal ageing. As the aging time increased, these stresses built up continuously, ultimately triggering interfacial failure and subsequent composite failure.

In summary, prolonged thermal aging induces molecular chain scission and structural damage within the material, which manifests as a decline in macroscopic mechanical

properties. However, the flexural modulus remained virtually unchanged, because the overall structure of the composite remained intact during aging. Specifically, the matrix retained its glassy state, with the molecular segments frozen and unable to slip. Even though microcracks may form within the matrix, they are typically discrete and insufficient in number to significantly reduce the overall density or continuity of the material.

Preparation of QF/PI@MWCNT+Fe₃O₄ Composites

To demonstrate the viability of this process even with the incorporation of fillers, particularly at high loading levels, multi-walled carbon nanotubes (MWCNTs) and Fe₃O₄ were selected as functional additives, as both are commonly used in microwave-absorbing materials. To this end, the filler loading was significantly increased (PI:MWCNT:Fe₃O₄=10:1:5) compared to conventional microwave-absorbing materials used to prepare QPMF composite materials.^[48–50] The preparation method is largely identical to that of the QP composites, with the key difference being that the fillers are first dispersed in a pure solvent (Fig. 4a). This filler dispersion was then added to the high-viscosity PAA solution, which not only diluted the PAA, but also ensured better compatibility and processability. Cross-sectional SEM and EDS images of the QPMF composite (Fig. 4b) confirm a dense, defect-free structure without any visible voids or delamination, validating the effectiveness of the proposed dispersion strategy.

Fig. S8 (in ESI) presents the relative complex permittivity and permeability of the QP and QPMF composites within the 2–18 GHz frequency range. Compared to the QP composite, the incorporation of MWCNTs and Fe₃O₄ significantly enhanced both the relative complex permittivity and permeability of the QPMF, which in turn contributed to a substantial improvement in its microwave absorption performance. To evaluate the microwave absorption capability of the composites, the reflection loss (RL) values were calculated based on transmission line theory as Eqs. (1) and (2):

$$RL = 20 \lg \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (1)$$

$$Z_{in} = Z_0 \left(\frac{\mu_r}{\epsilon_r} \right)^{\frac{1}{2}} \tanh \left[j \left(\frac{2\pi f d}{c} \right) (\mu_r \epsilon_r)^{\frac{1}{2}} \right] \quad (2)$$

Here, Z_0 and Z_{in} represent the characteristic impedance of free space and the normalized input impedance of the samples, respectively; f is the microwave frequency; c is the speed of light in free space; ϵ_r is the relative complex permittivity ($\epsilon_r = \epsilon' - j\epsilon''$); μ_r is the relative complex permeability ($\mu_r = \mu' - j\mu''$); and d is the sample thickness. In practical applications, microwave-absorbing materials are generally required to absorb 90% of the incident microwaves, which corresponds to an RL value of less than -10 dB.

The electromagnetic wave absorption performance of the reference QP sample (Figs. 4c1–4e1) was found to be negligible, confirming its poor microwave absorption capability. For the QPMF composite (Fig. 4c2), at a thickness of 1.5 mm, the minimum reflection loss (RL_{min}) reaches -55.07 dB, with an effective absorption bandwidth (EAB) of 1.9 GHz. The Z_{in} value approached 1 (Fig. 4d2), indicating that the QPMF composite exhibited outstanding microwave-absorption characteristics. Additionally, when the absorber layer has an appropriate

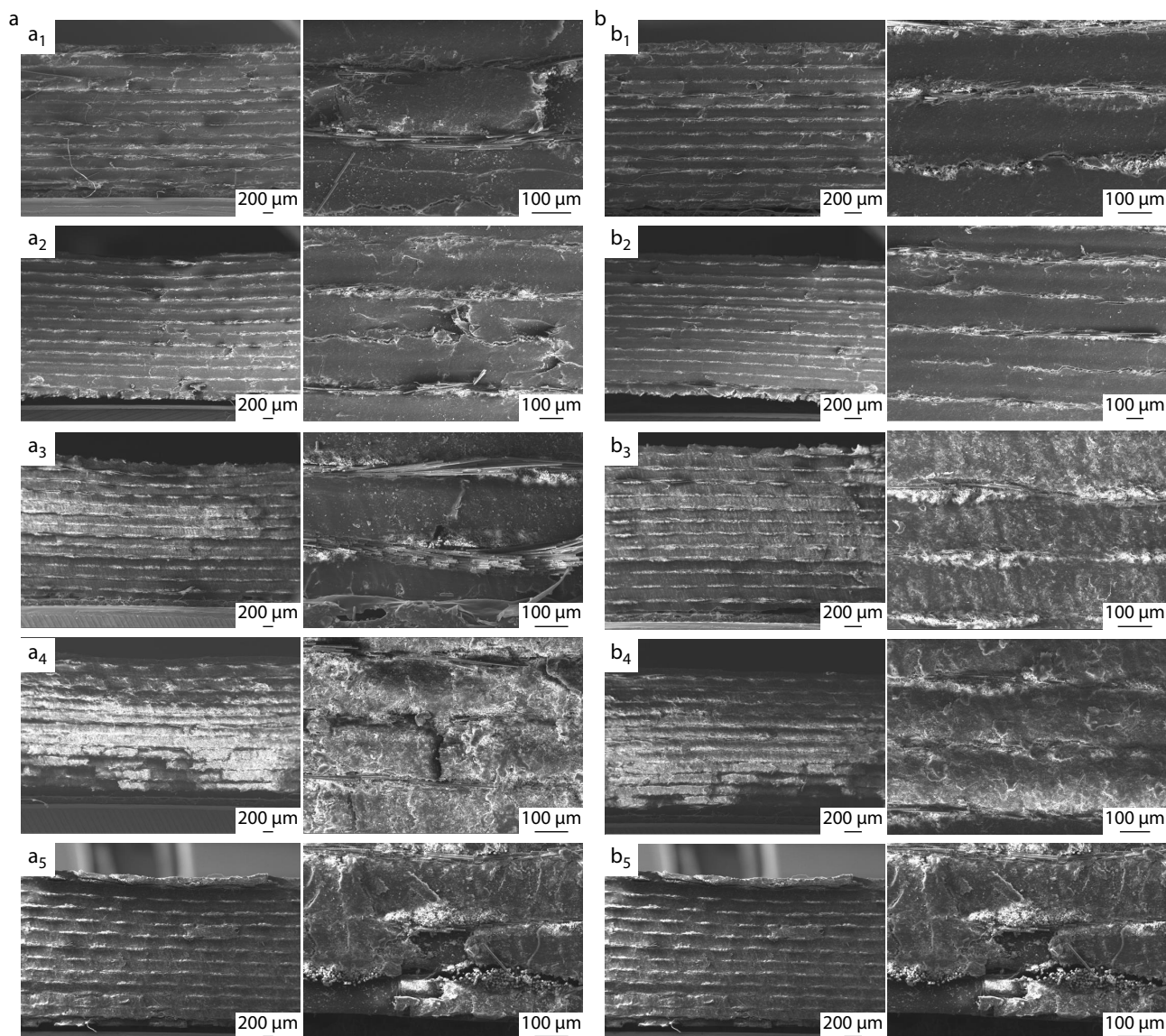


Fig. 3 (a) Fracture morphologies and (b) morphologies of QP composites after thermal aging: (a₁, b₁) 0 h; (a₂, b₂) 5 h; (a₃, b₃) 20 h; (a₄, b₄) 168 h; (a₅, b₅) 504 h.

thickness, specifically one-quarter of the incident wavelength, the phase difference between the incident wave at the air-absorber interface and the reflected wave at the absorber-metal interface is precisely 180° at the same frequency. Consequently, the electromagnetic wave (EMW) energies of the two components cancel each other out; this phenomenon is widely known as the quarter-wavelength cancellation model. This model enables an absorber layer with a specific thickness (t_m) to achieve minimal reflection at a specific EMW frequency (f_m). The mathematical relationship between t_m and f_m is described by the Eq. (3):

$$t_m = \frac{nc}{4f_m \sqrt{|\mu_r| |\epsilon_r|}} \quad (n = 1, 3, 5) \quad (3)$$

where f_m is the frequency corresponding to the $RL_{\min}$. Furthermore, the model reveals an inverse relationship between the peak frequency and absorber thickness. As shown in Fig. 4(e2), the 1.5 mm thick QPMF material precisely satisfied the quarter-

wave cancellation model. Additionally, after prolonged thermal aging at 300 °C, the surface morphology of the QPMF composite remained well preserved (Fig. 4f), with no significant degradation or structural damage observed. These findings demonstrated the excellent thermal stability of the composite under high-temperature conditions. For further details on the testing and characterization of the QPMF composite during thermal aging, please refer to Figs. S9–S11 (in ESI).

Universality

To verify the applicability of this preparation process to other polyimide systems, several common polyimide systems (BTDA/ODA, BPDA/MDA, and BPADA/TPE-Q) were selected, and their corresponding composites were fabricated using the aforementioned process. The curing temperature was adjusted based on the characteristics of each system. Specifically, BTDA/ODA and BPDA/MDA were cured at 350 °C for 60 min, while BPADA/TPE-Q was cured at 250 °C for 60 min. The cross-

sectional SEM images (Fig. 5) of these composites exhibited a dense, defect-free microstructure without visible voids or delamination, validating the suitability of this process for fabricating most thermoplastic polyimide composites. For the BTDA/ODA composite (Fig. 5a), the lay-up configuration was consistent with the PMDA/ODA system described in this work,

consisting of 12 prepreg layers and 39 adhesive film layers with a uniform distribution of both components. For the BPDA/MDA system (Fig. 5b), the composite was prepared with 9 prepreg layers and 30 adhesive film layers, which were also uniformly distributed. These results confirm that the preparation process proposed herein enables tailored control of the composite

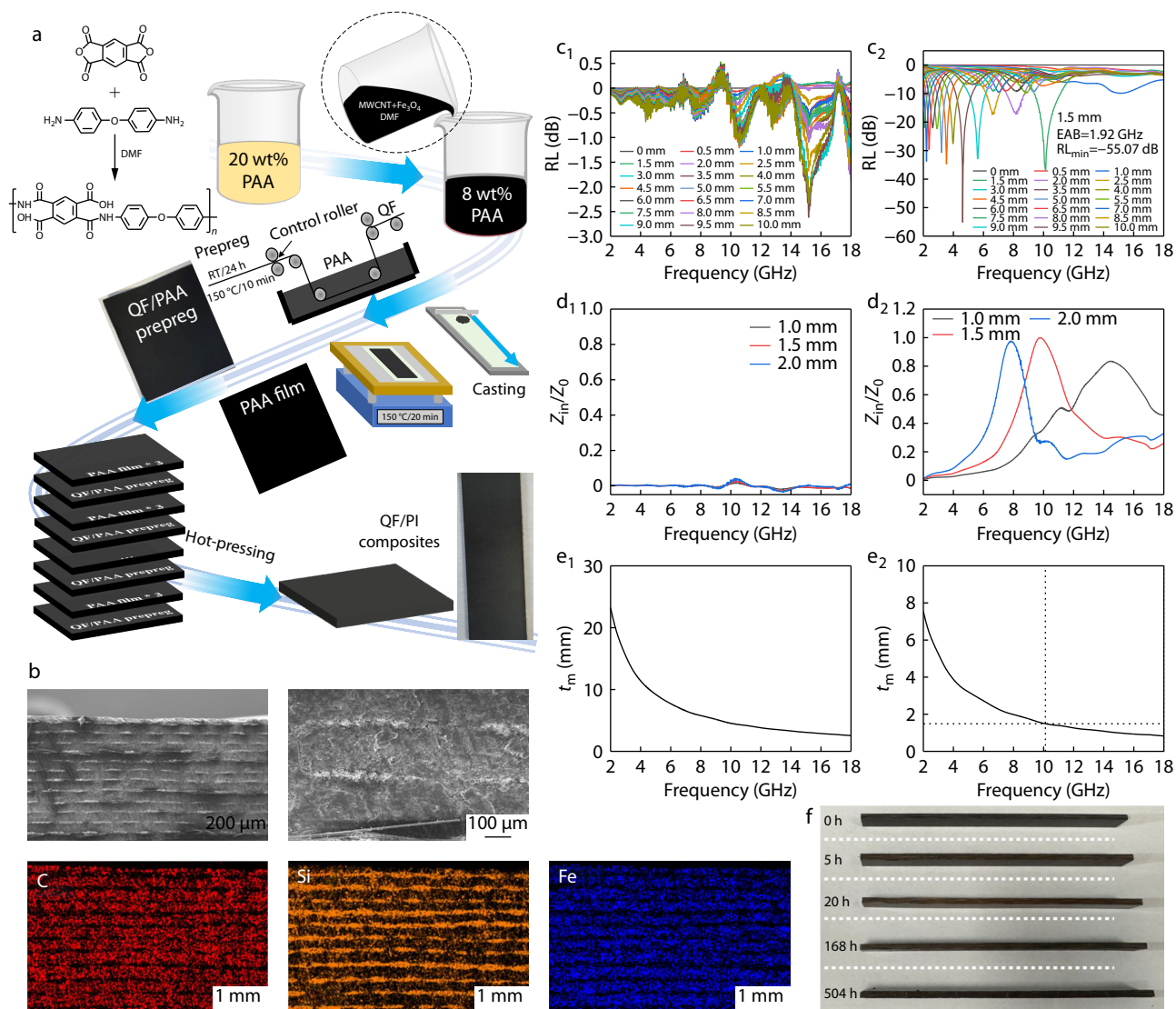
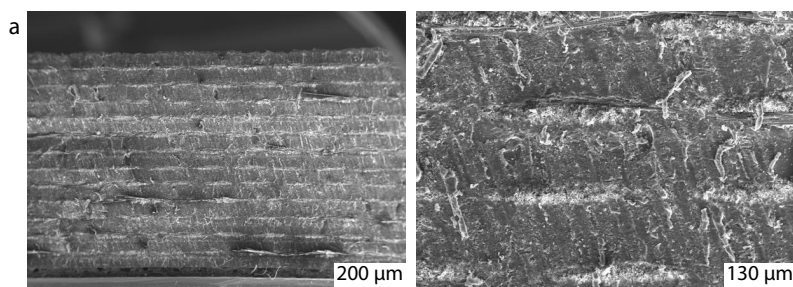


Fig. 4 (a) Schematic illustration of the preparation process of the QPMF composites; (b) SEM and EDS images of the QPMF composites; RL curves with different thicknesses of QP composites (c_1) and QPMF composites (c_2); Impedance matching characteristics values of QP composites (d_1) and QPMF composites (d_2); 1/4 Wavelength matching conditions of QP composites (e_1) and QPMF composites (e_2); (f) Digital photos of QPMF composites after thermal aging.



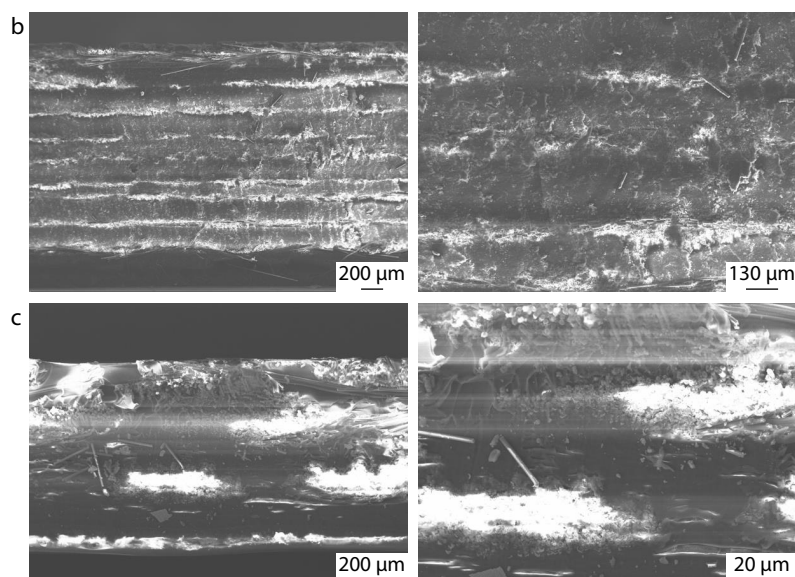


Fig. 5 Cross-sectional SEM images of quartz fiber-reinforced different polyimide composites: (a) BTDA/ODA, (b) BPDA/MDA, (c) BPADA/TPE-Q.

thickness by adjusting the number of prepregs and adhesive film layers as required. For the BPADA/TPE-Q system (Fig. 5c), the composite was constructed with three prepreg layers and 26 adhesive film layers in a non-uniform distribution, demonstrating that the process can also regulate the resin distribution within the composite by adjusting the distribution of adhesive film layers on demand. Owing to thickness limitations, only the ILSS of the BTDA/ODA composite was characterized, yielding a value of 41.44 MPa (Fig. S12 in ESI). This result further confirms that the inferior mechanical properties of the PMDA/ODA system originate from the low surface energy of its components, which impedes the interfacial adhesion.

CONCLUSIONS

This study proposed and validated a feasible preparation process for fiber-reinforced thermoplastic polyimide composites using quartz fibers and PMDA/ODA polyimide as model systems. The key design of this process is to significantly reduce the viscosity of the PAA solution, which inherently has a low solid content that hinders the prepreg preparation, thereby enhancing the fiber wetting efficiency. Subsequently, a PAA film intercalation method was employed to increase the resin content on both sides of the fibers, which in turn improved the interlaminar adhesion between the adjacent prepreg layers. Cross-sectional scanning electron microscopy (SEM) revealed a dense, defect-free microstructure devoid of voids or delamination. The thermal aging performance of QP composites was systematically investigated. After thermal aging at 300 °C for 504 h, the composites retained 70%–75% of their initial mechanical properties, with no macroscopic degradation or cracking observed. To validate the applicability of the process in fabricating functional composites, common microwave-absorbing fillers, MWCNT and Fe_3O_4 , were selected for incorporation. Another key design feature of this process involves dispersing the fillers in a pure solvent before adding them to a high-viscosity PAA solution, which ensures excellent compatibility and processability even at high filler loadings (PI:MWCNT: Fe_3O_4 =10:1:5). The resulting mi-

crowave-absorbing composite exhibited a dense, defect-free microstructure and outstanding microwave absorption performance ($\text{RL}_{\min}$ =−55.07 dB and EAB=1.9 GHz at a thickness of 1.5 mm), which is consistent with the quarter-wavelength absorber model, as well as high thermal stability. Furthermore, this preparation process yielded favorable results when extended to other thermoplastic polyimide systems, including BTDA/ODA, BPDA/MDA, and BPADA/TPE-Q. Notably, controllable composite thickness and resin distribution can be achieved by adjusting the number and distribution of the prepreg layers and adhesive film layers. Overall, this versatile preparation process provides a reliable technical pathway for the practical application of fiber-reinforced thermoplastic polyimides, facilitating their expansion into both structural and functional material fields.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3777-4>.

Data Availability Statement

Data supporting the findings of this study are available from the corresponding author upon reasonable request.

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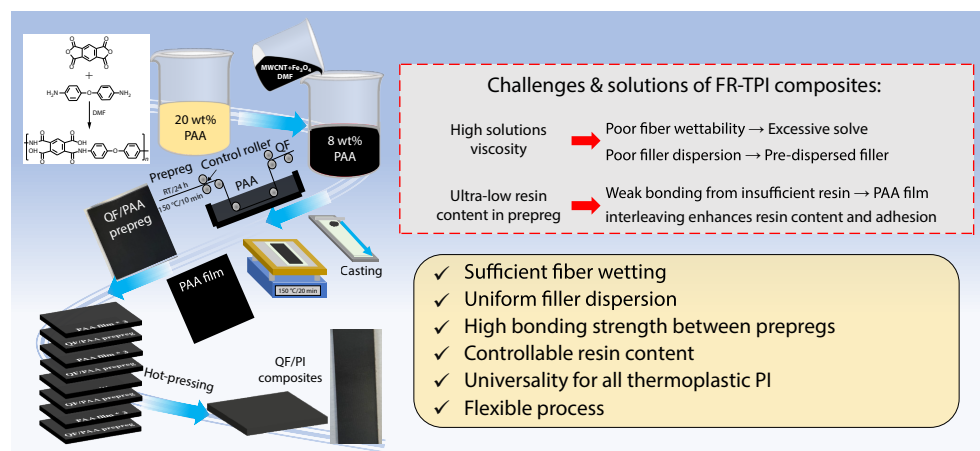
Graphical Abstract

Structural Regulation and High-temperature Thermo-oxidative Aging Behavior of Quartz Fiber/Thermoplastic Polyimide Composites

Xue-Yi Yu, Yue-Shu Gao, Liang-Hui Gong, Bin Wang, Chen-Yu Liu, Rui-Mei Xu, Wan-Juan Wang, Guo-Shan He, Ye Zhang, Xin-Zheng Huang, Run-Xin Bei, Si-Wei Liu, Ruo-Peng Liu, and Yi Zhan

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Fiber-reinforced thermoplastic polyimide composites exhibit poor fiber wettability and filler dispersion. This work proposes a facile process using diluted poly(amic acid) (PAA) and film intercalation to fabricate dense composites with excellent thermal stability, suitable for high-temperature aerospace applications.



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