DOI: 10.19884/j.1672-5220.202504014

Improved Interfacial Interaction of Carbon Fiber-Reinforced Polyamide 6 Composites by Sizing Agent of Blocked Isocyanate

DONG Fengyang, WANG Jindao, WANG Biao *
State Key Laboratory of Advanced Fiber Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

Abstract: To enhance the interfacial properties of carbon fiber (CF)-reinforced polyamide 6 (CF/PA6) composites, a novel blocked isocyanate (BI)/polyurethane (PU) sizing agent was prepared by dispersing BI in an aqueous PU emulsion. It was then applied to the CF surfaces for modification via a room-temperature sizing method. The results indicated that the BI/PU sizing layer significantly enhanced CF surface wettability, facilitating impregnation of PA6 resin onto fibers. With the increase in BI content, the interfacial shear strength (IFSS) of CF/PA6 composites was enhanced. The IFSS of the desized CF/PA6 composites was 46.8 MPa. When the sizing agent with a BI mass fraction of 3.0% was applied, the IFSS of the CF/PA6 composite reached 62.3 MPa, which represented an increase of 33.1% compared with that of the desized CF/PA6 composite. The proposed method offers an efficient and scalable surface modification strategy for high-performance thermoplastic composites.

Keywords: carbon fiber; sizing agent; blocked isocyanate; polyamide 6; interfacial shear strength
CLC number: TB33 **Document code**: A
Article ID: 1672-5220(2026)02-0059-06

Open Science Identity
(OSID)

0 Introduction

Carbon fiber (CF)-reinforced thermoplastic composites exhibit significant advantages, including excellent impact resistance, short molding cycles, and suitability for large-scale production, making them highly promising structural materials for aerospace and automotive applications[1-2]. Polyamide 6 (PA6) resin possesses high impact resistance and recyclability. Its high viscosity at processing temperatures hinders adequate impregnation onto the CF surface[3]. Furthermore, the inherent inertness of the CF surface results in weak interfacial interactions with PA6, limiting the application of CF-reinforced polyamide 6 (CF/PA6) composites in structural fields.

To address these challenges, surface modification of CFs is necessary. Current primary methods fall into two categories: changing the surface roughness and microstructure of CFs (namely, SR-MS modifying); introducing reactive functional groups onto CFs (namely, RFG grafting).

The SR-MS modifying method can produce the mechanical locking effect when it is combined with a resin matrix, so as to improve the interfacial properties of CF-reinforced composites[4]. Vautard et al.[5] formed a concave-convex structure of about 10 nm on the fiber surface after continuous vapor-phase thermochemical treatment of CFs. This enhanced the interfacial properties of the composite. Zhu et al.[6] deposited polyetherimide (PEI) nanoparticles on the surface of CFs by solvent evaporation. With the increase in PEI concentration, the size of PEI nanoparticles increased gradually. The presence of PEI nanoparticles could increase the specific surface area of CFs and enhance the mechanical linkage effect. Zhang et al.[7] introduced anhydride groups on the surface of CFs by plasma grafting polymerization. The modified CF surface was more hydrophilic, and the roughness increased, which enhanced the interaction between the fiber and resin. However, these methods often involve complex processes and offer limited precision in controlling interfacial properties.

RFG grafting methods can be used to introduce reactive functional groups (such as carbonyl, carboxyl, and hydroxyl) to enhance the wettability and chemical bonding between the fiber and resin. Li[8] significantly promoted the CF/PA6 interfacial interaction by oxidizing the CF surface with high-temperature ozone and increasing the carboxyl content. Chen et al.[9] successfully introduced carboxyl groups by treating CFs with nitric acid at 100 ℃, creating conditions for covalent polymer grafting and optimizing the interfacial properties. Nevertheless, these methods may reduce the fiber strength due to surface corrosion.

Consequently, developing methods that offer simple operation and efficiently enhance interfacial strength remains challenging. Compared to other techniques, sizing modification has proven to be the most convenient and effective strategy[10], as it can endow the CF surface

---

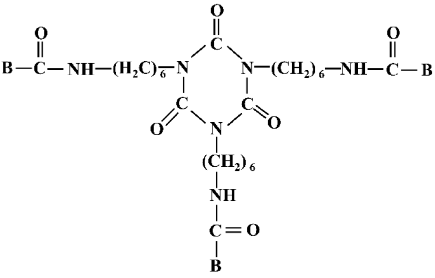
Received date: 2025-04-18

* Correspondence should be addressed to WANG Biao, email: wbiao2000@dhu.edu.cn

Citation: DONG F Y, WANG J D, WANG B. Improved interfacial interaction of carbon fiber-reinforced polyamide 6 composites by sizing agent of blocked isocyanate[J]. *Journal of Donghua University (English Edition)*, 2026, 43(2): 59-64.

with specific properties for different matrices and has the advantages of high design flexibility, low cost, and good implementation. Liu et al.[11] synthesized a modified epoxy emulsifier (MEE) as an aqueous epoxy sizing agent to treat the desized CFs. Surface grooves of CFs became shallow after being wrapped by the sizing agent, and the surface active groups increased. The epoxy groups improved the fiber wettability and formed chemical bonds, thus improving the interfacial interaction between the fiber and resin.

In this study, we dispersed a blocked isocyanate (BI), a latent cross-linking agent, into an aqueous polyurethane (PU) emulsion to prepare the BI/PU sizing agent. The chemical structure of BI is shown in Fig. 1. The active —NCO groups were designed to release from BI and react with active hydrogen atoms on both the CF and PA6, forming chemical crosslinks at the interface, thereby strengthening CF/PA6 interactions.



B— caprolactam blocked end.

Fig. 1 Chemical structure of BI

1 Materials and Methods

1.1 Materials

The CF (T700 SC PAN-based) was supplied by Toray Company, Japan. The CFs were desized in a desizing furnace at 500 ℃ before use. BI (Desmodur® BL3175) was purchased from Covestro Polymers (China) Co., Ltd. Its deblocking temperature is about 200 ℃. PA6 (Alphalon 27) was provided by Changzhou Polisen Plastics Technology Co., Ltd., China.

1.2 Modification of CFs

The desized CFs were modified via a room-temperature sizing method with an immersion time of 10 s. BI was dispersed into an aqueous PU emulsion to prepare the sizing agent. Due to the poor water solubility of BI, methyl ethyl ketone (MEK) was added as a dispersing aid to facilitate its uniform dispersion within the aqueous PU emulsion (a PU mass fraction of 3.0%). Four kinds of BI/PU sizing agents were prepared with the mass fractions of BI being 0.5%, 1.0%, 2.0% and 3.0%, respectively. The CFs were modified with the four sizing agents and dried at 80 ℃. The BI/PU-modified CF (BI/PU-CF) was denoted as BI0.5/PU-CF, BI1.0/PU-CF, BI2.0/PU-CF, and BI3.0/PU-CF, corresponding to the BI mass fractions of 0.5%, 1.0%, 2.0% and 3.0%, respectively. The desized CF (without BI/PU-modification) was designated as the control.

1.3 Characterizations

The scanning electron microscopy (SEM) images of each sample were recorded by using a Hitachi S-4800 instrument (Hitachi, Japan) at 5 kV. The Fourier transform infrared (FTIR) spectra were recorded by using a Nicolet 6700 FTIR spectrometer (Nicolet, USA) to analyze the chemical composition and reactions on the surface of each sample.

The schematic diagram of the test setup for interfacial shear strength (IFSS) and contact angle is shown in Fig. 2. The BI/PU-CF was first fixed in the center of the metal frame. Subsequently, the PA6 resin was heated to 280 ℃ until melting, and the molten PA6 microdroplets were then applied onto the BI/PU-CF. The samples were held at this temperature for 10 min and finally cooled naturally to room temperature to complete the preparation process. For the contact angle test, the length of the resin-embedded BI/PU-CF was controlled within a range of 30 to 50 μm. The tests were performed by using the HM410 composite interface tester (Toei Co., Ltd., Japan), as illustrated in Fig. 3. For each sample, 20 valid data points were collected and averaged to ensure the reliability of the results. The desized CF was tested as the control.

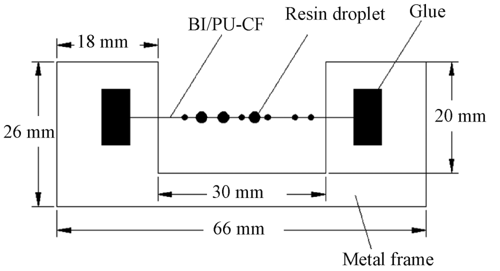


Fig. 2 Schematic diagram of test setup for IFSS and contact angle

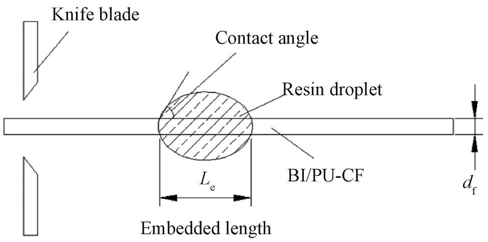


Fig. 3 Schematic diagram of IFSS and contact angle testing

During the IFSS measurements, the resin microdroplets on the CF surface were debonded by using a knife blade at a debonding speed of 1 μm/s. The IFSS was calculated as

$$I_{\mathrm{FSS}} = \frac{F_{\mathrm{m}}}{\pi d_{\mathrm{f}} L_{\mathrm{e}}}, \tag{1}$$

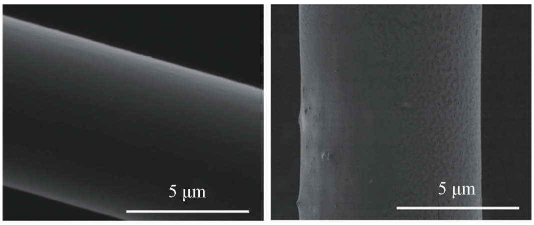
where I_{FSS} denotes the IFSS; F_{m} is the maximum tensile force; d_{f} is the CF diameter; L_{e} is the embedded length of the CF in the matrix. In this study, PA6 is the matrix.

For each sample, 20 valid specimens were tested, and the IFSS value was calculated as the average of the measurements.

2 Results and Discussion

2.1 IFSS of CF/PA6 composites

As shown in Fig. 4, the desized CF exhibits a smooth and groove-free surface with maintained fiber roundness, confirming that the treatment causes no structural damage or performance degradation. For BI/PU-CF, a uniform sizing layer forms on the CF surface, significantly enhancing surface roughness while achieving effective sizing coverage.



(a) (b)

Fig. 4 SEM images of different samples: (a) desized CF; (b) BI/PU-CF

The interfacial properties between CF and PA6 resin were evaluated through contact angle and IFSS tests. As depicted in Fig. 5, the contact angles of PA6 resin on BI/PU-CF surfaces exhibit a significant reduction compared to the desized CF. The contact angles decrease progressively with increasing BI mass fractions on the CF, from 49.6° (the desized CF) to 39.4° (BI3.0/PU-CF, a BI mass fraction of 3.0%), corresponding to a decrease of 20.6%. Owing to the favorable compatibility between BI and PA6 resin, BI functions as a latent cross-linking agent on CF surfaces to effectively improve interfacial wettability.

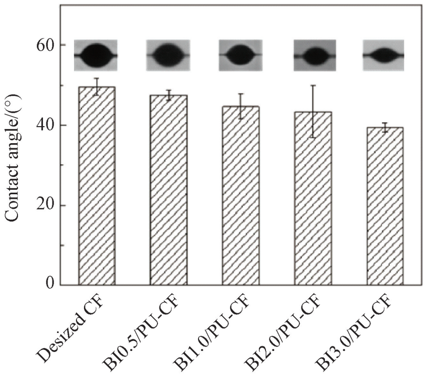


Fig. 5 Contact angles of PA6 resin on different CF samples

The micro-debond test was used to characterize the interfacial property between the CF and PA6 resin. As shown in Fig. 6, the IFSS increased progressively with the increase in BI mass fraction. At a BI mass fraction of 3.0%, IFSS reached 62.3 MPa, representing a 33.1% enhancement over the desized CF/PA6 systems (46.8 MPa). These results indicate that the released —NCO groups from BI during high-temperature processing enhance the interfacial property between the CF and PA6 resin.

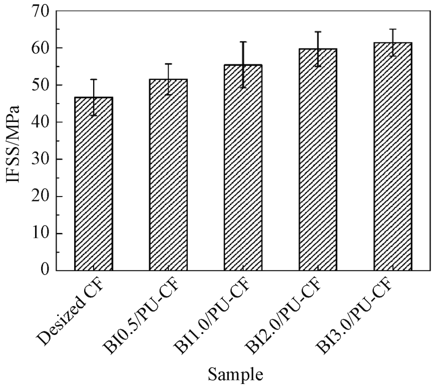
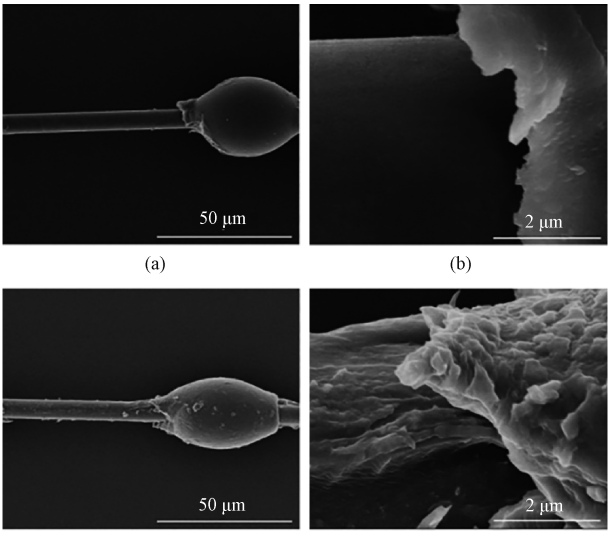


Fig. 6 IFSS of CF/PA6 for different CF samples

The fracture morphologies of CF surfaces after debonding from the matrix were characterized by SEM (Fig. 7). For desized CF (Figs. 7(a) and 7(b)), few residues of PA6 resin were on the fiber surface after debonding, indicating weak interfacial adhesion. In contrast, BI3.0/PU-CF (Figs. 7(c) and 7(d)) exhibited substantial PA6 resin retention after debonding, demonstrating enhanced interfacial bonding. These observations aligned with the IFSS results.



(a) (b)

(c) (d)

Fig. 7 Surface morphologies of CFs before and after PA6 microdroplet debonding: (a) desized CF before debonding; (b) desized CF after debonding; (c) BI3.0/PU-CF before debonding; (d) BI3.0/PU-CF after debonding

2.2 Interfacial interaction mechanism

In summary, the incorporation of BI significantly enhances the IFSS of CF/PA6 composites. During the 280 ℃ processing stage, BI undergoes deblocking to release reactive —NCO groups. These groups readily react with active hydrogen atoms from both CF surfaces and PA6 macromolecules, forming crosslinked networks at the fiber-matrix interface[12]. The underlying reaction mechanism is schematically illustrated in Fig. 8. After heating, BI releases isocyanate group (—NCO), which reacts with the carboxyl group (—COOH) on the surface of CF to form —NH—CO—O—CO—, which is unstable and decomposes into amide (—NHCO—) and carbon dioxide (CO_2)[13].

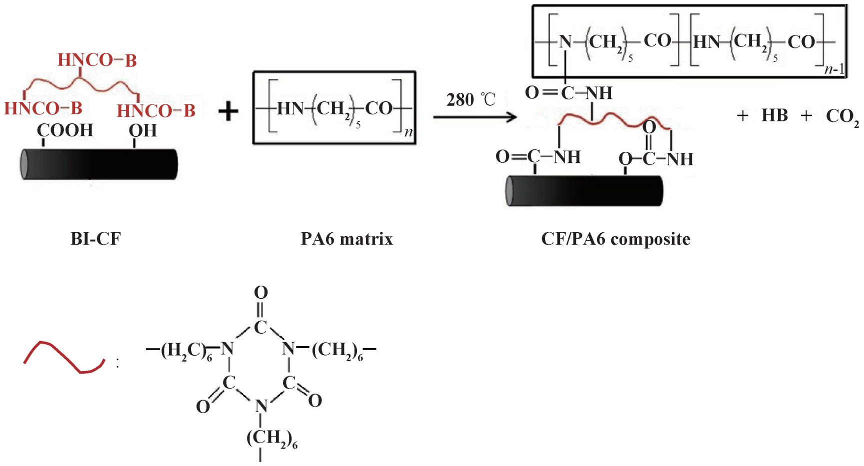


Fig. 8 Schematic illustration of chemical interactions among BI, CF, and PA6 resin

To investigate the chemical reaction mechanism between BI and CFs, BI was uniformly coated onto CF surfaces (denoted BI-CF). After vacuum drying at 80 ℃ for 24 h, the BI-CF sample was reacted at 280 ℃ for 10 min in a vacuum oven, and then cooled at room temperature, followed by washing thrice with MEK and dried to obtain the heated BI-CF sample.

Comparative FTIR analysis of the desized CF, BI-CF, and the heated BI-CF was performed (Fig. 9).

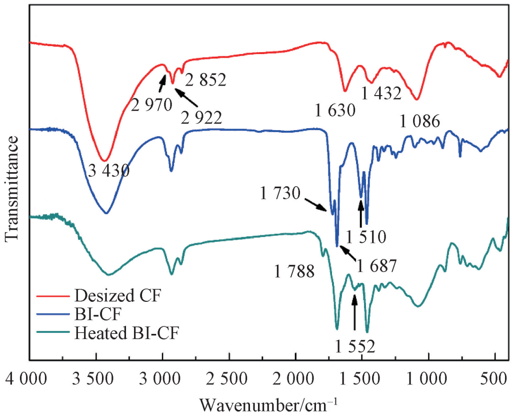


Fig. 9 FTIR spectra of desized CF, BI-CF, and heated BI-CF

For desized CF, the peak at 1 630 cm^{-1} is dominated by the H—O—H bending vibration of adsorbed water, while its broad profile suggests a contribution from surface C ═ O groups. Combined with the C—O stretching vibration at 1 086 cm^{-1} and the broad —OH stretching vibration at 3 430 cm^{-1}, these features collectively indicate the presence of —COOH and —OH groups, which serve as active sites for subsequent grafting. Upon BI coating (BI-CF), characteristic peaks emerged at 1 510 cm^{-1} (N—H bending vibration), 1 730 and 1 687 cm^{-1} (both attributed to C ═O stretching vibrations), confirming successful BI application on CF surfaces. After 280 ℃ heating, the deblocked —NCO groups reacted with active hydrogens from surface functionalities (—OH and —COOH) of the CF. A new peak at 1 788 cm^{-1} is assigned to C ═O stretching in newly formed amide linkages, and the peak at 1 552 cm^{-1} is assigned to N—H bending vibration. These spectral changes provide direct evidence for covalent bonding between —NCO groups and CF surface functionalities.

To investigate the chemical interactions between PA6 and BI, BI was coated onto PA6 films (denoted as BI-PA6). After vacuum drying at 80 ℃ for 24 h, the sample was heated at 280 ℃ for 15 min in a vacuum oven (denoted as heated BI-PA6), followed by the extraction of unreacted BI residues with MEK. Comparative FTIR analysis of PA6, BI-PA6, and heated BI-PA6 was conducted (Fig. 10). For PA6, the peak at 3 300 cm^{-1} is assigned to N—H stretching vibration; 1 639 and 1 545 cm^{-1} correspond to amide I and II stretching vibrations[14], respectively. The characteristic peaks at 3 420 cm^{-1} (N—H stretch) and 1 727 cm^{-1} (C ═O stretch) for BI-PA6 confirm the successful application of BI. The formation of urea linkages via reaction between the deblocked —NCO groups and the active hydrogen atoms on PA6 after heating at 280 ℃ was confirmed by FTIR analysis. A distinct new peak emerges at 1 683 cm^{-1}, assigned to the urea carbonyl (C ═O) stretching vibration, overlapping the characteristic urethane band. Meanwhile, a broad absorption band appears at 1 541 cm^{-1}, corresponding to the urea N—H bending vibration, partially overlapping the amide II band. The insolubility of this crosslinked product in MEK confirms covalent network formation on PA6 surfaces, demonstrating effective interfacial crosslinking by BI at processing temperatures.

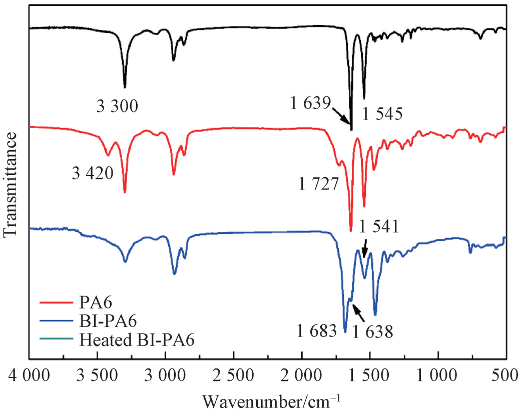


Fig. 10 FTIR spectra of PA6, BI-PA6 and heated BI-PA6

In order to further understand the cross-linking reaction between PA6 and BI after heat treatment, the solubility of BI-PA6 in formic acid before and after heating was compared. As shown in Fig. 11, the unheated BI-PA6 obtained after one day of placement is completely dissolved in formic acid. However, the heated BI-PA6 is not completely dissolved in formic acid solution, and there are obvious insoluble flocculent substances remaining. It can be seen that under the above heating conditions, certain cross-linked substances can be generated, and this result is basically consistent with the above FTIR analysis result that BI can cross-link with PA6. In general, BI can deblock and form a more stable crosslinking substance with PA6 resin at a processing temperature of 280 ℃.


(a) (b)

Fig. 11 BI-PA6 dissolved in formic acid: (a) before heating; (b) after heating

3 Conclusions

A novel sizing agent was developed by dispersing BI as a latent cross-linking agent in an aqueous PU emulsion for surface modification of CFs, to enhance interfacial properties in CF/PA6 composites. The BI/PU sizing layer improved fiber surface wettability, facilitating sufficient PA6 resin infiltration. After melt-compounding modified CF with PA6 resin at 280 ℃, IFSS was characterized via microdroplet debonding tests. The results revealed that a significant IFSS increased with the BI content. At a BI mass fraction of 3.0% on CF surfaces, IFSS of the modified system increased from 46.8 MPa (untreated control) to 62.3 MPa, representing a 33.1% enhancement. FTIR spectroscopy confirmed that deblocking of BI at the PA6 processing temperature (280 ℃) released reactive —NCO groups, which reacted with active hydrogen atoms from both CF surface functionalities and PA6 molecular chains to form interfacial crosslinked networks. This sizing strategy provides an efficient strategy for manufacturing high-performance thermoplastic composites.

References

[1] HASSAN E A M, YANG L L, ELAGIB T H H, et al. Synergistic effect of hydrogen bonding and π-π stacking in interface of CF/PEEK composites [J]. *Composites Part B: Engineering*, 2019, 171: 70-77.

[2] LIU L, JIA C Y, HE J M, et al. Interfacial characterization, control and modification of carbon fiber reinforced polymer composites [J]. *Composites Science and Technology*, 2015, 121: 56-72.

[3] KIM S W, PARK T, UM M K, et al. Effect of caprolactam modified phenoxy-based sizing material on reactive process of carbon fiber-reinforced thermoplastic polyamide-6 [J]. *Composites Part A: Applied Science and Manufacturing*, 2020, 139: 106104.

[4] LEE H, OHSAWA I, TAKAHASHI J. Effect of plasma surface treatment of recycled carbon fiber on carbon fiber-reinforced plastics (CFRP) interfacial properties [J]. *Applied Surface Science*, 2015, 328: 241-246.

[5] VAUTARD F, OZCAN S, MEYER H. Properties of thermo-chemically surface treated carbon fibers and of their epoxy and vinyl ester composites [J]. *Composites Part A: Applied Science and Manufacturing*, 2012, 43(7): 1120-1133.

[6] ZHU P, RUAN F T, BAO L M. Preparation of polyetherimide nanoparticles on carbon fiber surface via evaporation induced surface modification method and its effect on tensile strength and interfacial shear strength [J]. *Applied Surface Science*, 2018, 454: 54-60.

[7] ZHANG H X, LI W. Plasma-grafting polymerization on carbon fibers and its effect on their composite properties [J]. *Applied Surface Science*, 2015, 356: 492-498.

[8] LI J. Interfacial studies on the O_3 modified carbon fiber-reinforced polyamide 6 composites [J]. *Applied Surface Science*, 2008, 255(5):

2822-2824.

[9] CHEN Q, PENG Q Y, ZHAO X, et al. Grafting carbon nanotubes densely on carbon fibers by poly (propylene imine) for interfacial enhancement of carbon fiber composites [J]. *Carbon*, 2020, 158: 704-710.

[10] WU Q, ZHAO R Y, ZHU J F, et al. Interfacial improvement of carbon fiber reinforced epoxy composites by tuning the content of curing agent in sizing agent [J]. *Applied Surface Science*, 2020, 504: 144384.

[11] LIU F Y, SHI Z, DONG Y B. Improved wettability and interfacial adhesion in carbon fibre/epoxy composites via an aqueous epoxy sizing agent [J]. *Composites Part A: Applied Science and Manufacturing*, 2018, 112: 337-345.

[12] YIN S D, ZHANG X, HU G K, et al. In situ crosslinking of mechanically robust waterproof and moisture permeable cellulose diacetate nanofiber aerogels for warm clothing [J]. *Chemical Engineering Journal*, 2022, 444: 136528.

[13] ARNOLD R G, NELSON J A, VERBANC J J. Recent advances in isocyanate chemistry [J]. *Chemical Reviews*, 1957, 57(1): 47-76.

[14] YI C W, PENG Z H, WANG H P, et al. Synthesis and characteristics of thermoplastic elastomer based on polyamide-6 [J]. *Polymer International*, 2011, 60(12): 1728-1736.

封端异氰酸酯上浆剂改善碳纤维/聚酰胺 6 复合材料界面相互作用

董锋洋，王金刀，王　彪*

东华大学 先进纤维材料全国重点实验室 材料科学与工程学院，上海 201620

摘　要：为提高碳纤维增强聚酰胺 6(carbon fiber-reinforced polyamide 6，CF/PA6)复合材料的界面性能，将封端异氰酸酯(blocked isocyanate，BI)分散于水性聚氨酯(polyurethane，PU)乳液中，制备了新型上浆剂 BI/PU。采用室温施胶方法将其涂覆于碳纤维表面进行改性，结果表明，BI/PU 显著增强了碳纤维表面的润湿性，促进了 PA6 树脂在纤维上的浸渍。随着 BI 含量的增加，CF/PA6 复合材料的界面剪切强度(interfacial shear strength，IFSS)升高。去浆 CF/PA6 复合材料的 IFSS 为 46.8 MPa。上浆工艺中，当 BI 质量分数为 3.0%时，CF/PA6 复合材料 IFSS 达到 62.3 MPa，相较去浆 CF/PA6 复合材料的 IFSS 增加了 33.1%。所提出的方法为高性能热塑性复合材料提供了一种有效且可规模化的表面改性策略。

关键词：碳纤维；上浆剂；封端异氰酸酯；聚酰胺 6；界面剪切强度