Construction of Aramid Engineering Materials via Polymerization-Induced para-Aramid Nanofiber Hydrogel

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The processing of poly(p-phenylene terephthalamide) (PPTA) has long been a great challenge. This work reports a simple “monomers-nanofibers-macromolecular product” (MNM) hierarchical self-assembly approach to build 3D all-PPTA engineering materials. This approach mainly includes the preparation of polymerization-induced aramid nanofibers (PANFs) from monomers and the fabrication of all-PPTA materials from PANF hydrogel. Various 3D architectures, including simple solid bulks and sophisticated honeycombs (HCs), are obtained after the dehydration and shrinking of the PANF hydrogel. The tensile strength and compressive yield strength of PANF bulk are more than 62 and 90 MPa, respectively, which are comparable to typical engineering plastics. The compressive strength of PANF bulk with a density of 360 kg m$^{-3}$ is more than 24 MPa. The thermal stability of PANF bulk and PANF HCs are as good as that of Kevlar fiber and almost no decomposition occurred before 500 °C in a nitrogen atmosphere. Furthermore, the MNM process is performed under mild conditions, without high temperature, high pressure, or corrosive solvent. The MNM process is a novel strategy for the processing of all aromatic polyamide materials with complex structures and high performances and would be another development since the breakthrough of liquid crystal spinning technology of PPTA.

1. Introduction

Poly(p-phenylene terephthalamide) (PPTA) is a popular high-performance polymer known for its fiber form product with the commercial name of Kevlar. The excellent properties of PPTA derive from the intrinsic high rigidity and strong interactions of the all-aromatic amide macromolecular chains.[1-4] However, being neither soluble in common solvents nor fusible, PPTA is hard to manufacture unless through the liquid crystal spinning technology with concentrated sulfuric acid as the solvent.[5] PPTA fiber is usually made into composites for application in 3D structural materials.[6] The preparation of composites is challenging in practice, as it includes the design of the structure, long and tedious processes, modification of PPTA fiber, and enhancement of interfacial strength.[6-9]

The complicated process of building PPTA-fiber-based structural engineering composite materials can be reflected in the fabrication of aramid paper honeycomb (APHC), which is widely applied in the aerospace industry for vibration reduction and thermal insulation.[10,11] In the typical preparation process of APHC, aramid paper is first produced from differentiated products of PPTA fibers.[12] With an adhesive such as phenolic resin, aramid paper can be fabricated into honeycomb materials through the “expansion manufacturing process.”[10] This traditional technology leads to some problems of the products: 1) debonding between the two aramid paper sheets in the double cell wall might occur,[13,14] 2) the phenolic resin will affect the toughness of the honeycomb (HQ),[15] 3) the cell configurations of traditional APHC are limited,[16] and 4) the density of the APHC is usually less than 100 kg cm$^{-3}$ and high-density APHC is hard to obtain.[10] Therefore, a simplified approach for the direct production of all-PPTA 3D structures, including HCs, is needed.

The developments of nanotechnology and hierarchical self-assembly for the preparation of bulk materials[7,8] inspire the rational bottom-up design approach for high-order structures of PPTA. In recent years, aramid nanofibers have been successfully prepared through several strategies, such as chemical cleavage,[19,20] immersion rotary jet-spinning,[21] and polymerization-induced self-assembly.[22] The emergence of aramid nanofibers greatly expands the PPTA application range.[23] However, based on recent reports, product forms based on aramid nanofibers are mainly limited to 2D films[24-27] or 3D porous aerogel.[28,29] It is worth noting that theoretical models[5,8] recent observation results,[30] and the success of the cleavage of Kevlar fibers into nanofibers[31] all reveal the hierarchical structure in PPTA fibers, which indicates that 3D PPTA structures other than fibers might be achieved if the spatial self-assembly of the nanofibrils formed in situ is rearranged in a way different from the oriented spinning process.
Herein, we propose an original strategy for the preparation of 3D PPTA engineering structures through the spatial self-assembly of \( p \)-aromatic polyamide macromolecules. The whole approach is sketched as a “monomers-nanofibers-macroscopic product” (MNM) process, which consists of five simple steps (Figure 1). Utilizing the intrinsic aggregation tendency of PPTA molecule chains, we directly obtained polymerization-induced aramid nanofibers (PANF) through the polymerization method (Figure 1a–c). The PANF hydrogel was then obtained by the removal of excess water in PANF dispersion through vacuum assisted filtration (Figure 1d). The hydrogel was molded into desired 3D architectures based on its plasticity, without (Figure 1e) or with (Figure 1f) inner molds. Importantly, under mild drying conditions (no need for high and low temperature or special pressure treatment), densified all-PPTA PANF bulks and sophisticated HCs were successfully obtained after the shrinking of PANF hydrogel (Figure 1g,h). Through this approach, different macroscopic all-PPTA products could be obtained, such as a solid bulk with exquisite shape and surface pattern (Figure 1i), integrated PPTA workpieces (Figure 1j), and HCs with sophisticated cells (Figure 1k,l).

2. Results and Discussion

Our previous study demonstrated the feasibility of the polymerization-induced self-assembly strategy to prepare PANFs.\(^{[22]}\) In the current study, the polymerization without surfactant was performed and pure PANFs were successfully prepared by modifying the polymerization parameters, such as the monomer concentration, \( \text{CaCl}_2 \) concentration, and diluent amount. The length of the PANF is usually more than 5 \( \mu \text{m} \) (Figure 2a) and the average diameter is about 25.8 ± 6.4 nm (Figure 2b and Figure S1, Supporting Information). These results indicate that the average length-to-diameter ratio is greater than 200. This is helpful for the physical entanglement of and crosslinking between the PANFs and contributes to the formation of PANF 3D structures. After the repeated filtering-dispersing process (Figure S2a, Supporting Information), clean PANF dispersion, which is utilized for the preparation of PANF hydrogel and all-PPTA materials, can be obtained. The PANF dispersion (PANF concentration <0.5 wt%) was milk-white and had fine flowability (Figure 2c). When the PANF concentration increased to 2 wt% through the filtration process, the PANF dispersion transformed into a hydrogel state (Figure 2c). The PANF hydrogel could be easily shaped into different 3D structures using molds (Figure 2d and Figure S2b, Supporting Information) and transformed into solid bulks after drying and shrinking (Figure 2d). As shown in Figure S3 in the Supporting Information, the cubic hydrogel with a PANF concentration of 2% exhibited almost equal shrinkage ratios of about 75.5% in three directions when dried at a room temperature of 20 °C. The final size of PANF bulk depends on the original size of the molded hydrogel and the shrinkage ratio. It should be noted that the thickness of the relatively flat PANF hydrogel sample should be in a rational range; otherwise, as can be seen in Figure S4 in the Supporting Information, excessively thin samples suffer deformation. Interestingly, the geometric characteristics of the mooncake-shaped piece of PANF hydrogel were completely preserved, including the elaborate flower-like margin and detailed patterns on the hydrogel surface (Figure 2d). The precise retention of the morphology characteristics of the original hydrogel is similar to that obtained using the recent gel template technology\(^{[32,33]}\) and this retention of characteristics is helpful for the processing of PANF bulk products with sophisticated shapes or fine surface patterns.
In addition, the PANF bulk could not return to the original hydrogel state. When the PANF bulk was immersed in water for 24 h at 20 °C, the water absorption and the linear expansion ratio were 3% and 0.4%, respectively (Figure 2e), which reveals the strong interactions between PANFs.

The PANF bulk obtained via the MNM method could be further shaped through various mechanical processing methods, such as polishing, cutting, punching, and carving (Figure 2f,g). Also, as an example, the manufactured PANF bulk could be interlocked into a “Kong Ming Lock” (Figure 1j and Figure S5, Supporting Information), a traditional Chinese puzzle toy. The facile postprocessing of the PANF bulk further improves the PPTA processability.

The density of the PANF bulk obtained from the shrinking of the PANF hydrogel (initial PANF concentration = 2%, drying temperature = 20 °C) was measured as 1.40 g cm⁻³, which is close to the density of Kevlar 29 (1.44 g cm⁻³). As Figure 2h shows, PANF bulk with a density of 1.40 g cm⁻³ exhibited a compact structure in microscale and there are almost no obvious voids on the scale of a few nanometers. The increase of the initial PANF concentration will result in the slight decrease of the density (Figure S6a, Supporting Information). We suppose that the reduction of water content might to some extent weaken its driving force for the movement of PANFs. Furthermore, the increase of temperature also leads to the slight decrease of density (Figure S6b, Supporting Information), and this might be attributed to the decrease of capillary force of water at the elevated temperature, which also weaken its driving force for the movement of PANFs.

PANF bulk with a density of 1.40 g cm⁻³ exhibited excellent mechanical performance. Figure 3a is a typical tensile stress–strain curve of the PANF bulk. Its tensile strength reached 60.2 ± 2.0 MPa, which is comparable to those of some typical engineering plastics (Figure 3b and Table S1, Supporting Information). Figure 3c is a typical compressive stress–strain curve of the PANF bulk. The compressive yield strength of the PANF bulk was 87.1 ± 3.0 MPa, which also reaches the strength levels of engineering plastics (Figure 3d and Table S2, Supporting Information). The PANF bulk remained complete at a strain of 25% (Figure 3c, inset). In addition, the tensile and compressive strength of PANF bulk are related to its density (Figure S7, Supporting Information). The PANF bulk also exhibited
excellent hardness and elastic modulus in the nanoindentation test. Representative nanoindentation curves are displayed in Figure S8 in the Supporting Information. The hardness and elastic modulus of the PANF bulk reached 0.51 ± 0.03 and 9.2 ± 0.4 GPa, respectively, which were significantly higher than those of most commonly used polymers and polymeric composites (Figure 3e and Table S3, Supporting Information).

The PANF bulk also exhibited outstanding thermal performance. As demonstrated in Figure 3f, the PANF bulk and Kevlar 29 showed similar thermal decomposition profiles, and there was almost no thermal degradation before 500 °C for the PANF bulk. Furthermore, no transition was observed before 300 °C in the differential scanning calorimetry curves (Figure S9, Supporting Information) of both samples. The PANF bulk also showed excellent flame and heat resistance performance, which was demonstrated by the burning test (Movie S1, Supporting Information) and back-side temperature test (Figure 3g). During the burning test, the PANF bulk maintained its original shape and no melting or dropping occurred. The front side was burned but self-extinguished immediately after it was moved away from the fire. In the back-side temperature test, with the front-side flame temperature of ≈1000 °C, the back-side temperature of the PANF bulk plate with a thickness of 6.5 mm elevated only to 185.4 °C after 75 s (Figure 3g). The two sides involved in the back-side temperature test are presented in the insets of Figure 3g; the front side of the plate was carbonized, while the back remained intact. The excellent mechanical and thermal properties of the PANF bulk ensure its safety under harsh conditions.

The excellent performance of the PANF bulk should be due to the all-aromatic polyamide backbones of PANF and their strong interactions. The interactions between PANF were characterized via X-ray diffraction (XRD) (Figure 3h) and Fourier transform infrared (FTIR) spectroscopy (Figure 3i). Typical PPTA diffraction peaks, including (110), (200), and (004) reflections, existed in the profiles of the PANF bulk, PANF floc (obtained by freeze-drying of the PANF dispersion), and Kevlar 29 samples (Figure 3h).[19] The crystalline degree (Xc) values of the PANF bulk, PANF floc, and Kevlar 29 were 55.2%, 46.2%, and 71.3%, respectively (Figure S10a–c, Supporting Information).
Information). The $X_c$ of the PANF floc is consistent with the information reflected by the electron diffraction image and the high-resolution transmission electron microscopy images of the PANFs (Figure S11, Supporting Information), which indicates the semicrystalline state of the PANF. The increase of $X_c$ from the PANF floc to the PANF bulk might be attributed to the interface fusion of PANFs during the solidifying process, in which more H-bonds formed between the associated amide groups of PANFs under the stresses induced by the hydrogel drying. The diffraction image of the PANF bulk is shown in Figure 3g (inset), and those of PANF floc and Kevlar 29 are displayed in Figure S10 in the Supporting Information. The crystallite dimensions of the three samples are shown in Table S4 in the Supporting Information.

Characteristic PPTA bands emerged in the spectra of the three samples at about 3320, 1640, 1541, and 1260 cm$^{-1}$ (Figure 3i and Figure S12 and Table S5, Supporting Information).[19] Significantly, the C=O bands of the PANF bulk, PANF floc, and Kevlar 29 were located at 1643, 1651, and 1639 cm$^{-1}$, respectively (Figure S13a, Supporting Information). The difference in band location is related to the content ratio of the H-bonded C=O to the sum of the free and H-bonded C=O, which is defined as the association degree (AD).[20] By calculation, the ADs of the PANF bulk, PANF floc, and Kevlar 29 were 94.3%, 78.1%, and 98.0%, respectively (Figure S13b–d, Supporting Information). The increment of the AD from PANF floc to PANF bulk might also be due to the association of amide groups. Similar AD results were also obtained for the N–H bands (Figure S14, Supporting Information). Compared with the Kevlar 29, the PANF bulk is composed of the same PPTA molecules and has a similar molecular interaction degree, which might be the reason for its superior properties.

For a more practicable form of the all-PPTA material, we applied our MNM method to manufacture PANF HCs. By inserting orthohexagonal nylon columns in the PANF hydrogel as inner molds, we successfully built a periodic cellular structure consisting of all-PPTA cell walls after the controlled shrinking. The structure of the PANF HC was similar to that of commercial APHC (Figure S15, Supporting Information). PANF HC has many differences or advantages compared to traditional APHC in view of the preparation methods and characteristics of the products. First is the simplicity of preparation. The facile preparation process of PANF HC, as illustrated in Figure 4a, is quite simple compared to the traditional expansion process for APHC.[10] Second is the composition. In the MNM method, PANF hydrogel is the only raw material, and PANF HC was prepared without adhesives having poor heat resistance. Third is the structure. We can distinguish that the node (Figure 4b) and cell wall (Figure S16a, Supporting Information) of the PANF HC are integrated structures, while those of APHC are bonded composite structures (Figure 4c and Figure S16b, Supporting Information). Fourth is the flexibility of the MNM method. Except for the typical orthohexagonal honeycomb structure of APHC, PANF HCs with different structural parameters (Figures S17 and S18a, Supporting Information), various cell configurations (Figures 1l and 4d,e and Figure S18b–e, Supporting Information), and isotropic and anisotropic cell wall thicknesses (Figure 4b and Figure S19, Supporting Information).

![Figure 4](https://example.com/fig4.png)

**Figure 4.** Preparation process, structure, and properties of PANF honeycombs. a) Typical preparation procedures of PANF HCs; scale bars: 10 mm. b,c) Typical SEM images of microstructures of PANF HC and Nomex HC nodes, respectively; the red circles in (c) present the structural defects of Nomex HC; scale bars: 1 mm. d,e) PANF HCs with square cells and triangular cells, respectively; scale bars: 10 mm. f) Compressive stress–strain curves of PANF and Nomex HCs in T directions. g,h) Shear stress–strain curves of PANF and Nomex HCs in L and W directions, respectively. i) TGA and DTA curves of PANF HC-105 and Nomex HC-76.
Supporting Information) could be easily obtained through the MNM method; these are hard to achieve through the traditional aramid paper-based method. Finally, high-density PANF HCs could be prepared through the MNM method, while it is difficult for the traditional method. For example, the density of APHC with an inscribed circle diameter (D) of 4.8 mm is usually less than 100 kg m⁻³, which could be easily obtained through the MNM method.

Furthermore, the high-density PANF HCs showed excellent mechanical performance. Three kinds of high-density PANF HCs (PANF HC-105, PANF HC-210, and PANF HC-310) with the same D (4.8 mm) but different densities (105, 210, and 310 kg m⁻³, respectively) were prepared for mechanical performance evaluation. One kind of commercial APHC, Nomex HC-76 (D: 4.8 mm; density: 76 kg m⁻³), was used as the control sample. As shown in Figure 4f, the compressive strengths of these PANF HCs were more than 5 MPa and significantly increased with the density of the PANF HCs. Strain hardening, indicated by the uprising at the end of the plateau of compressive stress–strain curves, was observed for PANF HCs, which suggests their toughness. In contrast, the compressive strength of Nomex HC-76 was less than 5 MPa and the gradual decline of stress in the large strain region of the compressive stress–strain curve revealed the brittleness of Nomex HC-76. The shear performance of these HCs in the L and W directions showed similar tendencies (Figure 4g,h,i). The shear strengths of PANF HCs also increased with their densities and were all larger than those of Nomex HC-76. Furthermore, the specific strengths of PANF HCs and Nomex HC-76 are presented in Figure S20 in the Supporting Information. The specific strengths of PANF HC-210 and PANF HC-310 were larger than those of the Nomex HC-76 in both compression and shearing tests. The integrated node structure and the strong interactions among the PANFs were believed to be the main contributors to the improvement in specific strength.

The avoidance of adhesive resins in PANF HC not only effectively reduces bonding defects (Figure 4c) but also greatly improves the thermal stability. In Figure 4i, Nomex HC-76 started to decompose before 200 °C in thermogravimetric analysis as a composite of the Nomex paper and phenolic resin. However, the PANF HC showed almost no weight loss before 500 °C. The peak decomposition temperatures of PANF HC-105 and Nomex-76 HC were 566 and 464 °C, respectively.

3. Conclusion

Diverse all-PPTA 3D materials, including PANF bulks with different morphologies, and PANF HCs with different structures, could be successfully prepared via an innovative bottom-up MNM approach, which involved no high temperature, high pressure, or highly toxic solvent. The mechanical strengths of the PANF bulk were comparable to those of traditional engineering plastics and the mechanical strengths of PANF HCs were also excellent. Consisting of pure PPTA, the PANF bulk and PANF HC showed excellent thermal stability. Furthermore, the characteristics of being adhesive free and having high density were significant improvements in the preparation of the aramid HCs. The successful preparation of high-performance PANF bulks or PANF HCs, which have the potential to be applied as engineering materials, is a breakthrough in the processing of the aromatic polyamides for wider applications. This facile and scalable MNM approach built macroscopic materials with complex structures and high performances in mild ways, which is a successful combination of nanotechnology and hierarchical self-assembly.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

all-aramid bulk, all-aramid honeycomb, aramid nanofibers, “monomers-nanofibers-macroscopic product” method

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