Poly(lactic acid)/artificially cultured diatom frustules nanofibrous membranes with fast and controllable degradation rates for air filtration

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Abstract
The worldwide pandemic, coronavirus COVID-19, has been posing a serious threat to the global economy and security in last 2 years. The monthly consumption and subsequent discarding of 129 billion masks (equivalent to 645,000 tons) pose a serious detrimental impact on environmental sustainability. In this study, we report a novel type of nanofibrous membranes (NFMs) with supreme filtration performance and controllable degradation rates, which are mainly composed of polylactic acid (PLA) and artificially cultured diatom frustules (DFs). In this way, the filtration efficiency of particular matter (PM) and the pressure drop were significantly improved in the prepared PLA/DFs NFMs as compared with the neat PLA NFM. In specific, with incorporation of 5% DFs into fibers, PM0.3 removal with a filtration efficiency of over 99% and a pressure drop of 109 Pa were achieved with a membrane thickness of only 0.1 mm. Moreover, the yield strength and crystallinity degree of the PLA/DFs5 NFMs were sharply increased from 1.88 Mpa and 26.37% to 2.72 Mpa and 30.02%. Besides those unique characters, the PLA/DFs5 presented excellent degradability, accompanied by the degradation of 38% in 0.01 M sodium hydroxide solution after 7 days and approximately 100% in natural condition after 42 days, respectively. Meanwhile, the environmentally friendly raw materials of the composite polylactic acid and artificially cultured diatom frustules could be extracted from corn-derived biomass and artificially cultivated diatoms, ensuring the conformance to carbon neutrality and promising applications in personal protection.

Keywords Controllable degradation · Nanofibrous membrane · PM0.3 removal · Artificially cultured diatom frustules · Carbon neutrality

1 Introduction
The rapid spread of coronavirus disease 2019 (COVID-19) across the world has been acknowledged as one of the most severe global issues that poses a serious threat to public health at the present time [1–4]. Up to now, coronavirus cases worldwide have already surpassed 200 million, accompanied by a relative mortality rate of 2% as reported by the World Health Organization in 2021 [5]. Suspended virus particles (diameter ≈ 0.1 μm) that cause COVID-19 spreads mainly from person to person among those in close contact (within about 6 feet, or 2 m) [6–9]. To ensure interpersonal aerosol transmission protection, maintenance of social distance and air purification are considered essential even after vaccine protection. The air purification requires filter media with superior filtration efficiency and low cost [10]. According to recent research, conventional filter media, including melt blown non-woven fabric [11], glass fabric [12], and spun-boned fabric [13], are generally utilized for equipment and improvement in worker productivity. Currently, most people wear disposable medical masks (DMMs) or N95-certified masks, mainly composed of polypropylene, which can effectively protect humans from COVID-19 disease. However, it is difficult for the masks to realize high filtration efficiency due to their micron-sized fabric diameter [14]. Meanwhile, the available electret technologies that can inject charges into the as-prepared materials only via postprocessing are time-consuming. Furthermore, the daily production of more than six billion DMM production creates
a significant impact on environmental sustainability since the degradation of the DMMs requires more than 100 years. Hence, there is an urgent requirement for an efficient and versatile material to prepare nanofibrous filter media via a simple production method with an excellent filtration performance and subsequent rapid degradation properties [15, 16].

Compared with conventional technologies, electrospinning has emerged as a promising approach to fabricate the desired electret filter media owing to their distinct ability to generate nanoscale fibers and inject charges during the formation of the membranes [17, 18], whose process is fast developing from the single-fluid blending process [19] to coaxial electrospinning [20], modified coaxial electrospinning [21], tri-axial electrospinning [22], side-by-side electrospinning [23], and some other complicated processes [24]. Furthermore, the controllable fibrous diameter, arrangement, and morphologies ensure a high probability of optimization of the filtration performance and predominance of the filter media via this one-step method. Thus, electrospun fabric membranes with nano-sized fiber diameters have higher filtration efficiency than DMMs. Previous studies have shown that most of the petroleum-based polymers, such as polyamide 6 [25, 26], polyvinylidene fluoride [27–29], and polyvinyl alcohol [30], have been used as air filtration media by electrospinning; however, these applications have contributed to serious environmental pollution and fossil fuel resource depletion. Hence, sustainable green energy solutions have attracted increased attention in recent years.

Polylactic acid (PLA), as an environmentally friendly material, can be extracted from renewable starch raw materials, like corn, through polymerization and fermentation [31, 32]. To date, PLA has captured great interest for its good biodegradability and biocompatibility, with excellent mechanical properties. Additionally, PLA can be dissolved in many common solvents, showing great potential in green chemistry.

Under composting conditions, silica nanoparticles were deposited densely on the PLA fabric to enhance its surface roughness [33]. Silica has been recognized as the main representative of inorganic electrets by virtue of its excellent charge storage capacity and stability, expanding its applications in electrospinning [34]. However, the technique for preparing non-toxic silica with a large specific surface area and rough structure at low cost is a great challenge.

As representative natural nanomaterials with three-dimensional structures, diatom frustules (DFs) with ultrastructure and frustule morphology have been proposed as new functional biomaterials, due to their remarkable mechanical, optical, and chemical properties [35–38]. DFs, mainly composed of silica and covered with nanoholes around the shell, have good thermal and hydrothermal stability, high biocompatibility, and non-toxicity, extending their potential for broad application in macromolecular catalysis, biological processes, selective adsorption, and functional materials [39–42]. Furthermore, in our previous study, it was found that when compared with pure PLA, DFs can increase the degree of crystallinity and the modulus of the PLA [39].

In this work, we developed an efficient strategy to create PLA/DFs nanofibrous membranes (NFMs) with rapid degradation via electrospinning using the solvents chloroform/DMF (8/2, wt./wt.). Then, PLA/DFs NFMs with different DFs contents (0%, 5%, 10%, 15%, and 20%) were prepared by varying the ratio of the PLA/DF solutions. The morphology test demonstrated that DFs were distributed throughout within the PLA matrices. Moreover, it is also found that with an increase in DFs content, PLA/DFs NFMs have a smaller fiber diameter and smaller nano-sized pores, which were beneficial for improving the filtration efficiency. The filtration test indicated that DFs combined with high specific surface area and multiply hierarchical pores improve the removal of particulate matter (PM0.3) to 99.999% compared with the pure PLA NFMs. In addition, DFs can increase the degradation rate of PLA. The degradation test proved that PLA/DFs NFMs can be rapidly degraded in an alkaline solution and soil (7 days and 42 days, respectively), expanding the eco-friendly applications of the air filter media. Therefore, this design of a new facial mask made from these media conforms to the concept of carbon neutrality and demonstrates their potential application in personal protection.

2 Materials and methods
2.1 Materials

PLA (4032D, Nature Works, USA) with a density of 1.24 g/cm³ and the polydispersity of 1.7 was used in this study. DFs were obtained from Taili Energy Co., Ltd (Guangdong, China). The solvent of N,N-dimethylformamide (DMF) and trichloromethane was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). Sodium hydroxide (NaOH) and concentrated hydrochloric acid (HCl) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China).

2.2 Preparation of the polymer solutions

PLA solutions with 7 wt% concentration were prepared by dissolving PLA in a mixture of DMF/trichloromethane (with a mass ratio of 8:2) by stirring for 24 h at 90°C oil bath. After that, the DFs powders were added into as-prepared 7 wt% of PLA solutions by stirring for 4 h at room temperature, with a DFs percentage 0–20 wt%.
2.3 Electrospinning

NFMs were prepared using a HZ-10 electrospinning device provided by Huizhi Technology Co., Ltd (Shandong, China). The obtained polymer solutions were loaded into a 10 mL plastic syringe and extruded at a controllable speed rate (1.5 mL/h) through a stainless steel needle with an inner diameter of 0.9 mm. An electrospinning voltage (15 kV) was applied to the needle, placed on the top of collector with a distance of 20 cm. The obtained fiber deposited onto 10 cm × 15 cm aluminum substrate was vacuum-dried at 30°C for 72 h, then stored in a drying oven, waiting to be characterization. The preparation procedure was schematically shown in Fig. 1.

3 Characterization

3.1 Field scanning electron microscopy (FE-SEM)

The morphologies of PLA/DFs NFMS were acquired by VEGA 3 LMH scanning electron microscopy (SEM) (BrNo, Czech) with a 10 mm working distance at 10.0 kV acceleration voltage. The fiber diameter of FE-SEM image was determined using Image Jade software.

3.2 Nitrogen absorption–desorption test

According to the BET method, the specific surface area and mean pore volume of the samples were measured by N₂ sorption–desorption isotherm at 77 K using ASAP 2460, Micromeritics Instrument Co., Ltd (Norcross, USA).

3.3 X-ray photoelectron spectroscopy (XPS)

The XPS O 1s and Si 2p spectra of the PLA/DFs NFMS were analyzed by ThermoFisher ESCALAB Xi+ XPS (Massachusetts, USA), with the X-ray source of monochromatic AlKα (hν = 1486.6 eV).

3.4 Fourier transform infrared spectra analysis (FTIR)

Fourier transform infrared spectroscopy of PLA/DFs nanofibrous membranes was obtained through a PerkinElmer-L1600300 Spectrum Two FT-IR spectrometer (Massachusetts, USA).

3.5 Thermogravimetric analysis (TGA)

The thermal stability of PLA/DFs nanofibrous membranes was evaluated through a TA55 thermal gravimetric analysis (Delaware, USA) while heating under nitrogen environment at 25–200 °C, which the temperature programming is 10 °C/min.

3.6 Differential scanning calorimetry (DSC)

The thermal analysis of PLA/DFs nanofibrous membranes was investigated using METTLER DCS1 differential scanning calorimetry (Zurich, Switzerland). All samples with mass of 2–5 mg were heated from 25 to 200 °C at a rate of 10 °C/min, kept at 200 °C for 5 min, and then cooled down to 25 °C at a rate of 10 °C/min.

3.7 Tensile test

The mechanical properties were characterized by an LLY-06 electronic nanofiber strength tester (Gansu, China) with 10 mm/min at room temperature. All specimens had a size of 10 mm × 45 mm, which were kept in a closed drying oven under vacuum at 30 °C for 7 days before testing.

3.8 Surface potential test

The surface potential measures of the PLA/DFs nanofibrous membranes were decided on a handy digital electrostatic field meter (Model FMX-003, Simco-Ion). This meter can correctly measure static voltages within ± 20 kV range at
25 mm when two LED guide ring lights converge into a concentric circle. All samples needed to be tested ten times.

### 3.9 Air filtration test

The air filtration performance of PLA/DFs NFMs was evaluated by a TSI Model 8130 Automated Filter Tester (Hubei, China). 300 nm NaCl aerosol particles were counted at a flow rate of 96 L/min, corresponding to the face velocity of 5.3 cm/s. The membranes (100 cm² effective area) were placed on the air inlet.

### 3.10 The hydrolysis experiments

PLA/DFs NFMs were cut into quadrate samples with the size of 3.0 cm x 3.0 cm pieces and then were dry in vacuum at 30 °C for 7 days. Furthermore, PLA/DFs NFMs with different molar ratios were immersed in 0.01 mol/L NaOH, 0.01 mol/L HCl, and deionized water at room temperature (i.e., pH 12, pH 2, and pH 7). After each degradation period (1, 3, 5, 7 days), the samples were washed and dried in a vacuum oven at 30 °C for 7 days. The rate of weight loss was calculated according to formula (1).

$$W(\%) = \frac{M_1 - M_2}{M_1} \times 100$$

where $M_1$ is the weight of PLA/DFs NFMs before immersing. $M_2$ is the weight of PLA/DFs NFMs after immersing and drying.

### 3.11 Degradation in natural condition

The degradation performance was tested by burying neat PLA NFMs and PLA/DFs NFMs into soil with a burial depth of 30 cm at Tanglang Mountain, Shenzhen, China. The morphologies of all specimens were taken photos after removing from the soil at 0, 1, 2, 3, 4, and weeks.

### 4 Results and discussions

#### 4.1 Morphologies and chemical structures of DFs

The SEM images of the DFs before and after grinding are shown in Fig. 2a, b. The untreated DFs exhibit the characteristics of the centric diatom (diameter = 5 μm) with a hierarchical porous structure around the edges, ranging from 5 to 30 nm [43]. The morphology of the DFs after ball milling is uneven, ranging from 50 to 200 nm, with an average of 100 nm. However, the treated DFs have a small amount of particle agglomeration, some diameters of which exceed more than 1 μm in size.

Absorption isotherms of the DFs collected before ball milling (“untreated”) and after ball milling (“treated”) under a nitrogen atmosphere at 77.3 K are shown in Fig. 2c, d. After ball milling, the treated DFs show a remarkable increase in BET surface area from 66.2579 m²/g to 109.5830 m²/g and an absorption average pore diameter from 7.8213 to 10.0262 nm. These changes in microstructure would increase the PLA/DFs NFM’s surface membrane areas and decrease the time of degradation.

The surface properties of the DFs were further analyzed by XPS characterization. As shown in Fig. 2e–h, the XPS O 1 s and Si 2p spectra of the untreated and treated DFs were similar due to their consistent chemical composition. Through further analysis, no matter whether they are the treated or the untreated diatom shell, the chemical elements of both were composed of only Si and O (the atom ratio is 1:2), which proves that their components are SiO₂.

![Fig. 2](image_url)

*Fig. 2*  a, b SEM images,  c, d BET surface area,  e, f XPS O 1 s, and  g, h XPS Si 2p for untreated and treated DFs, respectively

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Combined with the SEM images and BET results, these results demonstrated that the ball milling was only a physical change; specifically, the treated DFs were only changed in morphology and the specific surface area increased, but their chemical properties did not change.

### 4.2 Morphologies of PLA/DFs NFMs

The concentration of nanoparticles has a significant influence on the morphology of the obtained nanofibrous membranes by electrospinning. The morphology and diameter distribution of the PLA/DFs NFMs with different blended ratios are depicted in Fig. 3. The diameter of the PLA/DFs NFMs appears as a normal frequency distribution, meaning that adding different DFs would not affect the uniformity of the fiber and could be evenly distributed inside the fiber. The fiber diameter (Fig. 3b1–e1) becomes thinner with increasing the concentration of the DFs, from 0.9 to 0.5 μm, indicating that the addition of diatom frustules can help reduce the fiber diameter. Interestingly, the image in Fig. 3a1 shows a uniform and smooth fiber. However, the addition of DFs resulted in the formation of a hierarchical pore structural combination with a thick and thin fiber. Furthermore, the SEM micrographs of PLA/DFs NFMs were investigated and showed the presence of several stacks in certain regions of the fibers, the size of which reached the micron level. All of the results proved that both agglomeration and homodispersion of the DFs appeared in the PLA/DFs NFMs. A similar phenomenon was found in PVDF/GPS@SiO₂ nanofibrous membranes [44].

![Fig. 3 SEM micrographs of the electrospun fibrous materials: a1 neat PLA, b1 PLA/DFs5, c1 PLA/DFs10, d1 PLA/DFs15, e1 PLA/DFs20 and a2, b2, c2, d2, and e2 with higher magnification; and a3, b3, c3, d3, e3 the relationship between the DFs content and the diameter distribution for the PLA/DFs NFMs](image-url)
4.3 Chemical structure and thermal stability analysis

The FT-IR spectrum of neat PLA, PLA/DFs NFMs, and the treated DFs are shown in Fig. 4a. The main characteristic bands of the treated DFs at 467, 799, and 1093 cm⁻¹ correspond to the bending vibration and symmetric stretching vibration of the Si–O bonds and antisymmetric stretching vibration of the Si–O-Si bonds, respectively, and the absorption peaks of the neat PLA nanofibrous membranes at 1183, 1749, 2947, and 2998 cm⁻¹ correspond to symmetric stretching vibration of the C–O–C group and stretching vibration of the C=O bonds, symmetric stretching vibration, and antisymmetric of the –CH₂ group [45]. It is important to note that the typical infrared absorption characteristic peaks of neat PLA were all present in the FT-IR spectrum of the PLA/DFs NFMs. Additionally, the typical characteristic peaks of the DFs could be found in the spectrum of the PLA/20%DFs NFMs, meaning that the DFs particles had been completely mixed into the PLA/DFs NFMs. Nevertheless, when the DFs content was less than 15%, it was difficult to observe the typical characteristic peaks of the DFs in the PLA/DFs NFMs due to the stretching of the Si–O-Si bonds and that the –OH group was weak or hard disappeared. This phenomenon might be due to the surface of the DFs being completely covered by PLA when the DFs content was relatively low. Hence, it was difficult to detect the existence of the DFs in the PLA matrix.

The crystallinity was analyzed by the initial heating DSC curves of the PLA/DFs NFMs shown in Fig. 4b, and the corresponding experimental results of the glass transition temperature ($T_g$), cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$), melt crystallization temperature ($T_{mc}$), melting enthalpy ($\Delta H_m$), and the degree of crystallinity ($X_c$) are summarized in Table 1. These results show that the $T_{cc}$ of the PLA/DFs nanofibrous membranes decreased, while it increased slightly when the DFs content reached 10% in comparison with the neat PLA nanofibrous membranes. Moreover, the crystallinity of the PLA/DFs NFMs was higher than that of the neat PLA NFMs. When the DFs content increased up to 5%, the crystallinity increased to 30.02%. This was because the DFs played a role as the nucleating agent during the crystallization process. However, the crystallinity of the PLA/DFs membranes decreased when the DFs content reached 10%.

### Table 1 DSC results for the neat PLA and PLA/DFs nanofibrous membranes

|          | $T_g$  | $T_{cc}$ | $T_{mc}$ | $H_m$  | $X_c$  |
|----------|--------|----------|----------|--------|--------|
| Neat PLA | 69.21  | 83.17    | 164.03   | 40.4   | 26.37  |
| PLA/DFs5 | 69.06  | 82.46    | 166.28   | 41.25  | 30.02  |
| PLA/DFs10| 64.74  | 81.95    | 166.77   | 38.87  | 29.45  |
| PLA/DFs15| 69.01  | 82.74    | 166.67   | 39.65  | 28.79  |
| PLA/DFs20| 69.37  | 82.92    | 166.56   | 35.33  | 27.62  |
DFs NFM shows an obvious decrease with an increasing of DFs content from 5 to 20%. This could be due to the DFs aggregating and inhibiting the formation of crystalline nuclei and thus inhibiting crystallization when the DFs were loaded at high levels [46].

The thermal stability of the PLA/DFs NFM was demonstrated by the TGA curves. As shown in Fig. 4c, there was only a slight change in weight before 300 °C, which might be caused by dehydration of the PLA/DFs NFM under heating. The initial thermal decomposition temperature of the neat PLA NFM was around 300 °C and the thermal decomposition finished at around 380 °C, with an undecomposable residue of DFs remaining [47]. Additionally, the initial thermal decomposition temperature of the PLA/DFs NFM decreased with increasing DFs content. Based on these data, the PLA/DFs NFM possessed good thermal stability, up to temperatures of about 300 °C.

4.4 Mechanical property analysis

The mechanical properties are some of the most important properties to make nanofibrous membranes more effective and practical for using as masks. The tensile stress–strain curves of the PLA/DFs NFM are shown in Fig. 5a. The values of the yield strength and elongation of the PLA/DFs NFM, calculated from the tensile stress–strain curve, are listed in Table 2. As the results indicate, the neat PLA NFM had a yield strength of 1.88 MPa and an elongation at break of 60.2%. When the DFs content increased up to 5%, the yield strength increased from 1.88 to 2.72 MPa with increasing DFs content. It is because DFs have a similar behavior like clay [48]; carbon nanotube can promote crystallinity of the PLA/DFs NFM as shown in Table 1. But continuous addition of DFs up to a higher concentration would lead to a decrease of breaking strength, due to the agglomeration of the DFs as shown in Fig. 5b. Additionally, it is worth noting that the elongation at break of the PLA/DFs NFM would decrease with an increasing in DFs when compared with the neat PLA nanofibrous membranes. From the microscopic view, this might be because the DFs nanoparticles are dispersed in the PLA/DFs mixture and form a discontinuous phase, generating weakness points. Therefore, the demands on the mechanical properties of the PLA/DFs NFM could be achieved by controlling the ratio of the DFs and PLA.

4.5 Filtration performance of PLA/DFs NFM

Three membrane characteristics were selected as the most important aspects that determine overall air filtration performance as follows: thickness of the membrane, the DFs loading percent, and the mean diameter of the fibers. Previous research has already been explored into mechanism of filtration. The air filtration efficiency of the nanofibrous membranes is the main performance characteristic to make an effective mask, protecting humans from bacteria and viruses. Hence, to explore the role of the DFs loaded on the fibers, the filtration efficiency of the PLA/DFs NFM with various DF concentrations was evaluated, as shown in Fig. 6a. The surgical mask, which is the control sample, has an efficiency of 89.98%. With incorporation of DF into fiber, the removal efficiency of PM0.3 of all PLA/DF NFM is over 99%. The neat PLA NFM is much lower, approximately 84.15% of filtration efficiency. These results were attributed to the increased surface roughness, remarkable specific surface area, smaller fiber diameter, and hierarchical pore structure that played a major role in particle interception. Meantime, it also could be explained that the smaller

| Sample   | Thickness (mm) | Yield strength (Mpa) | Elongation (%) |
|----------|----------------|---------------------|----------------|
| Neat PLA | 0.08 ± 0.01    | 1.88 ± 0.05         | 60.2 ± 1.2     |
| PLA/DFs5 | 0.09 ± 0.01    | 2.72 ± 0.06         | 57.9 ± 1.7     |
| PLA/DFs10| 0.08 ± 0.02    | 2.63 ± 0.05         | 53.1 ± 1.5     |
| PLA/DFs15| 0.09 ± 0.01    | 1.92 ± 0.08         | 39.1 ± 0.8     |
| PLA/DFs20| 0.08 ± 0.01    | 1.49 ± 0.09         | 26.8 ± 0.9     |
the fiber diameter with higher surface potential, the higher filtration efficiency. As shown in Fig. 6c, d, DFs as an additive exhibit unique characteristics similar to SiO$_2$ in reducing fiber and storing charge to enhance the surface potential. The high surface potential of the PLA/DFs NFMs has been proved that it could attach to tweezers tightly (Video S1). With increase in DFs concentration from 5 to 20%, there was insignificantly increase in filtration efficiency because of slightly increased in surface potential. It might be explained by filtration mechanism that the dominant mechanisms of the particle of sizes above 0.5 μm are gravitational sedimentation, inertia impaction, and interception, but the dominant mechanisms for the particles of size less than 0.2 μm are electrostatic attraction, shown in Fig. 6e. However, the filtration efficiency is not the only parameter that is considered for protection. Pressure drop needs to be kept as low as possible in addition to high filtration efficiency and air permeability for comfort. Otherwise, coatings that are 100%

Fig. 6  a PM$_{0.3}$ removal efficiency, b pressure drop, c surface potential, and d average fiber diameter for surgical mask and the PLA/DFs NFMs with different DFs concentrations. f Schematic illustration of five types of mechanisms that affect the collection process of aerosols. e Schematic of the PLA/DFs NFMs as the facial mask
efficient with no air permeability would be considered the perfect materials. Figure 6b shows the pressure drop of the PLA NFMs. When the DFs concentration increased from 5 to 20%, the pressure drop showed a gradually increasing trend, which is related to the decreasing diameter of the nanofibers. However, the PLA/DFs5 nanofibrous membranes represent a lower pressure drop (109 Pa) compared with those (122 Pa) of the neat PLA NFMs, which is close to pressure drop of surgical mask (106 Pa). With the high efficiency and low pressure drop, the PLA/DFs5 NFMs make it possible to be commercial (Video S2). Herein, PLA/DFs5 NFMs with 0.1 mm thickness have the ability to keep the virus from entering the human body (Fig. 6f) and which was higher than that of the KN95 mask standard.

4.6 Hydrolytic degradation performances of PLA/DFs NFMs

The degradation performance of membranes was observed by immersing neat PLA and PLA/DFs NFMs into an acid solution, water solution, and an alkali solution. The weight loss of five nanofilms at 20 °C during degradation under different degradation conditions is shown in Fig. 7a. According to the results of the hydrolytic tests, pH has a significant impact on weight loss. In fact, all the materials are more susceptible to weight loss at pH 12, while they appear to be less damaged at pH 7. PLA/DFs20 NFMs, in particular, appear to be the most sensitive material at pH 12, losing almost 100% of its initial weight after 7 days (Fig. 7b). Meanwhile, neat PLA NFMs lost only approx. 7% of their initial weight. These results demonstrated that adding DFs into PLA NFMs could expedite the hydrolysis degradation process, and that as the amount of DFs in the PLA nanofiber increases, the weight loss of the blended system increases progressively.

A similar pattern of activity was observed for systems that had been degraded at pH 7 and pH 2 (Fig. 7c). In particular, at pH 7, PLA/DFs20 NFMs appear to be the most sensitive material, losing about 7% of their initial weight after 7 days. However, neat PLA NFMs were minimally changed under this condition.

The above findings indicate that pH has a reasonably large influence on polylactic acid breakdown. The degradation of polylactic acid can be accomplished in three different ways: acid-catalyzed, base-catalyzed, and non-catalyzed hydrolysis of the ester groups [49–52]. As a result, we used the polymer degradation kinetic constant to assess the polylactic acid degradation performance. Höglund et al. [53] demonstrated that when the pH value increases from 1 to 10, the values of the measured constants initially decline, reaching a low at a pH of approximately 4, and a subsequent increase at higher pH values is evident. The rise is enormous in scope and size (about four orders of magnitude). The result was also corroborated by research findings in investigation.

The blended fabric membranes degradation behavior was obviously dependent on the relative content of the DFs and PLA. With the DFs fraction increasing, the weight loss
of PLA/DFs NFMs increased. This was because the DFs are made of SiO$_2$ with biological properties, they contain a higher number of hydroxyl group on their surface than silicon of industrial production. The fiber film surface will have more hydroxyl groups after adding diatom shells and this will improve the hydrophobic groups on the film surface, which will considerably improve the water absorption performance [53, 54]. Water might infiltrate the sample more quickly as a result, and weight loss can occur due to volume degradation rather than surface deterioration. Hence, the results showed that it is possible to adjust the breakdown rate of electrospun fabric membranes by varying the relative amounts of DFs and PLA used during the electrospinning process.

### 4.7 Natural degradation performances of PLA/DFs NFMs in soil

In most habitats, particularly soil and marine environments, the breakdown rate of PLA is generally slow, and it is strongly impacted by environmental parameters such as temperature, water content, the type of carbon sources available, and pH. For the most part, PLA has a slow disintegration rate, which is especially true during the first several months after burial. Take a 4032D PLA sample as an example, it takes more than 2 years to breakdown in soil. Furthermore, its decomposition rate in the presence of polylactic acid in the ocean is substantially slower, owing to the fact that saltwater has a much lower temperature than $T_g$ of the PLA [55].

The changes in morphology of neat PLA NFMs and PLA/DFs5 NFMs after 6 weeks are shown in Fig. 8. After 2 weeks, PLA/DF5 NFMs began to absorb water to form folds, with a considerable amount of soil and degradable holes in the surface. After 4 weeks, NFMs absorbed more water, with wrinkles on the surface, and they were degraded into two pieces. NFMs were fully degraded until 6 weeks, with no apparent full membrane, leaving a small amount of NFMs in the soil. However, there is hardly any change in the surface of neat PLA NFMs after degradation in 4 weeks. The surface of neat PLA NFMs began to absorb water, with soil and a little shrinkage. This indicates that DFs might function as a good degrade filler. Adding DFs with NFMs, the surface of NFMs would produce more hydroxyl group, improving the water absorption performance. Hence, the water mixed with bacteria in the soil could gain access to the NFMs quickly, finally forming volume degradation rather than surface deterioration.

### 5 Conclusions

In summary, PLA/DFs NFMs composed of biodegradable PLA and artificially cultivated DFs were developed via facile electrospinning. The hydrolytic degradation test demonstrated that the increased DFs concentration significantly accelerated the degradation rate of PLA/DFs NFMs in different media (pH 2, pH 7, and pH 12). In addition, a natural degradation test in soil also proved that DFs could improve the degradation rate of PLA NFMs. An air filtration test indicated that DFs can effectively improve the PM$_{0.3}$ particle removal of the filter even with a small DFs content, benefiting from a controlled fiber size and a favorable structure. The presence of the DFs could increase the number of hydrophobic groups on the film surface, resulting in an improvement in the water absorption performance to assist in the increased degradation rate. The air pollution removal efficiency of PLA/DFs NFMs (99.999%) is higher compared with neat PLA NFMs (82.156%). The tensile test confirmed that it can enhance the yield strength, while the elongation at break was within a controllable range when adding DFs. However, the yield strength will decrease when the DFs content...
was more than 5%. Therefore, with a fast degradation rate, enhanced mechanical properties, and high efficiency, PLA/DFs NFMs will find great potential as “green” materials for multifunctional and quickly degradable air filtration materials and pave a new path for large-scale fabrication of facial masks in accordance with a plastic ban and the current global carbon neutral goal.

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Competing interests The authors declare no competing interests.

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