Hierarchical porous poly(L-lactic acid)/SiO₂ nanoparticles fibrous membranes for oil/water separation

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Received: 19 May 2020

Accepted: 17 August 2020

Published online:

2 September 2020

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ABSTRACT

A two-step strategy has been developed to introduce silica nanoparticles into highly porous poly(L-lactic acid) (PLLA) nanofibers. Silica nanoparticles (SiNPs) were firstly synthesized and then modified to be hydrophobic. After PLLA/SiNPs composite fibrous membranes were electrospun and collected, they were re-crystallized by acetone at room temperature for a few minutes. With the re-arrangement of PLLA chains, the nano-/micro-electrospun fibres were transformed from non-porous ones to be porous ones with high surface area. Consequently, SiNPs that were completely covered by PLLA before acetone treatment showed up at the fibre surface. Higher PLLA crystallization also enhanced the Young's modulus and tensile strength (420 and 8.47 MPa) of the composite membrane. However, incorporation of SiNPs into porous PLLA membranes reduced their modulus and tensile strength (280.66 and 5.92 MPa), but an increase in strain to fracture (80.82%) was observed. Scanning electron microscopy (SEM), focused ion beam SEM, transmission electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction were applied to confirm the presence of SiNP in PLLA fibres. The presence of SiNPs inside and outside fibres enhances the hydrophobicity of PLLA/SiNPs nano-fibrous membrane as the water contact angle is greater than 150°. The oil absorption of these porous composite membranes was also tested using four different oils, which can reach the highest absorption capacity when the weight ratio of PLLA and SiNPs is 1:1. The flux of prepared membranes was investigated, and results indicated that SiNPs-loaded membrane effectively enhanced the flux (5200 Lm⁻² h⁻¹).

Handling Editor: Yaroslava Yingling.

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Introduction

The realizing of promise of nanotechnology is dependent on efficient technology for producing nanosized objects which should be prevented from aggregating into larger objects. The optical, catalytic or electrical properties of nanoparticles are different from those of the bulk material [1]. Appropriate strategies are necessary to keep nanoparticles apart and avail nanoparticles properties over long time duration. Functional nanoparticles that are incorporated within fibres are an important topic in electrospinning research [2]. Electrospinning is a versatile technology to fabricate ultrafine polymer fibres with diameters ranging from micron to nano-scale [3–7].

Thanks to the small diameter of nano-/micro-fibres, the electrospun fibres and fibrous membranes possess very high surface area and have a wide range of applications [5, 8–10]. In order to further increase the surface area of electrospun products, many methods have been tried to generate pores on the surface of polymer fibres, such as phase separation, breath figures, removal of selected polymer or particles and crystallization via introduced solvent [5, 11–15]. Phase separation is mainly caused by temperature change and non-solvent induction [13, 16]. Under a dramatically decreased temperature, some pores are formed on polymer fibres due to the volatile solvent evaporation. However, this method is complex and time-consuming, so it is not suitable for mass production. For the non-solvent induction, the phase separation and porosity can be achieved by the addition of a poor solvent, and this method is simple and energy-efficient [14, 15, 17, 18]. Breath figure mechanism is usually carried under a humid environment (normally above 50%). During the electrospinning process, evaporative cooling of the polymer solvent condenses water molecules in the environment on the surface of electrospun nanofibres; tiny water droplets on the surface of fibres finally evaporate to leave holes [11, 12, 16, 19]. Pore formation based on selected particles or polymers is easy to understand, namely, one sacrificial solvent or one kind of particle is blended with an electrospinning solution. After the nanofibres are electrospun, the fibres are immersed into an appropriate solution to dissolve and remove the sacrificial polymers or particles [20, 21]. For the crystallization via an introduced solvent, a specific solvent is applied to destroy

the fibre molecule structure and entangle the polymer chains, which can crystallize the polymer to form pores [22–24]. Based on our previous published studies, the electrospinning process of poly(L-lactic acid) (PLLA) fibres and the solvent-induced recrystallization of PLLA fibres were well explained [25, 26]. Acetone with a similar solubility parameter to PLLA was applied to contribute its recrystallization and swell fibres. The results show the novel porous PLLA fibres can be prepared through acetone post-treatment. The surface area of these porous fibres is increased to some extent, but porous fibres with greater surface areas still need further study.

In addition to the porous structure of fibres, nanoparticles such as TiO_2 nanoparticles, SiO_2 nanoparticles and Al_2O_3 nanoparticles can also be introduced into electrospun fibres for special functions or better mechanical properties [27–29]. As an inorganic material, silica has several unique properties, for instance, non-toxicity, chemically inert and low thermal conductivity [30–33]. Silica nanoparticles (SiNPs) can be applied in filtration, sensors, drug delivery and energy saving materials [31, 32, 34–41]. Numerous researchers have paid attention to the SiNP and various electrospun polymer fibres. There are three usual methods to incorporate silica nanoparticles within nano-/micro-polymer fibres. First, the polymer fibres are coated with SiNPs via physical or chemical methods. For instance, Gu et al. built a superoleophilic and superhydrophobic SiNPs/poly(lactic acid) (PLA) non-woven fabric via dopamine modification for oil and water separation [39]. The disadvantage of this method is that it is hard to deposit particles uniformly on the fibre surface. Second, the precursor of silica is mixed with the electrospinning solution so that the formation of the particles and the fibres are simultaneously performed. For example, Yanilmaz et al. used this method to fabricate silica/polyacrylonitrile membrane in the application of lithium-ion batteries and the loading of SiO_2 enhances ionic conductivity and thermal stability [42]. Although the in situ generated SiO_2 particles have good dispersion inside the polymer fibres, the load of nanoparticles is quite low and it is difficult to control the particle size. Third, nanoparticles are mixed directly into electrospinning polymer solutions. For instance, Obaid et al. used the method to prepare polyvinylidene difluoride/SiNP membranes for desalination technology. The SiNPs can enhance wettability and tensile strength of

membrane [43]. However, for the general polymer-SiNP composite fibres, most SiNPs were covered by a polymer layer, which limits the function of these inorganic particles. Therefore, a novel strategy is needed to solve the issues mentioned above.

Hydrophobic PLLA can be obtained from natural sources, for example, rice, corn and so on; thus, it is eco-friendly with good biocompatibility and biodegradability [44–48]. Efforts have been made to prepare porous PLLA fibres. Two main methods have been used to contribute to pore formation in PLLA fibres. First, a high volatile solvent is applied for PLLA electrospinning. For instance, Bogwitzki et al. [20] reported dichloromethane to leave pores on the surface of polylactic acid (PLA) fibres. Casasola et al. [49] reported that chloroform could also be used as a volatile solvent for the formation of porous PLA fibres. Second, poor-solvent induction is used for pore formation in PLA fibres. For example, Natarajan et al. [50] prepared porous PLA fibres via adding dimethyl formamide as a non-solvent into electrospinning solution. However, most of these pores were formed only on the fibre surface.

Herein, we report a two-step strategy for porous PLLA nanofibrous membranes loaded with modified silica nanoparticles prepared via electrospinning and recrystallization. This work focused on the preparation of materials and morphology of membranes. This kind of porous fibrous membrane shows a novel structure which has highly porous structures and whilst silica nanoparticles are uniformly distributed inside and outside porous fibres. These structures are not reported in previous publications. The oil–water separation is only one function of PLLA/SiO₂ fibrous membranes. The flux of these composite membranes is investigated, and results show that the membrane have very high flux. This strategy and porous composite fibres and membranes have potential applications in oil/water separation.

Experimental section

Materials

PLLA ($M_w = 1.43 \times 10^6$) was supplied by Corbion (The Netherlands). Dichloromethane (DCM, 99.99%) and Oil O Red were purchased from Sigma. Dimethyl formamide (DMF, 99.80%), tetraethyl orthosilicate (TEOS, 99.00%) and ammonia hydroxide (NH₃·H₂O,

35.00%) were purchased from Fisher Scientific Ltd. Ethanol (99.97%), and acetone (99.70%) were purchased from VWR Science Co., Ltd. Vinyltrimethoxysilane (VTMO, 97.00%) and hexane (99.00%) were purchased from Acros Organics. Distilled (DI) water was obtained using USF-ELGA water purifier in the laboratory. Corn oil, hydraulic jack oil and diesel were purchased from local market. All reagents were applied as received without any further purification.

SiNP surface modification

Following published procedures, SiNP were synthesized from TEOS [51]. In short, 8 mL NH₃·H₂O, 3 mL DI water and 100 mL ethanol were added to a 250-mL flask and placed into the water bath. When the solution temperature reached 60 °C, 6 mL TEOS was added into the mixture under stirring. The system temperature was kept at 60 °C for 3 h. After producing uniform SiNP, these particles were modified using a silane coupling agent (VTMO). Firstly, a mixture was prepared using 10 mL ethanol, 1 mL NH₃·H₂O, 1 mL DI water and 1 mL silane coupling agent in the 250-mL round bottom flask. The solution was vigorously stirred in the water bath at 50 °C for 30 min. Then 60 g dispersed SiNP solution was placed into the flask at 50 °C for 3 h. The surface modified SiNPs (M-SiNPs) were washed thoroughly by DCM. In the modification process, VTMO first undergoes a hydrolysis reaction and then reacts with hydroxyl group on the surface of the silica nanoparticles, which reduces the number of hydroxyl groups, as shown in Fig. 1. The dispersibility of the modified silica nanoparticles in the organic solution was improved.

Figure 1 Illustration of surface modification of SiNPs with VTMO.

Preparation of porous PLLA/M-SiNP membrane

PLLA was dissolved and M-SiNPs were dispersed in DCM and DMF mixed solvent to prepare a transparent electrospinning solution at 50 °C under stirring on a hotplate for 1 h. The electrospinning solution was loaded into a 30-mL syringe (TERUMO SYRINGE), and the syringe was put on the syringe pump (TONGLI Tech Ltd.) with 5 mL/h feeding rate. 21G needle was used and 23 kV was applied to provide electric field between the needle and metal collector. The rotational speed of the metal collector was 200 r/min. The electrospinning process was carried out under room temperature (about 20 °C), and the humidity was controlled at 30%. The distance between the tip of needle and metal collector was 30 cm. After the electrospun membrane was collected from the metal collector, it was immersed into acetone for 5 min at room temperature and then dried in a fume cupboard. Five treated samples were prepared, namely, S0, S0.5, S1, S1.5 and S2. The number following the letter S indicates the weight ratio of M-SiNP to PLLA. For example, the ratio of M-SiNP to PLLA for sample S0.5 is 0.5:1. Several pristine samples without acetone treatment were also tested as control.

Characterizations

Fourier transform infrared spectroscopy (FTIR, NICOLET 5700) was applied to compare pristine SiNPs and M-SiNPs by analysing functional groups from special peaks. Morphologies of prepared composite nanofibres were examined using scanning electron microscope (SEM, Zeiss Ultra 55) at 1.5 kV and transmission electron microscopy (TEM, FEI Tecnai G2 20). The cross section morphologies of fibres were analysed by focused ion beam SEM (FIB-SEM, FEI Helios Nanolab 660) at 5 kV and 0.1 nA beam current. X-ray diffraction (XRD, PANalytical X'Pert Pro) was applied to analyse crystallization of fibres. Mechanical properties were performed by using Instron 3344L3927. Samples were cut into a $5 \times 20 \text{ mm}^2$ rectangular shape with 20 μm thickness and tested with 5 mm/min extension rate. Five pieces of each sample were prepared for testing, and analysis was based on the strain–stress curves. Drop Shape Analyzer (DSA100, KRUS) was employed to investigate the wettability of silica nanoparticles and

nanofibres surface at room temperature. UV Lambda 25 instrument was used to examine the composition of filtration. The analysis of diameter of fibres was based on ImageJ software, and all charts were drawn using Origin software.

Oil absorption capacity measurements

Corn oil was used to carry out the oil sorption measurements at room temperature according to the following procedure. First, 10 g of DI water was placed in a clean glass petri dish, and 1 g of oil was placed on the surface of water. Then the dried porous nanofibres were immersed into the oil for 30 s. After that, the membrane was removed from the oil–water mixture using tweezers and drained up to 10 s. The final oil absorption capacity of the nanofibres was calculated by the following equation.

$$Q = \frac{W_t - W_0}{W_0}$$

where Q is the oil absorption capacity (g/g), W_0 is the weight of the nanofibres before immersing into the oil–water mixture, W_t is the weight of the wet nanofibres after oil absorption for 30 s.

Flux measurement

In the flux measurement, the membrane was cut into round piece with 3 cm diameter. The oil/water mixture was consisted with 10 mL water and 10 mL dyed hexane. The mixture was poured onto the membrane, and the pass time was recorded. The flux was calculated according to the following equation:

$$\text{Flux} = \frac{V}{St}$$

where V is the volume of oil, S is the effective area of membrane, and t is the oil pass time.

Results and discussions

Pristine and modified SiNPs

SiNP produced was based on the solvent varying technology (SVT). The particle diameter could be controlled by changing solvent volume. In this work, the pristine particle diameter was controlled at about 150 nm, as shown in Fig. 2a. The surface-modified SiNPs were obtained by using silane coupling agent

Figure 2 **a** TEM image of prepared SiNPs, **b** FTIR spectra of pristine SiNPs and the modified SiNPs (M-SiNPs). The special peaks of these curves indicate differences between these SiNPs.

through loading functional groups onto pristine particles surface. The FTIR spectra of pristine SiNP and M-SiNP are illustrated in Fig. 2b. The peak at about 3400 cm^{-1} corresponds to the absorption peak of -OH groups [52]. However, it is obvious that this peak is weaker and even disappears for M-SiNP. This is because that the VTMO reacted with the -OH groups on the SiNP surface, which reduced the amount of -OH groups. After the modification, the peak at approximate 1700 cm^{-1} appears, which indicates the stretch vibration of vinyl group (-CH=CH_2) [52]. These results indicate that the surface of the pristine SiNPs have been successfully modified by VTMO. The peaks between 2000 and 2400 cm^{-1} mainly indicate the CO_2 in the environment.

Morphologies of PLLA/M-SiNP nanofibres

Figure 3a exhibits the morphology of M-SiNP which is approximately 150 nm in diameter. The pristine PLLA nanofibres show coarser surface and are randomly arranged on the metal collector, as shown in Fig. 3b. The coarser surface is related to the environmental humidity. The humidity during the preparation of this pure PLLA fibre was about 30% RH. As the evaporative cooling of DCM occurs, environmental moisture condenses on the surface of the injected solution to form droplets. After the water droplets leave via natural evaporation, a few wrinkles or pores formed on the surface of nanofibres. Other SEM images show morphologies of PLLA/M-SiNP composite nanofibres with different amounts of M-SiNPs. Similarly, the surface of these composite nanofibres is coarser, whilst it is observed that the M-SiNPs are evenly distributed on the fibres. For the relatively low M-SiNP amount, the distribution of M-SiNPs on the S0.5 (Fig. 3c) and S1 (Fig. 3d) is

relatively wider. However, for S1.5 (Fig. 3e) and S2 (Fig. 3f), due to the high M-SiNP amount, it can be observed that each fibre is evenly covered with many M-SiNPs. Furthermore, a few pores formed on the surface of these PLLA/M-SiNP fibres. As mentioned before, after the droplets formed by the water vapour condensation leave via natural evaporation, the pores form on the surface of fibres. In this case, the porous composite nanofibres can be formed by controlling the environment humidity. However, the pores are not uniform and limited in number. The inserts of Fig. 3 clearly show that the M-SiNPs are still covered by the thin PLLA fibres, which adversely affects the final function of the nanoparticles. This is a common problem in producing composite membranes of nanoparticles and polymers using electrospinning. Thus, it is important to find a method to produce uniform pores so that the M-SiNPs can be exposed to improve the composite membrane performance.

Morphologies of nanofibres after acetone treatment

In order to solve the common problem mentioned above, post-process was applied to increase the exposure of M-SiNPs. Figure 4 shows the morphologies of pure PLLA nanofibres and four PLLA/M-SiNP composite nanofibres with different amounts of M-SiNPs after post-processing. It can be seen that numerous nano-size pores are formed on the surface of nanofibres which is quite different from that in Fig. 3. Moreover, it indicates that the nanopores can be uniformly generated from inside to outside of single fibres with good internal connections, as shown Fig. 4f. The pore size and distribution are important to electrospun fibres; however, the hierarchical porous PLLA fibres have not been reported

Figure 3 **a** SEM image of M-SiNPs with 150 nm diameter. **b** SEM image of the pure PLLA membrane (S0). **c–f** SEM morphologies of PLLA/M-SiNP nanofibres with different M-SiNP amount (S0.5, S1, S1.5 and S2). There are few pores formed on the surface of fibres, and M-SiNPs are covered in the fibres.

before. For pore size distribution, two typical measurements, namely, Brunauer–Emmett–Teller (BET) and Mercury intrusion porosimetry (MIP) tests, were applied. However, these two methods cannot indicate internal pore distribution. Additionally, BET is for analysing the pore size distribution of micropores and mesopores. MIP is for determining the pore size distribution of a portion of the mesopores and macropores [53]. Although there is no optimum measurement to analyse these properties, in our previous study, we also tried to analyse fibre's surface area by BET ($> 90 \text{ m}^2/\text{g}$) and porosity (80%) [25, 54]. However, because the hierarchical pore structure throughout the porous fibres is very complex, and the pore distribution is quite wider, from a few nanometers to hundreds of micrometers, none of BET and MIP can reveal the real pore size and pore size distributions of the PLLA/SiNPs composite fibrous membranes. By SEM and FIB, it can be observed the porous structure inside the fibres. However, it is still a difficult problem to measure and

analyse them now. And these methods are only used to measure surface pores property and the internal pores property cannot be measured. Therefore, there is no precise method to analyse the size distribution of these pores.

We can only roughly measure the pore size on the fibre surface using ImageJ software. Several pores were measured randomly, and the distribution image was drawn below. From Fig. S1 (support information), it can be seen that the range of pores diameter is wide. Smaller pores (under $d = 10 \text{ nm}$) are difficult measured just use this software. Therefore, the wide diameter distribution makes it impossible to measure by ordinary methods. This porous structure could significantly improve the oil flux when the membrane is applied as filter.

Figure 5 shows the internal structure of pristine PLLA fibres and porous PLLA fibre. It indicates that the M-SiNPs were coated by PLLA fibres and there is no porous structure formed (Fig. 5a). After acetone treatment, the porous structure was formed from

Figure 4 **a–e** SEM images of S0, S0.5, S1, S1.5 and S2 after immersed into acetone for 5 min. **f** TEM image of S2. There are a lot of pores formed inside and outside fibres. The added M-SiNPs are exposed from the fibre and uniformly distributed inside and outside fibres. The diameter of nanofibres is increasing with the increasing M-SiNP amount.

Figure 5 FIB-SEM images of cross sections of **a** random pristine, and **b** porous fibres (S1.5). Fibre surfaces were marked using red dots.

inside to outside and more nanoparticles were exposed. Although the diameter of the porous fibre is increased to some extent, there is less connection at the cross section than solid fibres. The internal pore structure is the same as the surface pore structure (Fig. 5b). As mentioned before, it is also difficult to measure internal pore property.

With the increasing amount of M-SiNP in porous PLLA fibres, the amount of exposed particles and the fibre diameter are both increased. The diameter

distribution is based on 50 random measurements for each sample. It can be seen that the diameter of S0 is approximately 1.48 μm (Fig. 4a). For the composite nanofibres, the pores also formed as the pure PLLA fibres, whereas the M-SiNPs with 150 nm diameter uniformly appear in the fibres and are exposed on the fibre surface (Fig. 4b–f). For the low amount of M-SiNP, the particles disperse widely in the fibres and are not apparent on the fibre surface. As the amount of M-SiNP increased, more particles appear

in the fibres and the diameters of fibres also increase, from 1.85 to 3.58 μm approximately. For all samples, M-SiNPs are uniformly dispersed inside and outside the PLLA fibres and the diameters of fibres are uniform. Overall, after the post-processing, pure PLLA and PLLA/M-SiNP composite fibres all show high number of pores and good internal connectivity.

Cross section of PLLA/M-SiNP fibres

In order to further analyse the internal structure of fibres, FIB SEM instrument was utilized to compare the pristine and porous PLLA/M-SiNP fibres, as shown in Fig. 5. The fibres were firstly coated with Pt and then ion beam was applied to the fibre cross section. From Fig. 5a, it can be seen that before the post-processing, a thick PLLA layer is formed which is noted using red dots and the M-SiNPs are covered by the fibre. However, after post-processing, pores are formed not only on the fibre surface but also inside the fibres, as shown in Fig. 5b. The surface pores contribute to M-SiNPs exposure, which promotes the function of M-SiNPs. The porous internal structure greatly improves the surface area and hydrophobic property of fibres.

X-ray diffraction and tension measurements

From the XRD spectra in Fig. 6a, the crystallization of these samples has been studied. For the pristine pure PLLA nanofibres, there is no obvious peak in its spectra, indicating low crystallization. After immersing the pure PLLA nanofibres into acetone, four peaks are observed, namely, $2\theta = 15^\circ$, $2\theta = 16.8^\circ$,

$2\theta = 19^\circ$ and $2\theta = 22.3^\circ$. In particular, the peak at 16.8° has the highest intensity. These four diffraction peaks are mainly formed from (010), (110)/(200), (203) and (015) planes, respectively, indicating the PLLA crystallization is the α formation which includes a 10_3 helical conformation [55–57]. This shows that amorphous PLLA nanofibres can be successfully crystallized by acetone at room temperature. Acetone also contributes to the crystallization of PLLA/M-SiNP composite nanofibres. The highest intensity peak (16.8°) also appears in the spectra of composite nanofibres. However, due to the addition of M-SiNP, the intensity of the peak of PLLA/M-SiNP is lower than that of treated PLLA. The other three peaks are lower as well, and the peak at 15° actually disappears. For the peak at 19° , as the M-SiNP amount increases, the peak shows right-side shift. For the peak at 22.3° , as the amount of M-SiNP increases, it first declines (S0.5, S1) and then increases gradually (S1.5, S2). These results can be attributed to XRD pattern of pure M-SiNP from Fig. 6b which indicates that the main peak has a wider distribution that is between 10° and 30° . This decreases the intensity of treated composite nanofibres' peaks and causes the peak at 19° to shift slightly to the right (Fig. 6a). It indicates that the loading of M-SiNP occupies space both inside and outside the fibres, which affects the intensity of crystallization of PLLA. As acetone has similar solubility to PLLA, when fibres immersed into acetone, acetone can swell fibres to give molecules free space for movement. However, M-SiNP loading obstructs free space for molecules movement, which reduces the crystallization

Figure 6 **a** XRD spectra of six different samples, and **b** M-SiNP. Lines show the pristine pure PLLA nanofibre, the treated pure PLLA porous fibre (S0), PLLA/M-SiNP composite fibre with different M-SiNP amounts (S0.5, S1, S1.5 and S2).

intensity. Overall, acetone treatment is an effective method to increase crystallization for both pure PLLA nanofibres and PLLA/M-SiNP composite nanofibres.

The crystallization of fibres affects their mechanical properties [25, 54]. The stress–strain patterns of fibres before and after acetone treatment are exhibited in Fig. 7. It is observed that pristine pure PLLA fibres have higher Young's modulus than that of pristine PLLA/M-SiNP fibres (S2). Although the pristine pure PLLA fibres show similar break strain to the pristine PLLA/M-SiNP fibres, the pristine pure PLLA fibres show higher break stress (4.31 ± 0.67 MPa). On the other hand, as mentioned before, after acetone treatment, porous fibres show higher crystallization and M-SiNP are exposed both inside and outside the porous fibres. The higher degree crystallinity increases the rigidity of the porous fibres. The porous PLLA and PLLA/M-SiNP fibres both show higher

Young's modulus, which indicates that porous fibres become more rigid than the pristine fibres. Although pure porous PLLA fibres show the highest break stress (8.47 ± 0.52 MPa), they have the lowest strain ($15.31 \pm 2.89\%$) which caused by the porous structure. The porous structure is not only on the fibre surface but also inside the fibres. It means that the pristine solid PLLA fibre is transferred to be a fully porous fibre from inside to outside. With loading of M-SiNPs, the Young's modulus and break stress are reduced to 280.66 ± 20.56 MPa and 5.92 ± 0.57 MPa, respectively. However, the break strain reaches $80.84 \pm 4.94\%$. This phenomenon is mainly attributed to M-SiNP loading decreasing crystallization. Pore formation causes M-SiNP exposure whilst M-SiNP loading contributes to the formation of flexible chain fibres and reduces the mobility of PLLA fibres. These results indicate that compared with pristine PLLA fibres, crystallization enhances porous

Figure 7 a Stress-strain curves, b peak stress, c elongation, and d Young's modulus analysis of fibres, before and after acetone treatment.

fibres' Young's modulus and uniform M-SiNP loading in PLLA fibres plays an important role in enhancing fibres' tensile strength.

Wettability measurement and oil absorption

The wettability of membrane surface is dependent on the polymer chemistry, surface roughness and fibre porosity [39, 43, 58]. In this work, membrane wettability is expressed by water contact angle (WCA). The results are shown in Fig. 8a; with increasing amount of M-SiNP in PLLA nanofibres, the WCA is slightly increased until the mass ratio of PLLA to M-SiNP is 1:1 (S1). When the M-SiNP amount increases further, the WCA decreases but is still larger than that of pure PLLA membrane. As mentioned before, many factors affect the wettability of these membranes, for instance, surface morphology, surface chemistry, fibre diameter and porosity. According to previous studies, decreasing fibre diameter, increasing surface roughness or decreasing porosity can enhance WCA [59]. PLLA is a hydrophobic material, and the contact angle of pure PLLA nanofibre is $137.60^\circ \pm 1.04^\circ$. M-SiNPs are also hydrophobic. The contact angle of the composite fibres can be increased with the loading of M-SiNP. Compared to the pure PLLA membrane (S0), the contact angle is increased by about 3.60%, 10.54%, 7.49% and 5.50% for S0.5, S1, S1.5 and S2, respectively. The highest contact angle can reach $151.50^\circ \pm 0.27^\circ$, when the mass ratio of PLLA and M-SiNP is 1:1. As discussed in “Morphologies of nanofibres after acetone treatment” section, the fibre diameter increases with increasing M-SiNP amount. Thus, as the M-SiNP loading increases, the diameter of fibre increases and the WCA decreases. Although

the contact angles of the PLLA/M-SiNP composite fibres, especially S1.5 and S2, decrease slightly as the fibre diameter increases, they are still greater than that of the pure PLLA nanofibre. It is worth mentioning that the loading of M-SiNP and their exposure can improve membrane hydrophobicity.

The oil absorption capacities of prepared membranes are presented in Fig. 8b. Four different kinds of oils were applied in this test. For different porous composite membranes, the oil absorption capacities are different. The absorption capacity is related to the volatility of oils. For example, diesel and hexane are both highly volatile solvents, which contributes weight loss of the final wet fibres and reduces the final absorption capacity. Thus, the absorption capacity of other stable oils is higher than that of these volatile oils. As the M-SiNP amount increases, the oil absorption capacities improve, although the oil absorption and the amount of M-SiNPs are not proportional to each other. When the mass ratio of M-SiNP and PLLA is 1:1 (S1), the oil absorption capacity reaches the highest values for all oils. When the amount of M-SiNP increases further (S1.5, S2), the oil absorption capacity decreases. This corresponds with the value of WCA and the balance between pores and SiNP amount. High M-SiNP amount affects the pores in the fibres and increases the fibre diameter, decreasing the oil absorption capacity. These results are mainly attributed to the strong hydrophobic and oleophilic properties of PLLA/M-SiNP composite membranes and the porous structure.

Figure 8 **a** Influence of M-SiNP on the water contact angle for acetone-treated pure PLLA membrane and PLLA/M-SiNP composite membranes with different M-SiNP amounts. **b** Oil

absorption capacities of pure PLLA nanofibre (S0) and PLLA/M-SiNP composite membranes (S0.5, S1, S1.5, S2).

Evaluation of superhydrophobic membrane in oil/water separation

All fabricated composite membranes were applied in hexane/water mixture separation process. 10 mL water and 10 mL dyed hexane were mixed to simulate the oil/water mixture and the thickness of each membrane was fixed at 30 μm . When the mixture was poured into the glass device, the oil was quickly filtrated through the membrane and the water was left on the membrane (video 1, support information), as shown in Fig. 9a, b. UV spectroscopic results indicate that the curve of filtrated hexane exactly lies on the curve of the dyed pure hexane, which shows that the solution filtrated from the prepared membrane is consisted of pure hexane. From Fig. 9d, it can be seen that the flux of proposed membranes is increased as the increase of M-SiNPs loading. When the mass ratio of PLLA and M-SiNPs is 1:1 (S1), the flux can reach the highest value ($5095.54 \pm 143.84 \text{ Lm}^{-2} \text{ h}^{-1}$), which is much higher than other SiNP-

loaded membranes ($3032.4 \pm 234.6 \text{ Lm}^{-2} \text{ h}^{-1}$) [60]. However, when the M-SiNPs loading further increases (S1.5, S2), the flux decrease. This is related to the balance between pores and nanoparticles loading. High particles loading blocks pores and then affects the hexane's passing speed. Thus, the flux is also reduced. These results indicate that M-SiNPs loading can promote the flux; however, excessive particles loading reduces the final flux.

Mechanism of pore formation

Based on the previous publications, it is clearly explained the acetone treatment theory for PLLA fibres [25, 26, 54]. At the initial stage of the electro-spinning process, the polymer solution jet of DCM/DMF is homogeneous and has no phase separation. When the solution jet is further stretched, most of the DCM is volatilized and most of the DMF is remaining because DCM has higher saturated vapour pressure than DMF. Because DMF is a non-solvent for PLLA

Figure 9 a, b Demonstration of oil/water separation: the film (30 μm) was fixed in separation cell and tilt 45°, and then, a hexane/water mixture was poured into the device. c UV spectroscopy analysis of pure hexane, filtrated hexane and water. d Hexane flux ($\text{Lm}^{-2} \text{ h}^{-1}$) of prepared membranes.

Figure 10 Illustration of preparation of porous PLLA/M-SiNP composite fibres. **a** Electrospun PLLA/M-SiNP fibre; **b** porous PLLA/M-SiNP fibre after acetone treatment at room temperature (RT) for 5 min.

especially PLLA with very high molecular weight, phase separation occurs between PLLA and DMF. When PLLA reaches the collector as fibres, some DMF is still trapped inside the fibres. After the remaining DMF is completely volatilized, it leaves some channel-like space or phase interface in the dry PLLA fibres. The M-SiNPs are uniformly distributed in the fibre, as shown in Fig. 10. When the fibres are immersed into acetone, the channel-like structure enables acetone to permeate into PLLA fibres. As acetone has similar solubility to PLLA, it can swell PLLA fibres to give molecules free space for movement. Some random and entangled polymer chains folded, which induces crystallization and pore formation. The pores are formed both inside and on the surface of the fibres and are interconnected. Additionally, the M-SiNPs are uniformly exposed in the pores and inside fibres, which improves the mechanical and hydrophobic properties of the composite fibre.

Conclusions

In this work, porous PLLA/M-SiNP nanofibres were successfully fabricated using electrospinning and post-processing by acetone. The SiNPs were firstly modified with silane coupling agent so that the M-SiNPs could be uniformly dispersed in the organic polymer electrospinning solution. M-SiNPs were distributed uniformly inside and on the surface of porous PLLA fibres, and the diameter of PLLA/M-SiNP fibres increased with increasing M-SiNP amount. XRD spectra of porous nanofibres showed four obvious peaks, indicating the fibres were crystallized into α formation. Acetone treatment folds

random and entangled polymer chains, which crystallizes PLLA amorphous phase. However, the addition of M-SiNP partly reduced the crystallization of treated PLLA fibres and caused right-side shift of its XRD spectra. High crystallization enhanced the Young's modulus of porous fibres and the uniform M-SiNP loading in PLLA fibres improved the fibres' tensile strength. The porous PLLA/M-SiNP nanofibres showed good oil absorption capacity and enhanced flux and have good potential for oil–water separation applications.

Acknowledgements

We acknowledge the help from Zhiying Xin, Xiangli Zhong and Hugh Gong. Thanks for the support of the Electron Microscopy Centre and XRD suite in The University of Manchester. The project was supported by The Chinese University of Hong Kong and The University of Manchester joint research fund. Finally, the authors thank to Corbion (The Netherlands) company for their supply of PLLA materials.

Compliance with ethical standards

Conflict of interest There are no conflicts to declare.

Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s10853-020-05115-2>) contains supplementary material, which is available to authorized users.

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