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Preparation of porous poly(L-lactic acid)/tobermorite composite membranes via electrospinning and heat treatment

Tatsuya Okuyama · Hirotaka Maeda ·
Emile Hideki Ishida

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Abstract A novel poly(L-lactic acid) (PLLA)/tobermorite composite porous membrane for use as filter materials was synthesized by electrospinning a mixture of tobermorite modified by poly(dialyldimethylammoniumchloride) (PDDA) and PLLA. X-ray diffraction patterns of the sample indicated the existence of tobermorite in the sample. Scanning electron micrographs of the sample showed that the nonwoven membrane consists of a few microscopic fibers despite the existence of tobermorite particles. This was due to repulsive force and surface tension. However, no tobermorite particle was exposed at its fiber surface. Thermal analysis showed PLLA of the sample pyrolyzed with two steps of weight loss (44% at around 170 °C and 34% at around 270 °C). Heat treatment of the sample at 130 and 250 °C led to crystallization of a part of amorphous PLLA in the fiber and elimination of the remaining amorphous PLLA, respectively. After the treatment, the membrane maintained its porous structure and was coated with tobermorite particles at the fiber surface.

Introduction

Tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) is a type of crystalline calcium silicate hydrate that is synthesized under hydrothermal processes [1–4]. Its ideal structure comprises infinite double layers of Ca–O polyhedra linked on both sides to chains of silica tetrahedral running along the *b*-axis. This assembly is stacked in the *c*-direction, which consists of interlayer regions that accommodate exchangeable cations and water molecules [1–3, 5–8]. Tobermorite has been shown to have potential applications in wastewater treatment and removal of heavy metals from water because of its cation exchange property [2–4, 6–8].

The synthesis of porous materials containing tobermorite with excellent properties leads to increase applications for environmental friendly materials. The sintering process is not suitable for synthesis of porous tobermorite materials because tobermorite transforms to wollastonite at about 850 °C [9]. Ceramic combined with polymer may lead to improved mechanical properties such as superior ductility.

Electrospinning has been reported as a method for synthesizing nonwoven porous polymer membranes, which consist of fibers in the range of nano to micro-meters. The introduction of successive pores into the materials contributes to it becoming lightweight, breathabile, and filterable, which are needed as a filter. The diameter of an electrospun fiber can be easily controlled by electrospinning parameters, such as applied voltage, distance from tip to collector, and a concentration of the polymer solution [10–12]. Poly(L-lactic acid) (PLLA) has attracted attention because of its botanical origin and biodegradability [13, 14]. Preparation of electrospun PLLA composite membranes containing hydroxyapatite nanoparticles [15], montmorillonite nano-sized platelets [16], and bioactive glass nanofillers [17] has been reported.

The diameter of an electrospun PLLA fiber is reported to be in the broad range of a few hundred nanometers to a few micrometers, depending on the viscosity of the PLLA solution [18]. It is well known that, among all the biodegradable polymers, PLLA exhibits relatively better mechanical

T. Okuyama · E. H. Ishida
Graduate School of Environmental Studies, Tohoku University,
6-6-20 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

H. Maeda (✉)
Center for Fostering Young and Innovative Researchers,
Nagoya Institute of Technology, Gokiso-cho, Showa-ku,
Nagoya 466-8555, Japan
e-mail: maeda.hirotaka@nitech.ac.jp

strength. Therefore, we focused on PLLA as a matrix. We considered that microscopic tobermorite particles are exposed to the PLLA fiber surface by controlling the fiber's diameter. Our strategy for the synthesis of a novel PLLA composite membrane suitable for the purification of effluents is to introduce successive pores into the polymer membrane to realize high permeability, and to coat the skeleton surface of the membrane with tobermorite for the removal of harmful matter. The objective of this study is to synthesize PLLA/tobermorite nonwoven composite membranes using the electrospinning method.

Experimental

Preparation of composite membrane

The average particle size of tobermorite (Japan Insulation Corporation, Ltd) used in this study was measured to be 12 μm by a laser diffractometer. To prevent the aggregation of tobermorite particles, a cationic surfactant; poly(dialyldimethylammoniumchloride) (PDDA, SIGMA-ALDRICH Corporation, 20 wt% in water) was added to the slurry consisting of tobermorite powders and distilled water (mass ratio of solid/water = 30 mass%), and the mixture was then dried in a desiccator. The mass ratio of PDDA/tobermorite was 20 mass%. Plate crystals, which are a crystal habit of tobermorite, were observed in the scanning electron microscopy (SEM) image, as shown in Fig. 1. It is proposed that the addition of PDDA has little effect on the shape of tobermorite.

Crystalline PLLA (Mitsui chemicals, Inc., LACEA, H-100, 170 kDa) was used as the polymer material in this study. PLLA was adjusted to a 6.3 mass% solution using chloroform (Wako Pure Chemical Industries, Ltd.) as a solvent. Chloroform is reported to be easy to use during electrospinning because of its appropriate evaporation [19]. The modified tobermorite powders were added to the PLLA solution and the mixture was stirred for 1 h. The mass ratio of tobermorite/PLLA was 60 mass%.

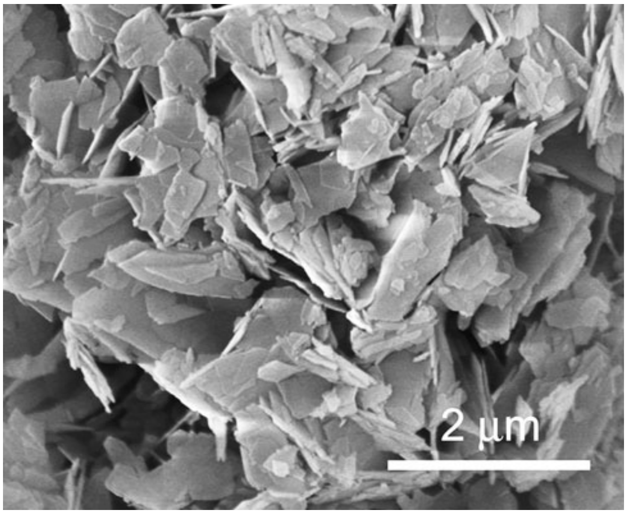

Fig. 1 SEM image of surface-modified tobermorite

The mixture was poured into a glass syringe with an 18 G stainless steel needle. Electrospinning was carried out at a voltage of 15 kV applied to the needle using a high voltage supplier. The fibers were collected on a grounded plate that was covered with aluminum foils located at a distance of 15 cm from the needle. The mixture was loaded at a feed rate of 0.6 mL/h for 1 h.

Characterization of the composite membrane

The membrane structure was examined by SEM (Hitachi Corporation, S4100). The fiber diameter was measured for at least 300 points by image-editing software: Scion Images (Scion Corporation). Viscosity of the mixture was measured using an ultrasonic viscometer (Fuji Ultrasonic Engineering Corporation, FUV-1, Model-104) at 20.0 °C. Thermogravimetric differential thermal analysis (TG-DTA) (Rigaku Corporation, TG8120) and a differential scanning calorimeter (DSC) (Rigaku Corporation, DSC8230) were used for the analyzing thermal properties at a heating rate of 5 °C/min in air (flow rate: 20 mL/min). The crystalline phases were identified by X-ray diffraction analysis (XRD) (Rigaku Corporation, RINT-2200VL) using CuKα radiation.

Results and discussion

Figure 2 shows XRD patterns and pictures of a (a) pure PLLA membrane, (b) PLLA/tobermorite membrane, (c) PLLA/surface-modified tobermorite membrane, and (d) PLLA membrane prepared by the casting method. The XRD patterns revealed that tobermorite exists in both PLLA/tobermorite and PLLA/surface-modified tobermorite composite membranes. Crystalline PLLA peaks were clearly observed in the XRD pattern of the PLLA membrane prepared by the casting method. On the other hand, few crystalline PLLA peaks were observed in the three samples prepared by the electrospinning method despite crystalline PLLA being used as the starting material. This implies that amorphous PLLA was formed during electrospinning. Figure 3 shows thermogravimetric (TG) analysis of the (a) pure PLLA membrane, (b) PLLA/tobermorite membrane, (c) PLLA/surface-modified tobermorite membrane, and (d) PLLA membrane that was prepared by casting method. The thermal decomposition of the PLLA membrane prepared by the casting method occurred only at around 270 °C. Note that we observed two instances of weight loss,

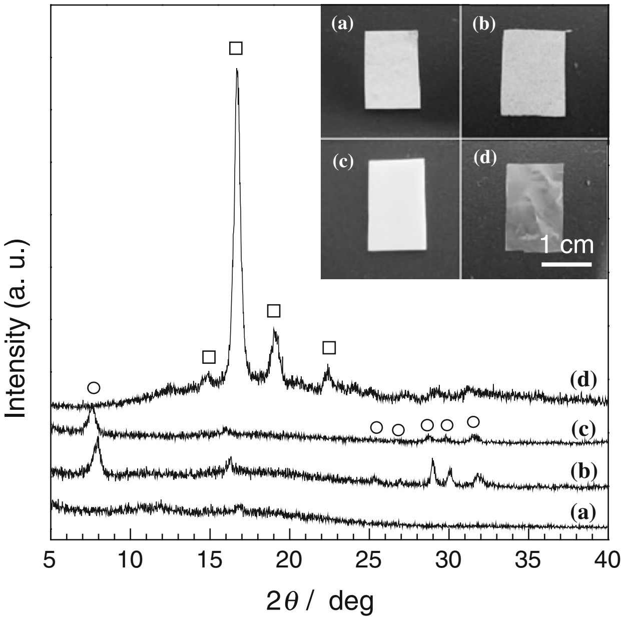

Fig. 2 XRD patterns and pictures of *a* electrospun pure PLLA membrane, *b* electrospun PLLA/tobermorite membrane, *c* electrospun PLLA/surface-modified tobermorite membrane, and **d** casted PLLA membrane. *Open circle* indicates Tobermorite and *open square* indicates PLLA. Pure PLLA membrane and PDDA-free tobermorite/PLLA membrane (tobermorite/PLLA = 60 mass%), prepared under the same experimental conditions, were used as control materials for comparison with the sample (PLLA/surface-modified tobermorite membrane). To examine the effect of electrospinning, a pure PLLA membrane was prepared by casting pure PLLA solution

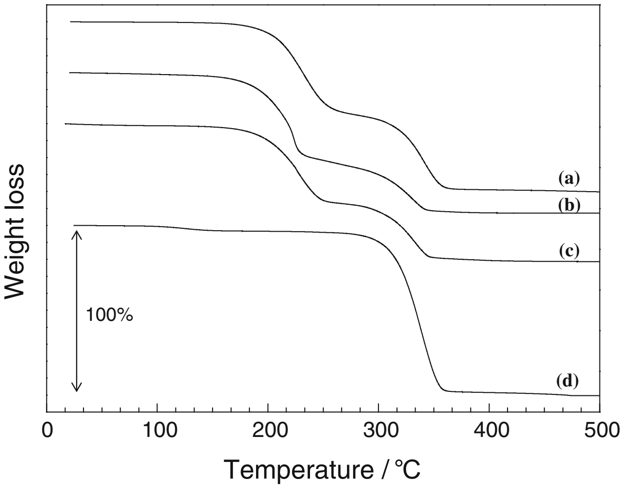

Fig. 3 TG curves of *a* electrospun pure PLLA membrane, *b* electrospun PLLA/tobermorite membrane, *c* electrospun PLLA/surface-modified tobermorite membrane, and *d* casted PLLA membrane

at around 170 and 270 °C, in all the samples prepared by the electrospinning method: (a) 55%, (b) 43%, and (c) 44% at around 170 °C; (a) 45%, (b) 34%, and (c) 34% at around 270 °C. The two instances of weight loss, at 170 and 270 °C, in the TG curve of the sample are believed to be due to the decomposition of amorphous and crystalline PLLA, respectively. During the electrospinning process, rapid evaporation of chloroform causes the amorphous formation in a part of PLLA. This evaporation is supposed to occur more rapidly at the fiber surface. That is, the fiber constructs two layers that have a core–shell structure, which is in the crystalline phase at the center of the fiber and the amorphous phase at the surface. TG analysis for tobermorite showed about 11% of weight loss by 500 °C, and gave an estimate of 22.4 mass% of tobermorite content in the sample.

Figure 4 shows SEM micrographs and fiber diameter distribution curves for the (a) pure PLLA membrane, (b) PLLA/tobermorite membrane, and (c) PLLA/surface-modified tobermorite membrane. The pure PLLA membrane consists of both uniform and smooth fibers. The PLLA/tobermorite composite membrane represents irregular lines of rough fibers. This roughness is expected to be due to the inclusion of tobermorite. The PLLA/surface-modified tobermorite composite membrane consists of relatively narrow fibers. This fiber also has a rough surface, which is due to the inclusion of tobermorite. No plate crystals, which are a crystal habit of tobermorite, are observed at either PLLA/tobermorite or PLLA/surface-modified tobermorite fiber surface in the SEM micrographs. Therefore, in the composite membrane, tobermorite was covered with the PLLA fibers. Table 1 shows the average fiber diameter D_{50} of these samples and the viscosity of the mixture solutions before electrospinning. The average fiber diameter D_{50} of the sample was determined to be about 2.6 μm, which was about one-tenth of 27.4 μm for the PDDA-free tobermorite/PLLA composite membrane that contain 22.0 mass% tobermorite as the same content of samples, which was prepared under the same experimental conditions. In general, the diameters of electrospun fibers increase with increasing viscosity of the solution. However, the fiber diameters of the samples decreased despite the increasing viscosity of the precursor solutions that contained surface-modified tobermorite. It is reported that the diameter of an electrospun fiber decreases when charge density increases [20]. These tobermorite particles in the mixture may repel each other because of the cationic repulsive force that is due to the PDDA coating on tobermorite. The repulsive force causes an increase in the charge density of the solution, leading to a decrease in the diameter of the fiber in the samples. The average fiber diameter D_{50} for PLLA/surface-modified tobermorite composite membrane is also smaller than the average fiber diameter D_{50} for the only PLLA membrane prepared under the same conditions as a control (11.5 μm). The fiber diameter tends to decrease as surface tension decreases [21]. The surface tension of the precursor solution is proposed to be reduced because of the introduction of

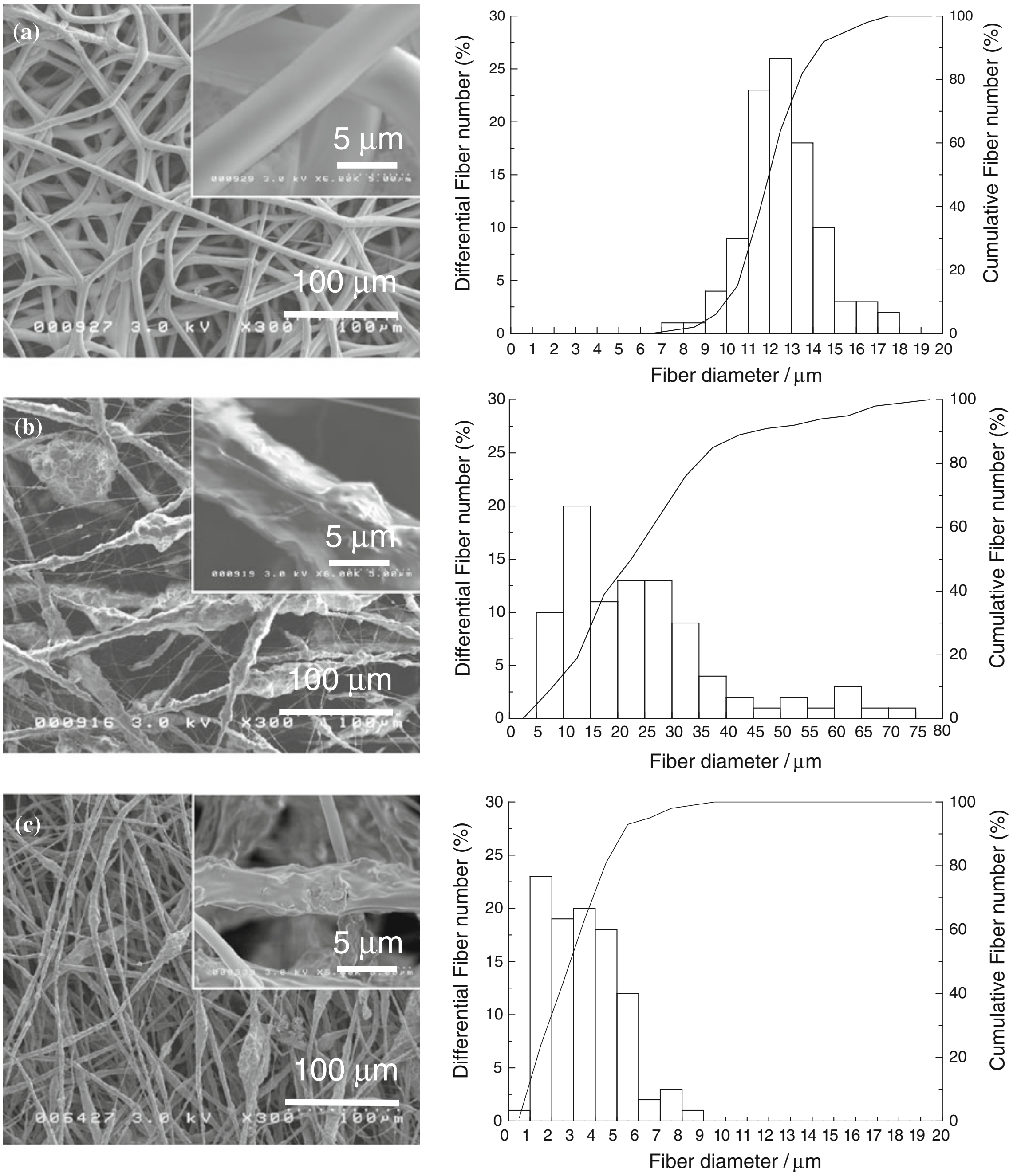

Fig. 4 SEM images and fiber diameter distribution curves for **a** pure PLLA membrane, **b** PLLA/tobermorite membrane, and **c** PLLA/surface-modified tobermorite membrane

tobermorite coated with PDDA into the PLLA solution. The fiber diameter of the samples is shown to be controlled by not only an increase in repulsive force due to the PDDA, but also the decline in surface tension that is due to the introduction of tobermorite coated with PDDA.

Although no tobermorite particle was observed on the fiber surface of the PLLA/surface-modified tobermorite membrane, the fibers were sufficiently narrow. To expose tobermorite particles on the fiber surface, amorphous PLLA should be eliminated from the fiber surface by heat treatment, as shown in the thermal analysis (Fig. 4). However, the sample contained ~45% of amorphous PLLA. Hence, elimination of amorphous PLLA could lead to the collapse of the membrane structure. To minimize this risk, we attempted to increase the ratio of crystalline PLLA in the sample. Crystalline PLLA was reported to exhibit higher chemical durability as compared with amorphous PLLA [22]. Crystalline PLLA is more favorable for use as

Table 1 PLLA/PDDA/tobermorite ratio in the precursor solutions, viscosity of solutions measured by ultrasonic viscometer at 20 °C, and average fiber diameter D_{50} of samples measured by SEM images and image-editing software, Scion Images (Scion corporation)

	PLLA/PDDA/tobermorite ratio (w/w/w) in the precursor solution	Viscosity of solution (mPa S)	Average fiber diameter (μm)
PLLA	100/–/–	74.1 ± 3.8	11.5 ± 2.2
PLLA/tobermorite	100/–/60	102.2 ± 8.1	27.4 ± 15.6
PLLA/surface-modified tobermorite	100/12/60	127.2 ± 4.8	2.4 ± 2.1

a filter material. In our preliminary experiments, the glass transition, cold crystallization, and melting temperatures (T_g, T_{cc}, and T_m, respectively) of the PLLA/surface-modified tobermorite membrane were observed at ~40, ~70, and ~160 °C, respectively, by DSC measurement. The PLLA/surface-modified tobermorite membrane underwent crystallization treatment at 130 °C for 10 h. Figure 5 shows the XRD pattern and a picture of the PLLA/surface-modified tobermorite membrane after crystallization treatment. A broad peak at around 16° (2θ) that corresponds to amorphous PLLA decreased after crystallization treatment. The TG thermograph of the sample after crystallization treatment showed that weight loss decreased from ~45 to ~17% at around 170 °C. On the other hand, the rate of weight loss of crystalline PLLA at the higher temperature of about ~250 °C increased by 28%. It is reported that the structure of tobermorite stabilizes up to 300 °C [9]. Consideration was given to exposing tobermorite at the fiber surfaces by heat treatment at 250 °C to eliminate the remaining amorphous PLLA.

After crystallization treatment at 130 °C, the PLLA/surface-modified tobermorite membrane was heated at 250 °C for 1 h (amorphous PLLA elimination treatment). In the TG curves of the sample after elimination treatment, no weight loss was observed at around 170 °C. This indicates that treatment with the two different temperatures is successful in the elimination of amorphous PLLA. Figure 6 shows XRD pattern and a picture of the PLLA/surface-modified tobermorite composite membrane after elimination treatment. The XRD pattern shows the existence of crystalline PLLA and tobermorite after elimination treatment, following which the membrane shrunk by 55% for the area and colored by the degradation of carbon compound. The membrane exhibited flexibility even when bent by fingers. Therefore, it is expected to be sufficiently strong for handling. Figure 7 shows the SEM micrograph and fiber diameter distribution curve for the PLLA/surface-modified tobermorite membrane after elimination treatment. It is clear that the fiber structure was maintained even after elimination treatment above T_m, and numerous plate-like tobermorite powders were observed at the fiber surfaces. After elimination treatment, the sample exhibited about 3.9 μm of the average fiber diameter D_{50}. When comparing the fiber diameter distribution of the sample before and after crystallization and elimination treatment (Figs. 4c, 7), the percentage of fibers having diameters below 3 μm decreased after the treatment, while the percentage with diameter above 3 μm increased. Narrow

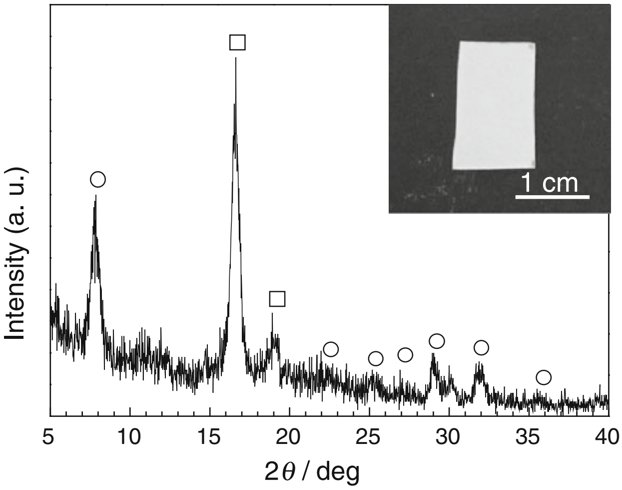

Fig. 5 XRD pattern and picture of PLLA/surface-modified tobermorite membrane after crystallization treatment. *Open circle* indicates Tobermorite and *open square* indicates PLLA

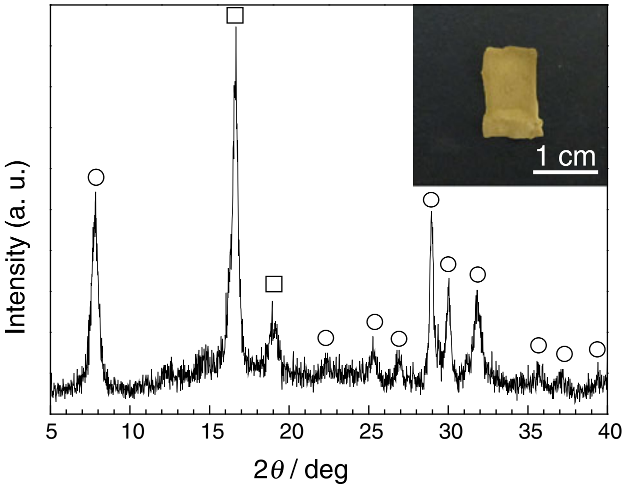

Fig. 6 XRD pattern and picture of PLLA/surface-modified tobermorite membrane after elimination treatment. *Open circle* indicates Tobermorite and *open square* indicates PLLA

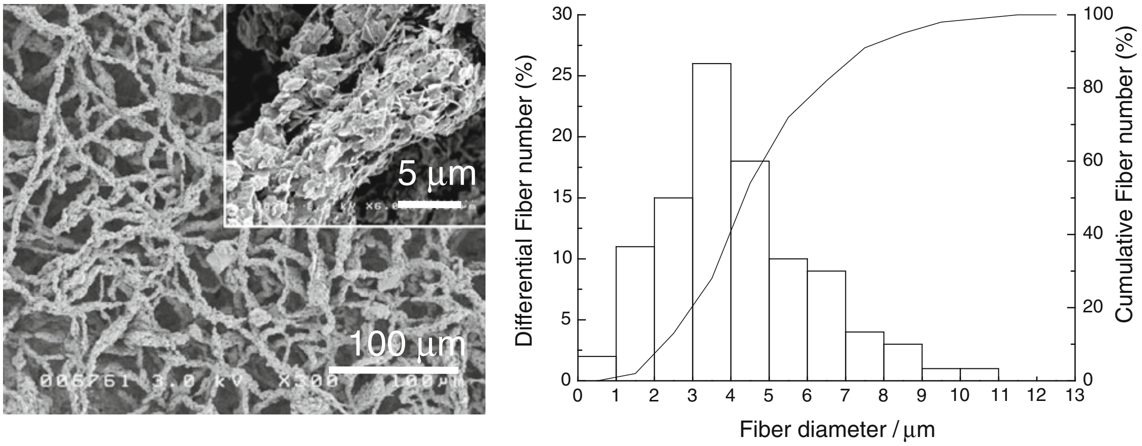

Fig. 7 SEM images and fiber diameter distribution curve for PLLA/surface-modified tobermorite membrane after elimination treatment

fibers containing a few tobermorite particles melted easily with treatment above T_m. On the other hand, thick fibers containing a specific amount of tobermorite maintained a fiber structure because of the presence of tobermorite. Melted narrow fibers are proposed to bind with the adjacent thick fibers, resulting in an increase in the fiber diameter. The composite membrane having numerous ~10 µm interconnected pores is capable of passing water and removing impurities. The electrospun fibrous crystalline PLLA/tobermorite composite porous membrane that has undergone elimination treatment is a promising filter material for wastewater treatment because of its porous structure and the existence of tobermorite particles at the fiber surface. In our preliminary experiments regarding the size of the composite membrane, a larger membrane was obtained after electrospinning for a long time, while a shorter membrane obtained after electrospinning for a short time. Further research on the size control of the composite membrane is currently in progress.

Conclusion

A novel nonwoven composite membrane consisting of fibers having several microscopic diameters were prepared by electrospinning using a mixture of PDDA surface-modified tobermorite and PLLA. The repulsive force of the cationic surfactant and the reduction of surface tension in the mixture solution played an important role in the preparation of fibers with microscopic diameters. Heat treatment in two stages at 130 °C (crystallization of amorphous PLLA) and 250 °C (amorphous PLLA elimination), led to the exposure of tobermorite at the fiber surfaces. The membrane structure was maintained by crystalline PLLA and tobermorite.

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