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RESEARCH ARTICLE

Mechanical and degradation properties of polycaprolactone/ zeolite electrospun membrane

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Abstract

Polycaprolactone (PCL) is one of the synthetic polymers used in biomedical applications. PCL has several advantages including biocompatibility, biodegradability and mechanical flexibility. On the other hand, zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. Electrospinning is a promising technique to produce membranes by applying high voltage electricity. In this research, an electrospinning technique was used to fabricate the electrospun membrane based on PCL and zeolite. In order to produce electrospun membrane, 15% (w/v) of PCL polymer solution was dissolved in acetone and 20% (w/v) zeolite was incorporated into the PCL polymer solution. The diameter range of fiber was 2-6 µm. Zeolite nanoparticles were distributed homogenously into the fibers. EDX spectrum confirmed the presence of zeolite throughout the membrane. Mechanical testing revealed that the bi-layered membrane had better mechanical properties than only PCL and PCL/Zeolite membrane. In-vitro degradation experiment was carried out for 21 days and the membranes were characterized after the experiment. The membrane can be potentially used as microfiltration unit to entrap silver contaminants in drinking water. Apart of that, the membranes are prepared with biodegradable, biocompatible, non-toxic materials which are eco-friendly.

Keywords: Polycaprolactone, zeolite, electrospinning, degradation

INTRODUCTION

Water plays an essential role in our life. Water is used in the human body for transporting, dissolving and replenishing nutrients and organic matters, while carrying away waste materials from the body. Furthermore, in the body, it aids the activities of fluids, tissues, cells, lymph, blood and glandular secretions (Homaeigohar *et al.,* 2014). Water supply from the ground sources inflicts a dilemma towards the human being nowadays with the presence of the heavy metal which leads into the health problem. The exploitation of the heavy metal causes water contamination to be well established and understood since thousands of years ago (Nalbandian *et al.,* 2016). Many researchers now have focused on using nanofiber membranes to overcome the problem. As an example, the consumption of polystyrene (PS)/TiO_2 composite nanofiber membrane by electrospinning process was made for removing Cu^{2+} from water (Wanjale *et al.,* 2016). Electrospinning is a promising technique to fabricate membrane. The consolidation of the electrospraying phenomenon, which is based on a physical and electrical mechanism, known as electrospinning technique (Hassan *et al.,* 2014; Nagamine *et al.,* 2016) is one of the methods of production of electrospun membranes. It is a simple and potential technique for the fabrication of multilevel ultrafine fibers by applying a high voltage to create an electrically charged jet of polymer solution from the syringe (Nasreen *et al.,* 2013; Li *et al.,* 2015).

In this research, polycaprolactone (PCL) and zeolites were used to produce composite membrane and the characteristics of the membranes were evaluated. PCL is one of the popular synthetic aliphatic polymers (Lim *et al.,* 2015). PCL has many advantages, including mechanical flexibility. However, high hydrophobicity and low water absorptivity have become its point of issues of PCL drawbacks (Hong *et al.,* 2011; Cooke *et al.,* 2016). On the other hand, zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. Their unique three-dimensional network of aluminium and silicon tetrahedral linked by shared oxygen atom structure produces specific pore sizes and large surface area. It can be used in advance application, for instance, molecular sieves, adsorbents, catalysts and etc (Mallapur *et al.,* 2013). It is expected that the membranes fabricated from PCL, PCL/Zeolite and bi-layered PCL/Zeolite membrane will be advantageous to remove silver in drinking water due to their suitable morphology and mechanical properties, as well as slow degradation characteristics and based on ultrafiltration or nanofiltration technique as the membranes will contain micropores together with a well-known adsorbant, Zeolite.

EXPERIMENTAL

Materials

Poly (caprolactone) (PCL) (MW: 70,000-90,000) was purchased from Sigma and Beta Zeolite Powder (0.55-0.70 nm pore) (MR: 40)

was purchased from ACS Material. Acetone was analytical grade and used as solvents. Silver nanopowder (<100nm particle size) and PVP (MW: 107.87) were purchased from Sigma.

Fabrication of membrane

In order to produce 15% w/v of poly(caprolactone) solution, 1.50g of PCL was dissolved in 10ml of acetone and magnetically stirred at 300 rpm and 50°C for an hour. On the other hand, 20% w/v or 0.30g of zeolite powder was added into the PCL solution and stirred magnetically to produce PCL/Zeolite solution. After that, the mixture solution of PCL and Zeolite was homogenized at the speed of 16,000~20,000 /min for 3 minutes. The membrane was fabricated by electrospinning technique.

Ultrafine nanofibers from micro to nano scale and varied morphologies can be fabricated with ease by a versatile technique called electrospinning. The syringe containing pure 15% PCL polymer solution was placed on a syringe pump. An aluminium foil of $10cm \times 10cm$ size was placed as a collector plate and electrospinning was conducted using the parameters described elsewhere (Rusli *et al.,* 2017).

For the fabrication of layer by layer (PCL and PCL/Zeolite) membrane, all the steps involved in the electrospinning process were repeated and the parameters were remained constant. The duration for the electrospinning process was 1 hour for PCL solution. After that, the same collector was used to collect PCL/Zeolite membrane on top of the PCL membrane. The duration for electrospinning process (PCL/Zeolite) took 1 hour as well and the whole process to fabricate the PCL and PCL/Zeolite layer by layer took about 2 hours.

Morphology of fabricated membranes

A scanning electron microscope (SEM, Hitachi TM3000, Japan) was used to observe and characterize the morphology of membrane. An ImageJ software was utilized to measure the diameters and pore sizes of membranes. 40 reading of the diameter measurements were taken, and the averages were calculated.

Elemental analysis of membranes

An energy dispersive X-ray (EDX) was used for the elemental analysis of the sample. Apart from that, EDX mapping was also carried out to find out the presence of specific elements that were interpreted in different colors.

Mechanical analysis of membranes

Mechanical testing was carried out on PCL, PCL/Zeolite and bi-layered PCL, and PCL/Zeolite membranes. The experiment was conducted by using the universal testing machine (LRX 2.5kN tensile tester, Lloyd Instruments Ltd) at the speed of 10 mm/min.

In vitro degradation and water uptake

In vitro degradation testing was carried out to investigate the weight loss of membrane and to test biodegradable polymer-based membrane integrity. All the samples were cut into 10×10 mm^2 (Fig. 1) pieces and placed into a centrifuge tube filled with a model water containing silver nanoparticles. Similar methods were described previously to study the adsorption kinetics (Liu *et.al,* 2010). The tubes were then placed inside a water bath at room temperature for several weeks. The silver containg model water was prepared by mixing 0.005g of silver nanoparticles in 100 ml of distilled water to mimic the water contaminated by silver metal. The pH of the model water was 7.0. The observation was made on day 7, 14 and 21 for all fabricated membranes. Before the experiment started, the initial weight of the PCL, PCL/Zeolite, as well as PCL-PCL/Zeolite layer by layer membrane was determined by weighing membranes.

$$\text{Weight loss (\%)} = \frac{Wi - Wf}{Wi} \times 100 \quad (1)$$

Where Wi and Wf are the specimen weights before and after soaking in silver containing water.

After a specific time, membranes were removed from the model water. The membranes were then washed out with distilled water to remove any residual silver and dried until it reached the constant weight. After the membranes were dried out, they were weighed. The readings of the membranes were recorded and compared with the initial reading obtained at the beginning of the experiment. Water uptake was measured using distilled water according to the equation below (Sultana *et al.,* 2012):

$$\text{Water uptake (\%)} = \frac{Ww - Wd}{Wd} \times 100 \quad (2)$$

Where Wd is the initial weight and Ww indicates the measured weight wet condition.

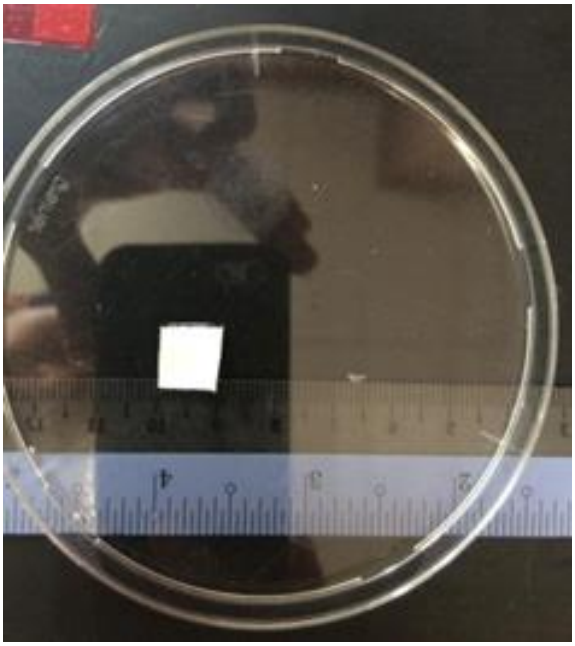

Fig. 1 Sample specimen (10×10 mm^2).

RESULTS AND DISCUSSION

Membrane morphology should remain unchanged after in vitro degradation experiment to be used in microfiltration application. Fig. 2 shows the membranes morphology after undergoing *in-vitro* degradation tests for 7days, 14 days and 21 days. The morphology of the membranes remained unchanged after 21 days. No broken fibers were observed after the degradation test in silver containing water. These findings proved that the membranes did not degrade during the time period. Polymer degradation occurs due to the hydrolysis of polymer bonds caused by the hydrolytic attacks of water in polymer membrane (Sultana *et al.,* 2012). Zeolites were still incorporated in the membranes as the EDX spectrum in Fig. 3 confirmed the presence of Zeolite and silver that diffused to the membrane after the degradation period. The elemental analyses were presented in Table 1.

Table 1 Summary result of EDX spectrums of PCL/Zeolite nanofiber.

Element	Weight %	Weight %	Atomic %
Carbon	57.589	0.651	65.999
Oxygen	36.477	0.661	31.384
Aluminum	0.289	0.049	0.147
Silicon	4.827	0.116	2.366
Silver	0.819	0.158	0.104

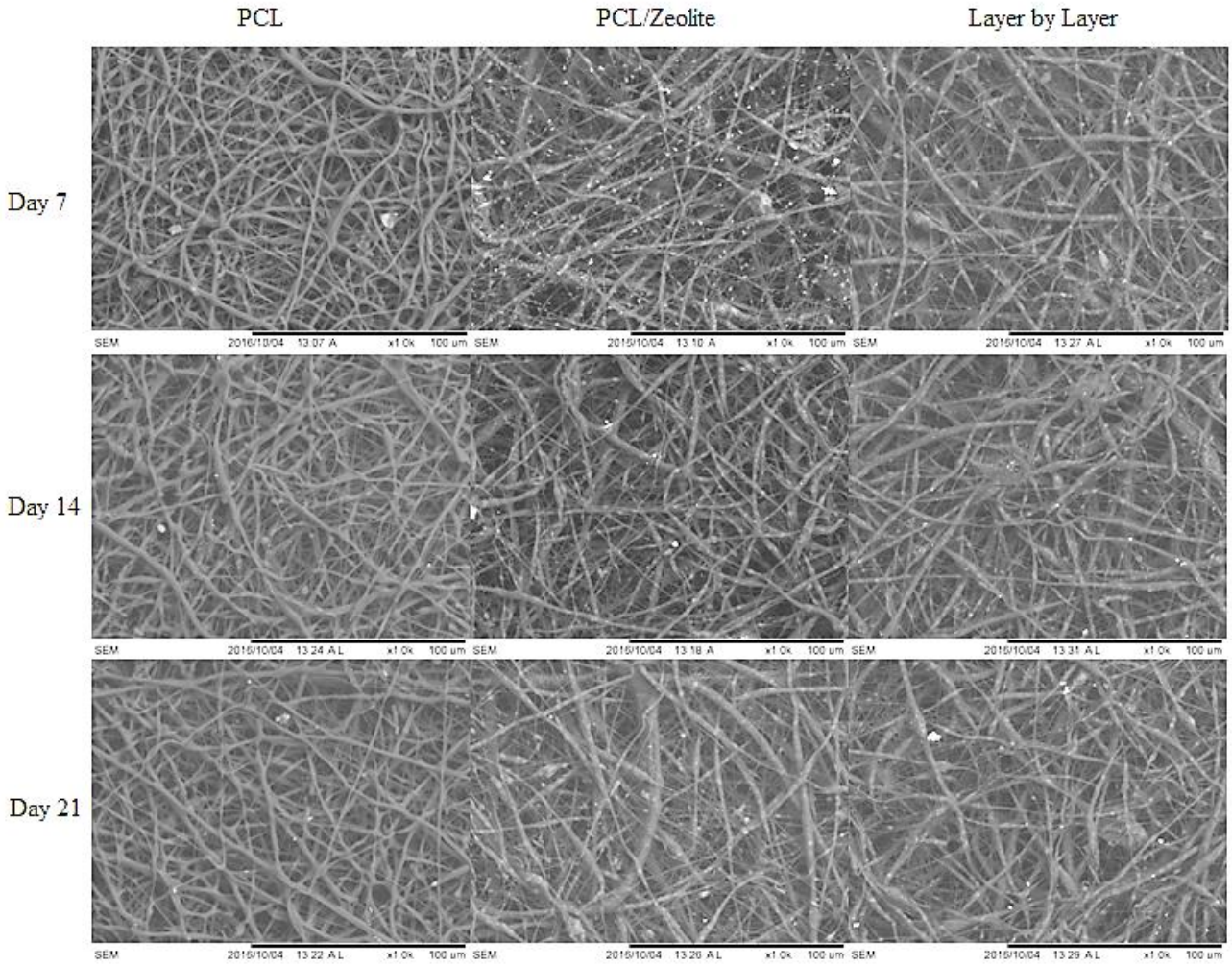

Fig. 2 SEM micrographs of membranes after in vitro testing of 7days, 14 days and 21 days.

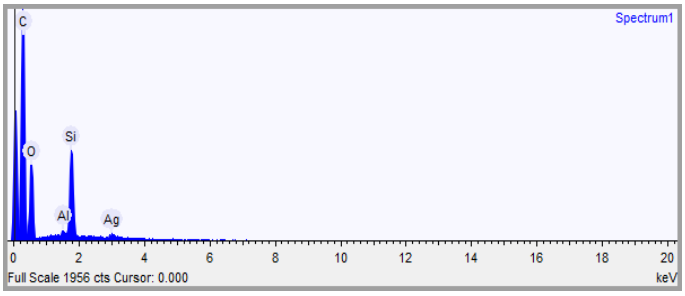

Fig. 3 EDX spectrum of PCL/Zeolite membrane with entrapped Ag.

Mechanical properties can be influenced by various factors such as spinning voltage, polymer solution concentration, and electric properties of the polymer solution (Tan *et al.*, 2005). These factors can affect the phenomenon of deformation of the membranes. Fig. 4 shows the stress–strain curves obtained for PCL, PCL/Zeolite and layer by layer of PCL and PCL/zeolite fibrous membranes. From Fig. 4, the maximum stress recorded for as-fabricated PCL, PCL/Zeolite as well as PCL and PCL/Zeolite layer by layer membrane was 1.94 MPa, 1.88 MPa and 2.02 MPa, respectively. The Young's modulus calculated for PCL membrane and PCL/Zeolite membrane was 3.16 MPa and 2.03 MPa.

On the other hand, bi-layered PCL and PCl/Zeolite had a modulus of 5.8 MPa. This result proved that the bi-layered membrane had better tensile properties than only PCL or PCL/Zeolite membranes. After degradation, the mechanical properties remained unchanged.

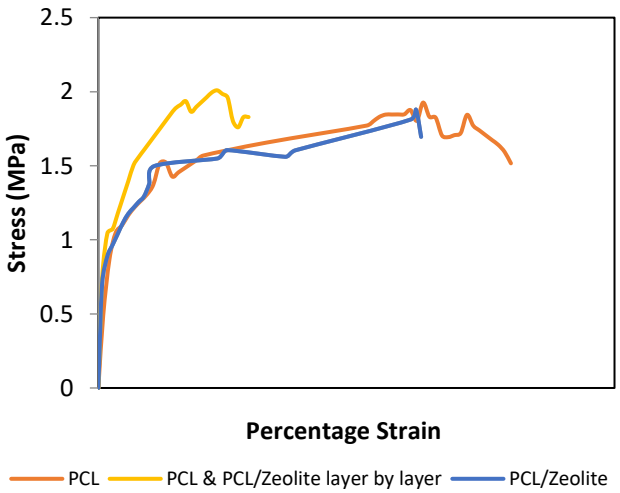

Fig. 4 Tensile stress-strain diagram for different fibers.

The water uptake behavior of the membranes is an important property for the membrane fabricated from biodegradable polymers. As the membranes are going to be used in molecular sieve application, swelling of the membrane can occur. The swollen membranes can lose their mechanical strength properties. However, PCL is well known for its hydrophobicity and low water absorption characteristics (Hong *et al.*, 2011). PCL has slow degradation rate (Lim *et al.*, 2015). It can retain its properties for a long time period. The degradation products of PCL polymers are nontoxic if they are being used continuously. Figure 5 displays the percentage of water uptake for PCL, PCL/Zeolite and PCL and PCL/Zeolite layer by layer membrane. As shown in Figure 5, PCL membranes absorbed less water compared to PCL/Zeolite membrane. At the end of 60 minutes, PCL and PCL/Zeolite layer by layer reached the highest percentage (149%) of water uptake while PCL and PCL/Zeolite membranes obtained water uptakes of 89% and 194%, respectively.

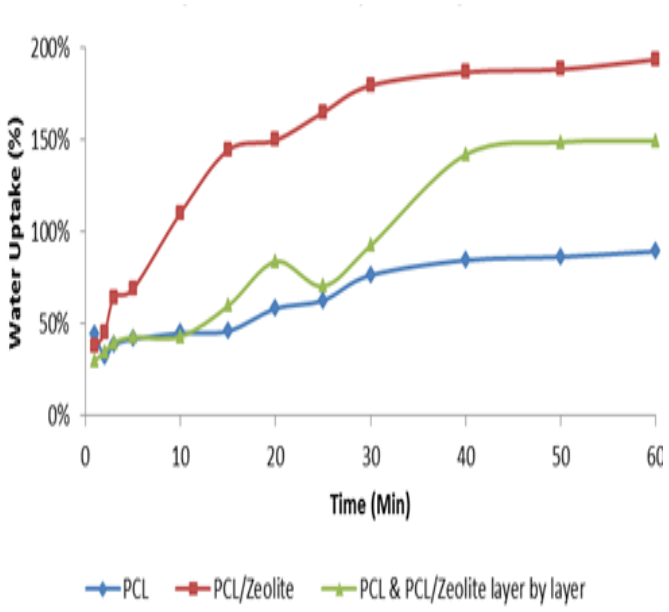

Fig. 5 Percentage of water uptake and time.

Comparison of the fiber diameter was done by determining the diameter of the as-fabricated membranes and the membranes after degradation experiment. The purpose of this comparison was to check the durability of the membrane after the immersion phase for 21 days. Damaged membranes will show the characteristics of erosion or swollen. Figure 6 shows the fiber diameter distribution for PCL, PCL/Zeolite as well as PCL and PCL/Zeolite layer by layer membrane respectively for as fabricated and degraded membranes. By comparing these findings, it was observed that the distributions of the fibers were not significantly different. From the results of PCL membranes, the average diameter for as-fabricated membrane was 2.29µm while the average diameter of PCL membrane was increased to 2.31µm after 21 days of degradation test. However, the change is not significant and still within specified scale that suitable for molecular sieve application (Pillay *et al.*, 2013). For PCL/Zeolite membrane, average fiber diameter at the initial state was 2.62µm, slightly decreased to 2.39µm. Meanwhile, PCL and PCL/Zeolite layer by layer membrane's average diameter was increased slightly to 2.57µm after the degradation test, compared to the initial value which was 2.45 µm.

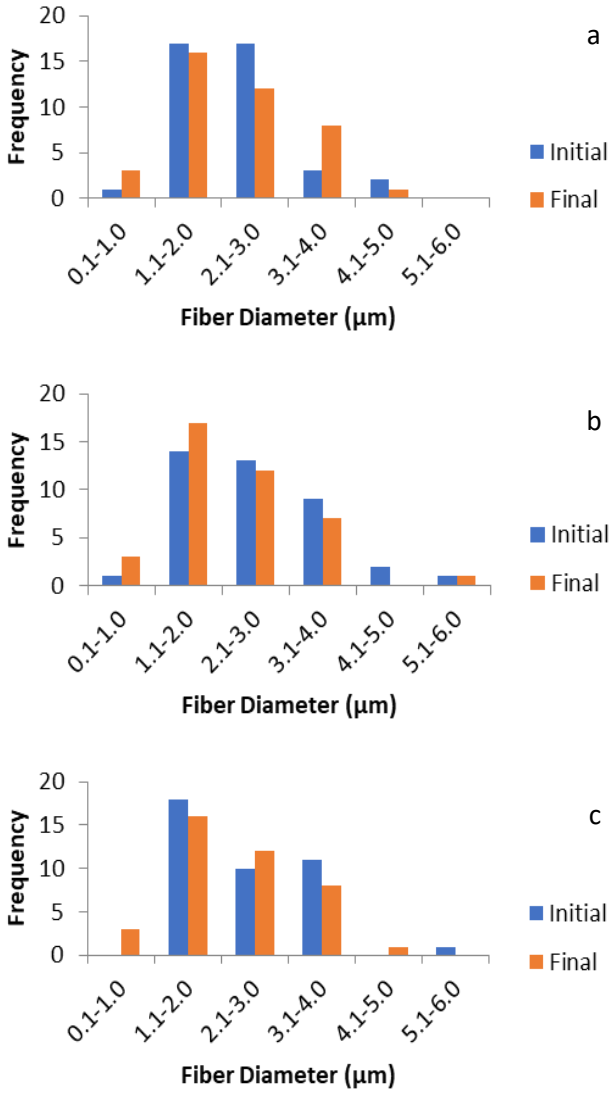

Fig. 6 Fiber diameter of as-fabricated (initial) and degraded (final) membranes: (a) PCL, (b) PCL/Zeolite, and (c) Layer by layer.

CONCLUSIONS

Electrospun membrane based on biodegradable polymer PCL and Zeolite was successfully fabricated and characterized. The young modulus was higher in bi-layered membrane than that of PCL and PCL/Zeolite membranes. As PCL has slow degradation rate, no weight loss or no change in morphology was observed during 21 days of in vitro degradation test. Water uptake was increased with time due to the capillary action and the presence of pores in the membrane. PCL/Zeolite and layer by layer membrane has higher water uptake than pure PCL membrane. No significant change in fiber diameter was observed during the experimental time period.

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