

Fabrication of Biodegradable Poly(caprolactone) (PCL) and Poly(3-Hydroxybutyrate-Co-3-Hydroxyvalerate) (PHBV) Electrospun Composite Membrane for Oil-Water Separation

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Abstract

The biodegradable polymer demonstrates significant potential for addressing the critical environmental challenges associated with oil spills; however, the cellular film structure and hydrophobic characteristics of the polymer restrict their efficacy. In this study, a biodegradable thin membrane composed of a blend of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(caprolactone) (PCL) was fabricated utilizing the electrospinning technique. The membrane exhibited an adsorption capacity for cooking oil of 10.8 g/g, and Fourier-transform infrared spectroscopy (FTIR) analysis confirmed the anticipated chemical structures, revealing no evidence of chemical interactions between PHBV and PCL. This research presents an environmentally friendly and straightforward approach for fabricating biodegradable membrane structure with exceptional oil-water separation capabilities.

Keywords

Poly(caprolactone), Poly(3-Hydroxybutyrate-Co-3-Hydroxyvalerate), Electrospinning, Biodegradable Membranes, Oil-Water Separation

1. Introduction

The membrane technology has been demonstrated to be one of the most effective methods for the separation of oil from oil-water mixtures, and it has found

extensive application in various industries, including food processing, pharmaceuticals, desalination, and fuel cells. When compared to traditional methods such as chemical treatment [1]-[3], membrane separation technology provides superior oil removal efficiency, consistent effluent quality, and reduced energy costs. Consequently, it is regarded as one of the most efficient approaches for separating oil-water mixtures across a diverse array of industrial effluents [4] [5].

Electrospinning is a widely utilized technique for the fabrication of porous polymeric matrices composed of submicron fibers. Poly(ϵ -caprolactone) (PCL) is a polyester characterized by its considerable mechanical strength and flexibility, in addition to its biodegradable, biocompatible, and non-toxic properties [6]-[8]. Similarly, Poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) exhibits biodegradability and biocompatibility, making it applicable in diverse fields, including the plastic products and drug releasing systems [9]. However, despite these advantageous characteristics, PHBV presents certain limitations that hinder its application in load-bearing contexts, notably its insufficient flexibility and high brittleness. To enhance the mechanical properties of PHBV and expand its range of applications, the incorporation of other polymers is warranted. The blending of PCL with PHBV represents a promising strategy to create a structure that is relatively elastic, physically stable, and better platform of cellular activities, thereby broadening its potential applications.

Recent research in oil-water separation technology has increasingly focused on the application of electrospinning techniques to develop nanofibrous absorbent and filtration membranes [10]. Over the past three decades, these electrospun nanofibers have garnered significant attention for their utility in oil-water separation processes [11]. The unique characteristics of electrospun nanofibers, including their high specific surface areas [12], interconnected pore structures, nanoscale pore sizes, and the ability to merge active chemical functionalities at the nanoscale [13], contribute to their effectiveness. Furthermore, these membranes exhibit low initial solid densities, which enhances their permeability during oil-water separation process. This combination of properties not only improves separation efficiency but also simplifies the process requirements. Additionally, the ability to control fiber diameters, which can range from tens of nanometers to micrometer scale, makes electrospun fibrous membranes particularly valid for oil-water separation.

The development of efficient and straightforward methods for the separation of oil/water mixtures continues to pose significant challenges that remain unresolved. Recent literature has documented advancements involving polymer-based filtration membranes created through phase separation techniques with adjustable pore sizes [14]-[16]. However, these membranes are hindered by issues related to low flux and fouling. Recently, nanofibrous membranes, characterized by high porosity and surface area to volume ratio, have demonstrated considerable capacity for the separation of emulsified oil/water phase structure [17]-[19]. Various fabrication methods for nanofibrous membranes exist, with electrospinning

emerging as the preferred technique due to its relative simplicity. Electrospun nanofiber membranes represent a leading category of advanced fibrous materials, offering advantages such as tuneable wettability, extensive surface area, and high porosity [20] [21].

Huang *et al.* proposed an innovative and scalable methodology for the synthesis of in situ superhydrophobic and superoleophilic electrospun nanofibrous membranes, which effectively facilitate the separation of water-in-oil micro-emulsions. These membranes exhibit exceptionally high flux, favorable antifouling characteristics, thermal stability, and endurance [11]. Subsequently, Tang *et al.* developed a membrane characterized by high thermal stability and outstanding mechanical properties, achieved through a straightforward integration of electrospun poly(m-phenylene isophthalamide) (PMIA) nanofibers with an in situ polymerized F-PBZ functional layer that incorporated SiO₂ nanoparticles for gravity-driven oil-water separation [22]. In addition, nanofibrous membrane exhibiting superhydrophilicity and underwater superoleophobicity, which was fabricated by electrospinning cellulosic modified polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) [23]. Furthermore, a superhydrophobic and superoleophilic electrospun nanofibrous membrane that exhibited remarkable oil/water separation behaviour, featuring a self-cleaning surface and commendable recyclability [24].

In this study, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was chosen for its potential to enhance oil-water separation performance when combined with Polycaprolactone (PCL). Among various promising alternatives, PHBV is notable for its production via bacterial fermentation of biomass. This linear isotactic polyester is formed from hydroxy acid units and is capable of undergoing composting in industrial environments; it also demonstrates degradability in specific ecological contexts, which increases its attractiveness in terms of sustainability. Furthermore, the composition, chain length, and physicochemical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) can be altered by manipulating bacterial strains, nutrient resources, and cultivation conditions, resulting in a diverse array of mechanical and thermal properties.

The objective of this research was to fabricate a PHBV membrane blended with the bio-polyester PCL in a weight ratio of 3:1 through the electrospinning technique, with the intention of reducing energy consumption and mitigate thermal degradation during the processing phase. Polycaprolactone (PCL) was selected as the blending polymer owing to its advantageous miscibility with polyhydroxybutyrate-co-valerate (PHBV) and co-solubilization in chloroform. Additionally, a review of the existing literature reveals a lack of studies concerning polymer membrane composed of both PHBV and PCL.

2. Materials and Methods

2.1. Electrospinning Process

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), characterized by a composition ratio of 1:1 for hydroxybutyrate (HB) to hydroxyvalerate (HV) and a

molecular weight of 30,000 kDa, was procured from Cheng Jin Plastics Co. Ltd. Dongguan, Guangdong, China. PHBV powder was mixed with Polycaprolactone (PCL) powder (Cheng Jin Plastics Co. Ltd.) with molecular weight of 35,000 kDa in 3:1 (w/w). The polymers were co-dissolved in chloroform (GR grade, 99.8% purity, RCI Labscan Ltd., Bangkok, Thailand) to create a homogeneous solution at a concentration of 12 wt. %. Prior to the electrospinning procedure, the solution was transferred into a 20 mL glass syringe fitted with a metal luer lock tip (SAMCOTM, UK). The electrospinning parameters were meticulously controlled, including an applied voltage of 20 kV, a solution concentration of 12 wt. %, a flow rate of 1 mL·hr⁻¹, and a needle tip inner diameter of 0.21 mm. The distance between the needle tip and the cylindrical collector was maintained at 16 cm to establish a stable system, ensuring that the volume of fluid introduced into the droplet matched the average rate of fluid ejection from the jet. The polymer solution was housed in a standard 20 mL syringe (SAMCO Co. Ltd., Nuneaton, UK) and dispensed using an NE-300 single syringe pump (Model TL-F6, Tong Li Tech. Co. Ltd., Shenzhen, China). The needle tip and the rotating cylindrical collector were connected to a high-voltage power supply (Model TL-Pro, Tong Li Tech Co. Ltd., Shenzhen, China), which was capable of delivering a positive direct current voltage of up to 30 kV.

2.2. Properties of the Electrospun PHBV/PCL Membrane

Oil-Water Separation Process

6 g of cooking oil was added into 60 ml DI water and stirred vigorously for 1 min. to form oil-water double layer. The fabricated PHBV/PCL membrane (0.6 g) with 0.12 mm thickness was immersed in oil-water mixture for 10 sec and further removed from the mixture. The cooking oil was selected to evaluate the oil-water separation ability of the membrane.

3. Results and Discussion

3.1. Morphology of the Electrospun Membrane

A scanning electron microscopy (SEM) analysis was performed to investigate the morphology of the fibers and to confirm the absence of beads and defects. This analysis yielded additional data, including the mean fiber diameter, pore distribution, and the architecture of interconnected pores. The efficacy of the electrospinning technique was clearly demonstrated, as all fibers exhibited a cylindrical shape, continuity, and were devoid of defects. The SEM micrograph of the electrospun PHBV-PCL membrane is presented in **Figure 1**. The sample comprised fibers that were randomly organized, flawless, and characterized by a smooth surface without the presence of beads. Due to the elasticity and flexibility of PCL, PHBV incorporated with another flexible biodegradable polymer is generally in narrow diameter distribution and good uniformity compared to pure PHBV fibers [15]. The average fiber diameter for the PHBV/PCL membrane was determined to be 0.85 ± 0.44 mm.

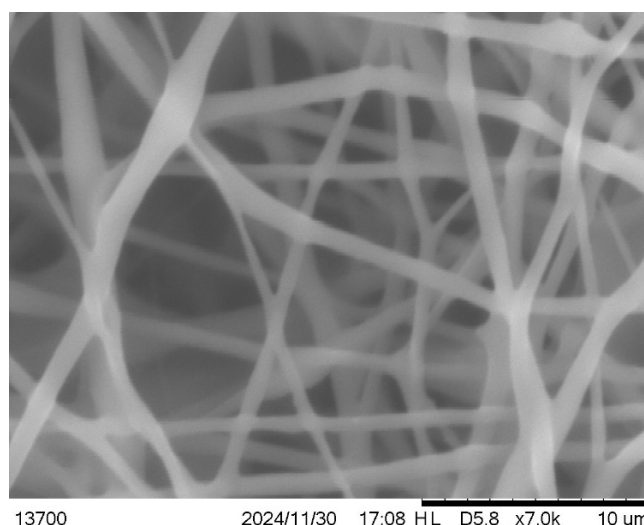


Figure 1. SEM micrograph of electrospun PHBV/PCL fibrous membrane.

3.2. Chemical Signature Using Fourier Transform Infrared (FTIR) Spectroscopy

The Fourier Transform Infrared (FTIR) spectrum of the electrospun membrane is presented in **Figure 2**. The FTIR spectrum for polycaprolactone (PCL) exhibits several notable characteristic bands: 1236 and 1157 cm^{-1} corresponding to asymmetric and symmetric C–O–C stretching, 1750 cm^{-1} for asymmetric and symmetric C=O stretching, 1175 cm^{-1} for OC–O stretching, and 2976 and 2866 cm^{-1} for asymmetric and symmetric CH_2 stretching, respectively. In the case of polyhydroxybutyrate-co-hydroxyvalerate (PHBV), the absorption bands at 1279, 1457, and 1750 cm^{-1} are indicative of the stretching vibrations of –COC–, bending vibrations of – CH_2 –, and stretching vibrations of –CO– in the ester functional group. The chemical functional groups present in PHBV and PCL exhibit a high degree of similarity, leading to significant overlap of the infrared bands in the polymer blend. Furthermore, no new absorption peaks were detected, nor were there any shifts in the peak positions. These observations suggest that the two polymers are well blended within the fibers; however, they do not exhibit any chemical interaction during both co-solubilization and electrospinning processes.

3.3. Separation of Oil-Water Mixture

In the case of cooking oil water mixture, PHBV/PCL showed excellent separation efficiency (>95%). This can be probably attributed to the wide diameter distribution of the fibers and porosity of the membranes. It is worth mentioning that PHBV/PCL membrane can separate water-and cooking oil effectively. This is because the density of cooking oil (0.933 g/ml) is less than the density of water, and so no water layer formed during the separation of the oil-water layer. Water droplets only wetted a very small fraction of the membrane so that the oil could contact and pass through the pores (**Figure 3**). The absorption capacity is approx. 10 g oil/g membrane.

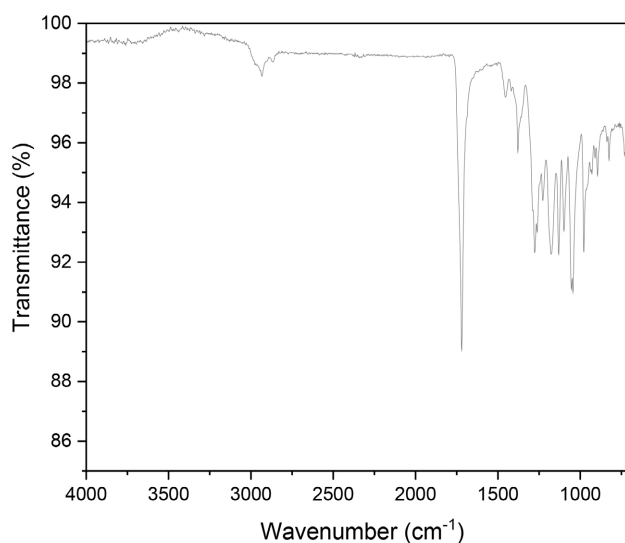


Figure 2. FTIR spectrum of electrospun PHBV/PCL membrane with corresponding IR bands.

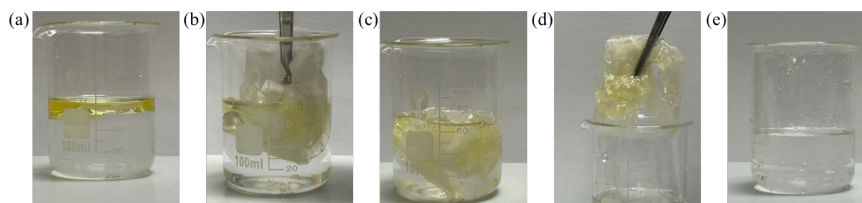


Figure 3. (a) The yellow cooking oil floated on the upper layer with high buoyancy. (b) The PHBV/PCL membrane is initially placed into the cooking oil-water mixture. (c) The membrane was immersed for 10 sec. (d) After 10 sec immersions, the membrane absorbed all given cooking oil layer. (e) The oil-water mixture becomes transparent (no yellowish cooking oil), only leaving water in the beaker.

4. Conclusion

This research utilized bio-based polycaprolactone (PCL) and polyhydroxybutyrate-co-valerate (PHBV) to effectively fabricate biodegradable composite membranes through an electrospinning technique. The resulting membranes exhibited remarkable performance in oil-water separation. The adsorption capacity was measured at 10 grams of oil per gram of membrane, while the membranes demonstrated minimal adsorption of deionized water. Furthermore, the foams exhibited exceptional cyclic durability, maintaining at least 95% of their initial adsorption capacity after 10 seconds of stirring. This study presents an ecological friendly and simple approach in the preparation of bio-based biodegradable membranes with outstanding oil-water separation capabilities.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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