

Robustly superhydrophobic polylactic acid nonwoven membranes for efficient oil/water separation

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Abstract

Oily wastewater is an urgent issue threatening the ecosystem and human health. Superhydrophobic porous materials are widely concerned as promising candidates for effective oil/water separation and oil adsorption. However, superhydrophobic porous materials are still confronted with frustrations such as complex preparation processes and secondary pollution to the environment. Superhydrophobic porous materials with biodegradability and a relatively simple preparation process are more attractive to practical application and environmental protection. In this work, biodegradable and industrially applied polylactic acid (PLA) nonwoven materials were used as porous membranes, then PLA nanoparticles were loaded on the membrane surface to construct the hierarchical rough structure. The modified PLA nonwoven membrane (Nano-PLA) shows superhydrophobicity and efficient oil/water separation performance. Moreover, strong mechanical strength and acceptable toughness are obtained. This work offers an easily controlled and industrially used pathway for the design of robust, highly selective, and biodegradable oil/water separation materials.

Introduction

In recent years, abundant oily wastewater generated in industrial fields such as textiles, food processing, metal smelting, leather reform, and petrochemicals, as well as crude oil waste caused by frequent offshore oil spills, have attracted increasing attentions due to the already revealed critical threats to the ecosystem and human health ^[1-3]. As a research hotspot, high-performance oil/water separation material shows excellent efficacy in the treatment of oily wastewater ^[4-6]. With a deep understanding of the special wettability, a membrane with the characteristic of selectively wetting provides a reliable method for achieving highly efficient oil/water separation performance ^[7, 8].

Theoretically, the wettability of a solid surface relies on two aspects, namely the free energy and the microstructure of the solid surface ^[9, 10]. The chemical composition essentially determines the intrinsic property of the free energy of the solid surface and plays a decisive role in the wetting characteristics of the material. The microstructure of the surface is represented by the roughness of the solid surface on a macro scale, which can amplify the original wetting characteristics of the material to a certain extent, thereby producing special wetting properties. Chen ^[11] et al. used suction filtration to make polystyrene composite microspheres (PS @ AuNPs) tightly packed and assembled to form a composite microsphere film. Then a hydrophilic carbon nanotube film was deposited on the microspheres film to obtain an underwater superhydrophobic multi-layer composite film. Zhang ^[12] et al. constructed a multi-level rough structure on polyacrylic acid (PAA) - grafted polyvinylidene fluoride (PVDF) (PAA-g-PVDF) microfiltration membrane by using a salt-induced phase inversion method. This superhydrophilic membrane could effectively separate oil/water mixture under the action of gravity.

Polymer membranes are the most studied and widely used oil/water separation materials due to their advantages such as easy processing, low price, high separation efficiency, and reusability ^[13, 14]. At

present, polypropylene nonwoven fabrics^[15], polyurethane foam materials^[16], and polyvinylidene fluoride porous membranes^[17] are commonly used as polymer-based oil/water separation materials. The above polymer membranes are usually difficult to degrade in nature. Especially the lipophilic oil/water separation material is easily contaminated in the treatment of oily sewage and the contaminants are difficult to clean up so that its recycling rate is extremely low. The secondary pollution to the environment and low utilization of superhydrophobic polymeric membranes have already been restricted in the application of oil/water separation.

The construction of environmentally friendly oil/water separation materials has practical necessity and urgency. Polylactic acid (PLA) is a more typical one of many biodegradable materials^[18, 19]. It has very good chemical stability, high mechanical strength, non-toxicity, and extensive sources, etc. In this study, the industrialized PLA nonwoven membrane was selected as the substrate to prepare superhydrophobic oil/water separation materials. Based on the theory of special wettability, PLA nonwoven membranes still have something to be desired for oil/water separation: (1) the water contact angle (WCA) of pristine PLA nonwoven membrane is around 120 ° which is far from reaching the superhydrophobic requirement; (2) the pore size is too large for the effective oil/water separation.

Therefore, the purpose of this work is to utilize an easily controlled method to fabricate the superhydrophobic PLA nonwoven membranes for efficient oil/water separation. In general, the PLA nanospheres with uniform particle size were prepared and attached to PLA nonwoven membranes with the help of chemical cross-linking of epoxy resin (ER). The hierarchical rough structure was expected to be constructed to improve hydrophobic performance as well as reduce pore size. The modified PLA nonwoven membrane was desired to be not only with high efficiency for oil/water separation but also no threats to the environment after use.

Experimental Section

Materials

All the materials used in this study are commercially available. The pristine PLA nonwoven materials (diameter 20-25 μ m) were kindly supplied by Zhejiang Hisun Biomaterials Co., Ltd. PLA nonwoven materials were rinsed off with anhydrous ethanol and dried thoroughly before using. PLA (4060D, NatureWorks LLC) with a density of 1.24 g/cm³ was used as raw materials for preparing PLA nanospheres. Epoxy resin (ER), curing agent, acetone, and anhydrous ethanol were purchased from Aladdin (Shanghai) Co., Ltd., China. N-hexane, petroleum ether, castor oil, silicone oil, and lubricating oil were received from Hangzhou Mike Chemical Plant Co., Ltd.

Preparation of PLA Spherical Particle

The specific preparation steps are as follows: a certain amount of PLA was dissolved in a mixture of acetone and ethyl alcohol under sonication for 10 minutes to obtain a well-mixed oil phase. The above oil mixture was slowly dropped into deionized water by strong mechanical stirring. After the acetone was

completely evaporated, the suspension was freeze-dried to obtain PLA nanospheres. The preparation process is shown in Figure 1.

Preparation of Superhydrophobic Coating

Under stirring mixing, ER and curing agent were mixed with a 2:1 mass ratio at room temperature to prepare ER solution. Then PLA nanoparticles (3 g) and KH-560 (1 g) were added into the ER solution successively. After diluted with 30 ml anhydrous ethanol, the mixture was kept stirring for 30 min at room temperature. Subsequently, the thoroughly rinsed PLA nonwoven material was submerged into the prepared PLA nanoparticles/ER mixtures. Finally, the resultant Nano-PLA nonwoven fabric was rigorously rinsed with ethanol to remove undecorated PLA nanospheres.

Characterization

Water contact angle (WCA) measurements were carried out at room temperature and 65% humidity by using the JY-82B video contact angle tester. The image was captured after the 60s of contact with the water drop and specimen. The surface wettability was determined by an average of ten measurements. Microscopic morphology of PLA nonwoven fabrics before and after coating was performed on field emission scanning electron microscopy (FE-SEM, Verios G4) at the voltage of 3.0 kV. The observed surface was sputter-coated with a thin gold layer to imaging. The diameter of PLA nanoparticles was investigated by using an LB-500v laser dynamic light scatterer and determined by the average of 3 measurements. Tensile properties were performed at room temperature by using an Instron-3369 universal testing machine (U.K.). The sample size was 30 cm×5cm and the cross-head speed was 50 mm/min. For each specimen, the reported value was calculated as an average of 10 independent specimens with a gauge length of 25 cm.

Results And Discussion

The Microstructure of PLA nanoparticles

The liquid precipitation method is usually used to prepare metal oxide nanoparticles, which is rarely applied for polymer nanoparticle formation. In this work, the modified liquid precipitation method was used for the PLA nanoparticles' preparation without emulsifier or precipitant^[20]. With changes in solubility, PLA precipitated from the solvent to form nanoparticles. Specifically, when the oil mixture was added to water, the water-soluble organic solvent in the oil phase diffused into the water phase and penetrated the oil/water interface rapidly. Due to the turbulence at the interface, surface tension reduced and oil drops continuously shrank to a smaller size. Water-insoluble PLA migrated to the interface, deposited, and solidified to form nanoparticles. The diameter of PLA nanoparticles was determined by two factors: (1) the volume fraction of alcohol in the oil phase; (2) PLA concentration in the oil phase. The solubility parameter of acetone and anhydrous ethanol is $10.0 \text{ cal}^{1/2} \times \text{cm}^{-3/2}$ and $12.7 \text{ cal}^{1/2} \times \text{cm}^{-3/2}$ respectively. The solubility of PLA decreases gradually with the increase of ethanol in the mixture solvent. It is very important to determine the critical composition ratio of the mixed solvent which can completely

dissolve PLA. Photographs of PLA solution with different ethanol content (f_e) are shown in Figure 2, which states complete dissolution of PLA with a transparent solution when $f_e \leq 30\%$. However, when f_e increases up to 40%, the cloudy solution indicates incomplete dissolution. In this work, the critical ethanol content in the mixed solvent was fixed as 30%. Figure 3 is a morphological view of PLA nanoparticles. The prepared PLA nanoparticles are relatively regular, spherical in shape, and uniform in particle size. The relationship between PLA nanoparticles' diameter and PLA concentration in the oil phase was carefully explored. As shown in Figure 4, the particle size decreases from 186.5 nm down to 102.3 nm when PLA concentration lessened from 2% to 0.5%. It is easier to form smaller-sized PLA nanoparticles when the concentration of PLA in the oil phase decreased, as the viscosity of the oil phase also decreased.

Surface morphology and wetting analysis

The hydrophobic properties can be enhanced with the reduction of surface free energy. However, even a smooth solid surface with the lowest surface energy has a WCA of only 119° . Constructing a hierarchical rough structure is particularly important for the acquisition of superhydrophobic properties. As shown in Figure 5(A), PLA fibers in pure PLA nonwoven material are quite smooth. After treatment with ER-coated nanoparticles, a large number of protrusions present on the fiber surface. As shown in Figure 5(B'), protrusions are formed by the agglomeration of different numbers of PLA nanoparticles, which increased the roughness of PLA fibers.

Due to the presence of a large number of hydrophobic ester groups in PLA molecules, the pristine PLA nonwoven materials present hydrophobic surface wettability with static WCA of 119.4° as shown in Figure 6(A). ER was used as a binder for the adhesion of PLA nanoparticles on the surface of PLA fibers. However, as shown by the SEM results, ER forms wrinkle morphology on the surface of PLA fiber. The effect of the crease structure formed by ER on the wettability of nonwoven materials is worth exploring. As shown in Figure 6(B), WCA increases to 133.2° after ER treatment. The WCA further increases to 140.8° after the adhesion treatment of PLA nanoparticles. This can be attributed to the increased surface roughness by the help of nanoparticles as confirmed by SEM results. The above hydrophobic surface was further treated with KH560 of low surface energy. Finally, the Nano-PLA nonwoven material turns superhydrophobic with a WCA of 152.1° as shown in Figure 6(D). This is the combined result of surface roughness construction and low surface energy treatment.

Mechanical property

Mechanical properties are the premise and foundation of material application. Especially in the fabric/nonwoven materials treatment process, mechanical forces and chemical reagents usually cause structural damage and mechanical performance degradation. The maintenance of mechanical properties is essential for the post-treatment modification of fabrics/nonwoven materials. The mechanical strength of nonwoven materials is commonly worse than that of woven fabrics as a result of disorderly arranged fibers. This also limits its use to some extent. As shown in Figure 7, the mechanical strength of pure PLA nonwoven material is only 114N. The mechanical strength of the nonwoven material treated with ER is

increased to 244N, which is more than twice the strength of the pure sample. The improvement of mechanical strength arises from the ER at the fiber junction acts like a chemical bonding effect. This can enhance fiber bonding strength and ultimately increase the strength of the modified nonwoven materials. Strength can further increase to 266N after adhesion treatment of nanoparticles. Although the elongation at break has decreased, it can still be maintained at around 17% with relative toughness. In short, superhydrophobic Nano-PLA nonwoven material has strong mechanical strength and certain toughness. Compared with the pure sample, the mechanical properties of the modified PLA nonwoven membrane have been greatly improved.

Application of superhydrophobic Nano-PLA nonwoven material

One of the applications of superhydrophobic materials is the rapid absorption of skim oil from oil-polluted water. Figure 8 shows the phenomenon of oil adsorption after the superhydrophobic Nano-PLA nonwoven material was placed in oil-contaminated water, by the way, organic n-hexane was dyed by red oil O for clear observation. Oil can be quickly absorbed by Nano-PLA nonwoven material. It is found that excess oil droplets are attached to the surface of the Nano-PLA nonwoven membrane, and they are difficult to drip. This shows that the modified material can selectively absorb oil from oil-contaminated water, and has a definite role in removing oil stains. When superhydrophobic materials are used for oil adsorption, the adsorption rate is an important factor to be considered. Therefore, the absorption capacity of different oils is further studied.

The oils used in daily life and production are diverse, and the density of oil can be varied within a wide range. It is necessary to figure out the absorption rate of modified Nano-PLA nonwoven material to different density oil products. The density of the oil used for testing is listed in Table 1, showing as 0.65 g/ml, 0.69 g/ml, 0.88 g/ml, 0.96 g/ml, and 0.97 g/ml for petroleum ether, n-hexane, lubricating oil, silicone oil, and castor oil, respectively. As shown in Figure 9, the oil absorption rate of the superhydrophobic material increases with the increasing density of the oil. The reason for this result may be that the adhesion and retention of the oil will increase with the increase in density. Specifically, the modified PLA nonwoven material can absorb castor oil 5.5 times its weight.

In addition to oil absorption properties, superhydrophobic materials can also be used for oil/water separation. Although the pure PLA nonwoven material has a WCA of 119° and has certain hydrophobic property, it fails to a high selectivity for water or oil. Both water and oil can penetrate PLA nonwoven materials which cannot be used for oil/water separation. This may also be related to the larger pore size $\approx 225 \mu\text{m}$ of the pure PLA nonwoven material. However, superhydrophobic Nano-PLA nonwoven material is highly selective to oil. For the n-hexane/water mixture, only red oil can wet and penetrate the Nano-PLA material to achieve oil/water separation with 96% separation efficiency as shown in Figure 10. In addition to its special surface wettability, the Nano-PLA nonwoven material also has a small pore size of about $100 \mu\text{m}$, which is reduced by half compared to that of the pure sample. As shown in Figure 11, the combination results of superhydrophobic surface and reduced pore size make Nano-PLA membrane effective in oil/water separation. Both the oil absorption property and oil/water separation performance

indicate that the superhydrophobic Nano-PLA nonwoven material has definite application advantages in oily water purification. Not to mention that the material is biodegradable and has the dual meaning of environmental governance and resource protection.

Conclusions

In summary, we have developed an easily controlled method to prepare superhydrophobic Nano-PLA nonwoven membranes by coating PLA nanoparticles onto PLA nonwoven materials. Through adjusting the dosage and curing time of adhesive ER, the adhesion fastness of PLA nanoparticles and the flexibility of the modified PLA nonwoven materials are balanced. The resulted Nano-PLA membrane shows excellent selectivity when they are employed as oil/water separation and oil absorption materials. Moreover, the mechanical strength is more than twice the pure PLA nonwoven membranes' value, and the flexibility is maintained. Such superhydrophobic Nano-PLA membranes with robust mechanical properties provide a good solution aiming at second pollution of the oil/water separation materials themselves.

Declarations

Acknowledgments

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Data Availability

The data that supports the findings of this study are available within the article.

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Tables

Table 1 The density of different oils.

Oil	Density [g/ml]
petroleum ether	0.65
hexane	0.69
lubricating oil	0.88
silicone oil	0.96
castor oil	0.97

Figures

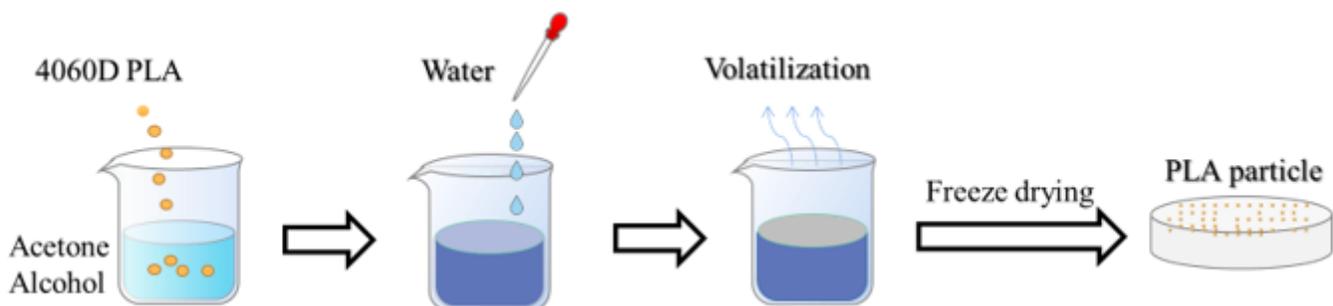


Figure 1

Diagram of PLA nanoparticle preparation process.

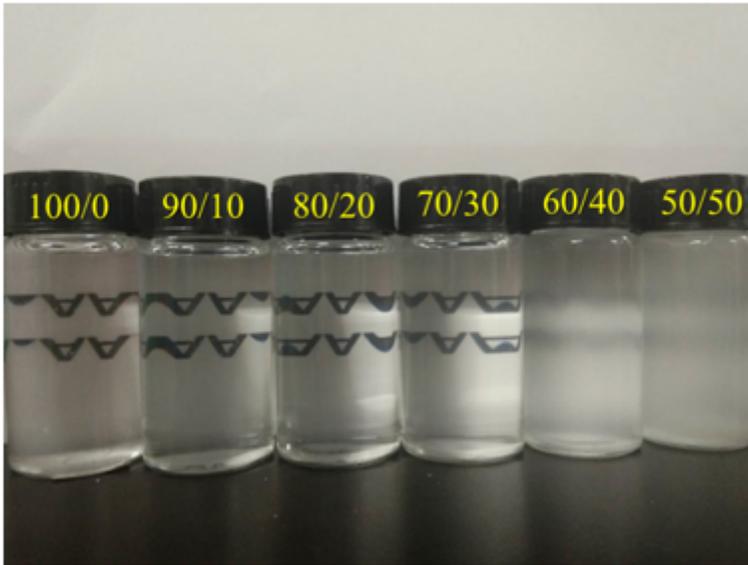


Figure 2

PLA solubility in acetone/ethyl alcohol mixed solvent.

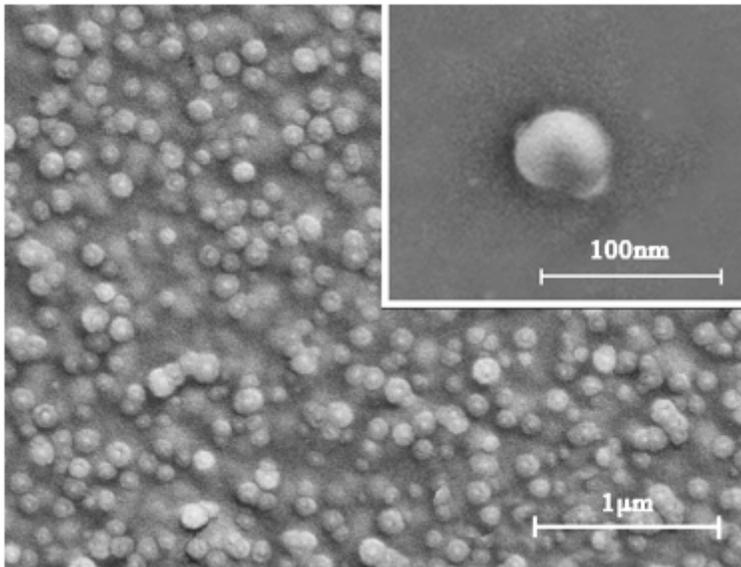


Figure 3

SEM micrographs of PLA nanoparticles.

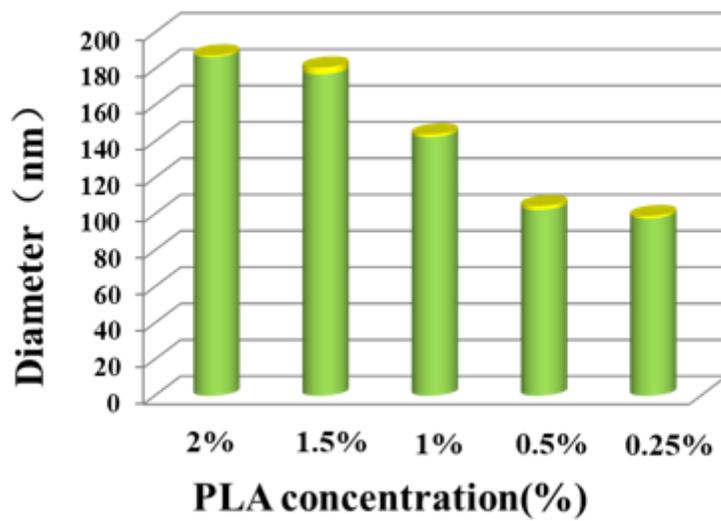


Figure 4

Relationship between PLA nanoparticle diameter and PLA concentration in the mixed solvent.

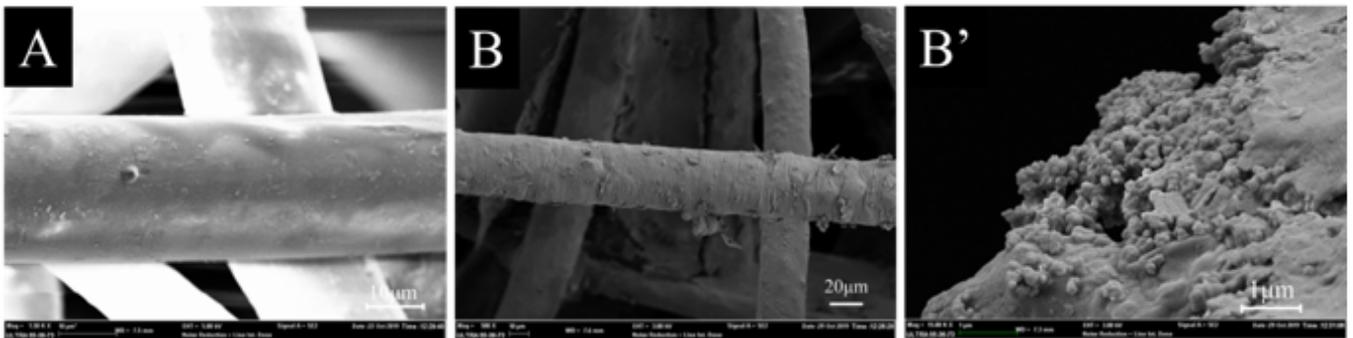


Figure 5

SEM images of the surface of (A) Pure PLA nonwoven membrane; (B) Nano-PLA membrane; (B') Enlarged image of (B).

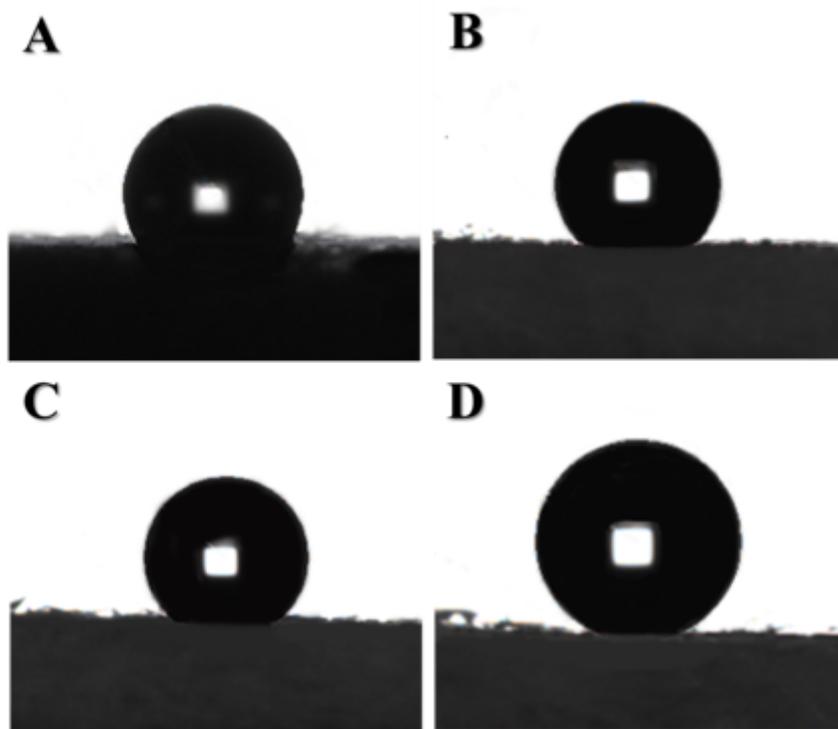


Figure 6

The WCA of the membranes (A) Pure PLA nonwoven membrane; (B) PLA/Epoxy membrane; (C) PLA/Epoxy/Nanoparticles membrane; (D) Nano-PLA membrane (further treated with KH-560).

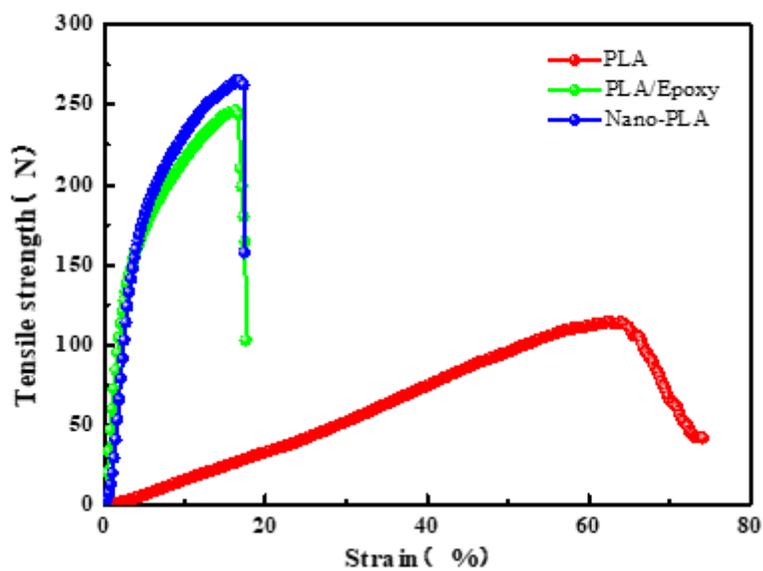


Figure 7

Tensile strength-strain curves of membranes before and after coating.

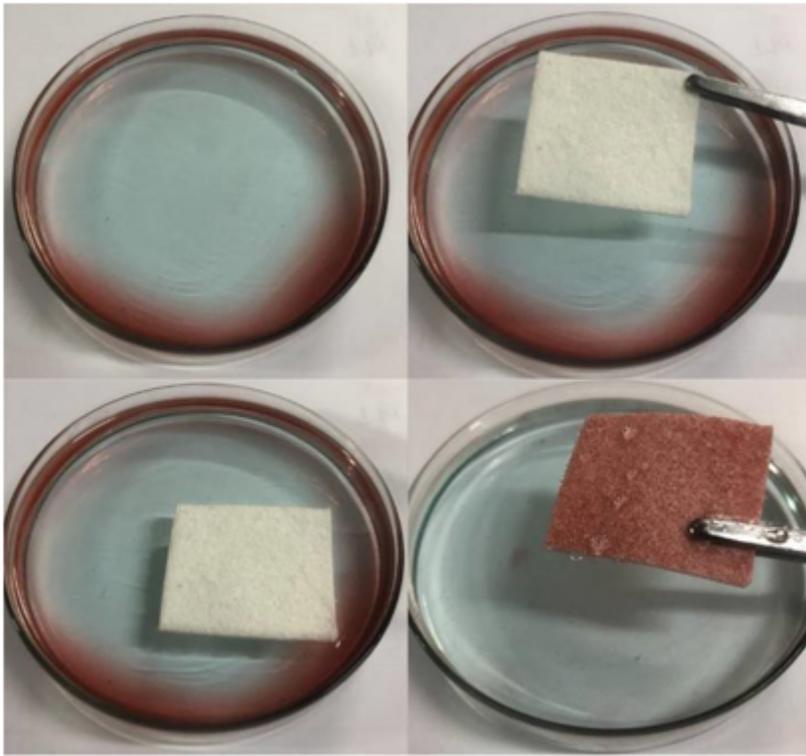


Figure 8

Schematic diagram of oil absorption effect.

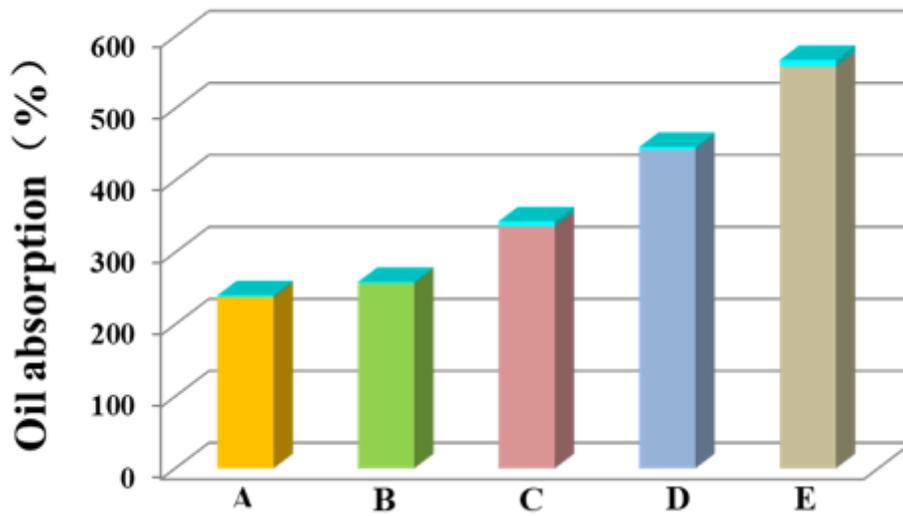


Figure 9

Oil adsorption rate of Nano-PLA membrane to different oils.



Figure 10

Photographs showing the separating process of hexane/water mixture by Nano-PLA membrane.

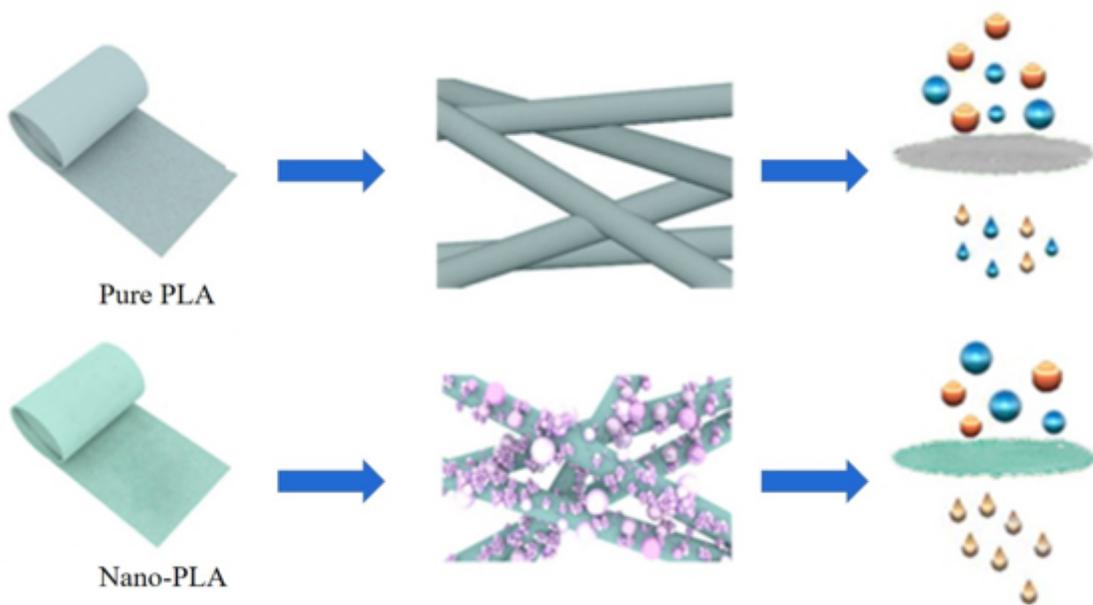


Figure 11

Schematic demonstration of the oil/water separation by Nano-PLA membrane.