Journal of Fiber Bioengineering and Informatics 9:2 (2016) 101–113
doi:10.3993/jfbim00234

Structures and Properties of Chitosan Based Porous Membranes ⋆

Yeping Xiang [a], Mo Yang [b], Liyun Xu [a], Ruiyun Zhang [a,*]

[a] *Key Laboratory of Textile Science & Technology, Ministry of Education, College of Textiles Donghua University, Shanghai 201620, China*

[b] *School of Economics and Management, Hebei University of Engineering, Hebei 056038, China*

Abstract

In order to improve some defects of pure chitosan membrane, such as the high brittleness and poor flexibility *etc.*. This paper adopted a simple and effective method to realize the performance optimization by blending with Poly Lactic Acid (PLA) and Poly (Vinyl Alcohol) (PVA). The result indicated that compared with pure CS membrane, moisture absorption rate and Water Vapor Transmission Rate (WVTR) of CS/PLAand CS/PVAblend membranes have been greatly improved. With a certain amount of the PLA or PVA, the breaking elongation of the blend membrane rise steadily. The physical properties of CS/PLA blend membrane are better than the CS/PVA's, so the research for CS/PLA blend membrane is expanded. With the Scanning Electron Microscopy (SEM) images, it observed that the CS/PLA blend membrane's porosity is improved after freeze-drying, and have better porous structure, the pore size and morphology with different blending ratios changed significantly. Besidethe SEM images, CS/PLA blend membranes' Fourier transform infrared spectroscopy (FTIR) reveal that the strong hydrogen bonds formed between CS and PLA, which is consistent with the conclusions of the Differential Scanning Calorimetry (DSC). The DSC curve analysis shows that the decomposition temperatures of the blend membrane decrease firstly and then increase with the decrease of CS content. The comprehensive property of the porous membranes is optimal point where the CS content is 60%. The good properties, such as moisture regain, porosity, and water vapor transmission rate, of the kind of CS/PLA or CS/PVA blend membranes suggested a potential application in wound dressing.

Keywords: Chitosan (CS); Poly Lactic Acid (PLA); Poly (Vinyl Alcohol) (PVA); Lyophilization; PorousMembrane; Biodegradation

1 Introduction

Biopolymer material contributed to the medical application is one of the widest application, the fastest development, and thehottest research materials [1]. Nowadays, biopolymer blending mod-

⋆Project supported by Shanghai Municipal Natural Science Foundation (14ZR1401000) and Shanghai University Students Innovation Project.

*Corresponding author.
Email address: ryzhang@dhu.edu.cn (Ruiyun Zhang).

1940–8676 / Copyright © 2016 Textile Bioengineering and Informatics Society
2016

ification has been increasingly investigated. The technology of blending preparation can choose the appropriate blending materials and the proportion of composition to improve the material defects, obtain good mechanical properties, the morphology, the permeability, degradation and so on. Polymer blended are physical mixtures of structurally different polymers or copolymers that interact with secondary forces without covalent bonding, such as hydrogen bonding, dipole-dipole forces, and charge transfer complexes for homopolymer mixtures [2]. In short, the characteristics of optimal combination of different polymers in one, a new performance the material does not have, not only simple and effective, but also considerable economic, open up a broad path for the research and development of polymer materials. The preparation of porous materials by freeze dryingcarried out cast and lyophilize technologyat the same time can maximize the biological and chemical structure of the products and the integrity of the biological activities.

Chitosan is soluble in acid or dilute acid solution, and has some excellent performances like adsorption, integration, and moisturizing membrane, non-toxic to humans, no immunogenicity and good antibacterial. Furthermore its biological compatibility, biodegradability, low toxicity, no allergic effects give it their natural advantages and has good effects of drugs and medical functions, which makes it occupy a larger market application in biology and medicine. But the chitosan molecule is so rigid that its film curls easily. In the dry weather, shrinkage cracking damaged the membrane structure; in the wet weather, absorbing water vapor decreased the membrane strength and the color yellowed [3]. PLA is composed of dehydrated and condensed lactic acid under the suitable conditions, a kind of completely biodegradable polymer. Under certain circumstance, PLA can be decomposed into carbon dioxide and water. PLA fiber and its fabric waste can be processed. However, the disadvantages of PLA due to its chemical structure, like high crystallinity and low crystallization rate, low strength, poor toughness, low thermal deformation temperature (usually only 60 degrees centigrade), high cost and less species, limit the large-scale application in industry [4, 5]. PVA whose performance depends on the degree of polymerization and alcoholysis, a regular molecular structure with molecular chain flexibility polymer, is non-toxic, harmless, and has chemical stability, no reaction with most organic solvents, andhydrophilic [6].

The experiment adopted good biological activity, degradation and absorption chitosan as matrix, and blended PLA or PVA to prepare the blend membrane. On one hand experiment improved the mechanical properties of CS, on the other hand adjusted the biodegradability and degradation of PLA and PVA. This paper carries on the theoretical analysis of polymer membrane, membrane preparation method, the relationship of the proportion of material and membrane structure to obtain the excellent performance and meet requirements of biomedical porous and degradable material. The purpose to prepare porous membrane in this experiment is to meet the requirements of biomedical porous material for wound dressings.

2 Experiment

2.1 Materials, Reagents and Instruments

Materials and reagents: CS (degree of deacetylation $\geq$90%) was purchased from Jinan Haidebei Marine Bioengineering Co. Ltd (China). Poly lactic acid (PLA): Laboratory synthesis; acetic acid, acetone, chloroform, N, N- methyl amide two, two dimethyl sulfoxide (DMSO), sodium hydroxide: analysis of pure, Boer Shanghai Chemical Reagent Co. ltd.

Instruments: Y802A eight basket oven thermostat magnetic stirrer; 85-2 SK3200H BCD-232EN; ultrasonic; refrigerator; FD-10-50 freeze dryer; YG141N digital fabric thickness tester; YG065; DSC PE7 thermal analyzer; NDJ79 viscosimeter; HH.CP-T type constant temperature incubator; FA1004 electronic balance.

2.2 Preparation of CS/PLA and CS/PVA Blend Porous Membranes

CS was dissolved in 2% HAc solution to prepare a 3% solution. A certain amount of PLA was dissolved in DMSO solution to prepare 5% (w/w) PLA solution. Different weights of PLA with DMSO were added into the 3% chitosan solution to obtain CS/PLA weight ratios of (100: 0), (90: 10), (80: 20), (60: 40), (50: 50) and (40: 60), and marked as CS100, CS90, CS80, CS60, CS50 and C40 respectively. The mixture solution was kept stirring for 1 hour until the PLA and chitosan completely reacted. And then the ultrasonic degassing processed the solutions. During the experiment, blending PLA with DMSO into CS solution with different mass ratios are observed that the color of the solution is from golden yellow to milky white gradually and the viscosity of the solution increase. The phenomenon indicates that adding the DMSO as a solvent into the blending solution, the solution miscibility is improved.

7% PVA solution was prepared by fully dissolving 7 g of polymer powder without further purification in 100 mL of de-ionized water under magnetic stirring at temperature of 90 °. Different weights of PVA were added into the 3% CS solution to obtain CS/PVA weight ratios of 8: 2, 6: 4 and 4: 6, and marked as CS80, CS60 and CS40 respectively. And then, the solution was poured into glass moulds for pre-frozen in the refrigerator for 24 h. After frozen into solid, the CS samples were placed into the vacuum freeze-drying machine for 5 h, until the porous CS/PVA films were formed.

3 Measurement and Characterization

3.1 Moisture RegainRate

The prepared the polymer blend membranes were cut into 20 mm × 20 mm samples and then humidified (20±2°C 65%±3%) for 24 h. The weights of the samples G0 and G1 were tested before and after drying them. The moisture regain rate was calculated as Formula 1.

$$rate = \frac{G_0 - G_1}{G_1} \times 100\% \tag{1}$$

3.2 Water Vapor Transmission Rate

Medical dressings should have sufficient water vapor permeability and prevent the wound fluid accumulation from causing serious consequences to the wound. Therefore, the good water vapor transmission provided the wounds for remaining relatively transparent environment, played a very important role in prolonging the dressing [7]. The polymer blend membranes were cut into 20 mm diameter circular specimens, and then smoothly covered on the test tube with some proper deionized water. Then the assembly was placed into the environment of temperature of 20 ± 2 °C, humidity 65% ± 3% for 24 h. The weight of films, liquid and test tube before and after

process were weighed on an electronic balance. The water vapor transmission rates of films were then calculated from Formula 2.

$$rate = \frac{W}{\frac{1}{4}\pi D^2} = \frac{4W}{\pi D^2} \tag{2}$$

3.3 Porosity Rates

Porosity is an important parameter of porous materials. Porous materials can provide a large surface area for the proliferation of adherent cells, make the nutrients and body fluid be more likely to reach the material deep, which benefit to provide nutrition, gas exchange, waste elimination environment for cells, space for cell proliferation and reproduction [8]. Therefore, the pore size of cell scaffold must be controlled, and there are strict requirements. The porosity rates of porous membranes were determined by dissolving the membranes in ethanol at room temperature. The cutout porous membrane was placed in a scaled test tube with the media (ethanol) until the sample was fully immersed without air bubble on the surface. Denoting V_1 as the initial volume of ethanol, V_2 as the volume of ethanol when the porous membranes were immersed in the test tube, V_3 as the volume of ethanol after the membranes was removed, after each porosity rate experiment was repeated 3 times, the average value P was taken as the porosity rates, calculated as formula 3.

$$P = \frac{V_1 - V_3}{V_2 - V_3} \times 100\% \tag{3}$$

3.4 Mechanical Properties

Using YG065 tester tested the mechanical properties of blend membranes. The prepared the polymer blend membranes were cut into samples 20 mm in width. The clamp length is 50 mm, tensile speed is 50 in/min and the pre-load is 2N.

3.5 Fourier Transforms Infrared Spectra (FTIR)

Cut the polymer film samples into particle whose size less than 40 um, KBr tablet compressed samples preparation, measured by NEXUS-670 Fourier transforms infrared spectra.

3.6 Thermal Performance

The DSC curves of blend membranes were measured in nitrogen atmosphere during the heating process. The heating rate was set 20°/min while the temperature range was between 30-400°.

3.7 Scanning Electron Microscopy (SEM)

The surface morphology of the films was analyzed by using the JSM-5600LV scanning electron microscope.

4 Results and Discussions

4.1 Moisture Regain Rate

The moisture absorption properties of materials mainly depend on the physical structure and the number of the hydrophilic groups. CS molecule contains hydroxyl and amidogen, can be combined with water molecules, but because CS itself contains a lot of ring structure, which is so dense that water molecules entereasily, therefore, the CS100 has a certain amount of moistureabsorption, moisture absorption performance is poor. Fig. 1 showsthe moisture regain rate of CS/PVA and CS/PLA porous membranes. It can be seen that the blend membranes adding PVA or PLA have better moisture absorption than pure CS membrane. The molecule structure of PVA has many hydroxyl groups, which can also form hydrogen bonds with hydroxyl groups on CS, and thus the moisture regain of porous membranes is enhanced. PVA is usually apt to form intermolecular hydrogen bonds in certain range of content, and would cause a slight decrease of moisture regain at over that range because of hydrogen bond association. With the increase in PLA content, moisture absorption in CS/PLA blend films first increase and then decrease; CS90 presents the best moisture absorption. The results suggest that the moisture absorption of the blend membrane can be improved. In the CS/PLA system, the water molecules penetrated into the blend membrane, mainly existed in the membrane pores, also bonded with a small amount of the hydroxyl groups of CS. Accessing PLA, the porosity of the membrane increased, so the wettability was improved. But due to the molecular chain of PLA contains a lot of ester bond, which is hydrophobic, with the increase of content of PLA, increased the density of the blend film of ester bond, so weaken the blend membrane hydrophilic ability, lowed water absorption. In addition, the increase of PLA content in the blend solution, it may be a certain degree of phase separation, result in CS and PLA formed gel precipitation, also made the water absorption of the blend films decrease.

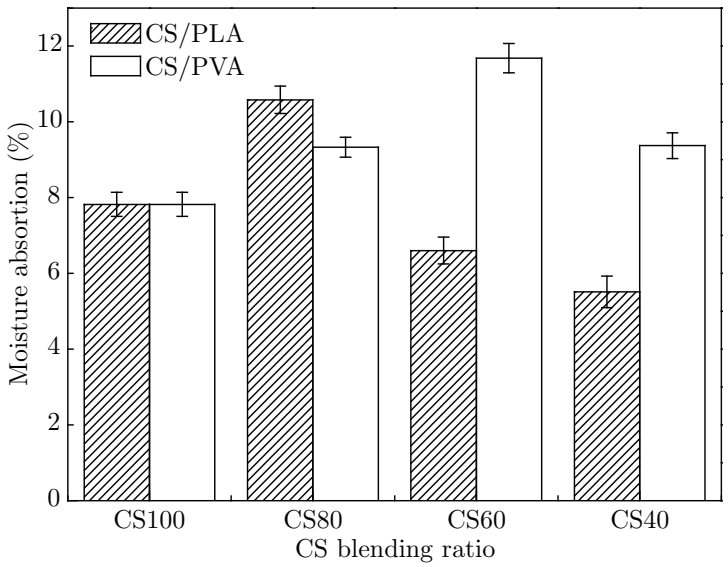


Fig. 1: Moisture regains of CS/PLA and CS/PVA porous membranes

4.2 Water Vapor Transmission Rate

In a certain temperature and humidity conditions, water vapors passthrough the porous membrane material in accordance with "adsorption-diffusion-desorption" method. Firstly, the water vapor molecules adsorb on the surface of porous membrane; subsequently, water vapor diffuses through the porous membrane; finally, water vapor desorbs in the other side of the porous membrane[9]. WVTRs of CS/PVA and CS/PLA porous membranes are shown in Fig. 2. With the increase of PLA content, the WVTR firstly increased and then decreased. The highest value reaches at 1810 when PLA content is 20wt% and the value is about 80% higher than that of CS40, which indicates the higher content of CS contributes the better WVTR of the blend membrane. The WVTR is closely related with membrane thickness, structure compactness and crystallinity degree, the thicker the blend membrane, the higher the structure compactness and crystallinity degree, while the lower the WVTR, and vice versa. The molecular interaction of CS and PLA results in difference of the density and crystallinity of different mass ratio of blend membranes, so that WVTR shows irregular change. With the increase of PVA content, water vapor permeability first increases the highest value where reaches at 1550 when PVA content is 40wt% and then decreases. Adding PVA would damage the CS original structure, regularity among molecules and increase molecular distance inevitably, which improves the water vapor adsorption capacity of porous membrane. Furthermore, the WVTR has close relationship with porosity. Adding more PVA would make membrane porosity decreased, structure compacted that the transfer resistance of membrane increase, so when PVA is 60wt%, the WVTR decrease distinctly. In addition, like adding PVA, PLA affect the permeability and then decrease the porosity rate of the membrane, relatively the lower WVTR of the blend membrane. Likewise the difference of the hydrophilicitybetween PVA and PLA affect the membrane pore size and quantity and the blend solution properties *etc.*, which also have equally important influences on WVTR.

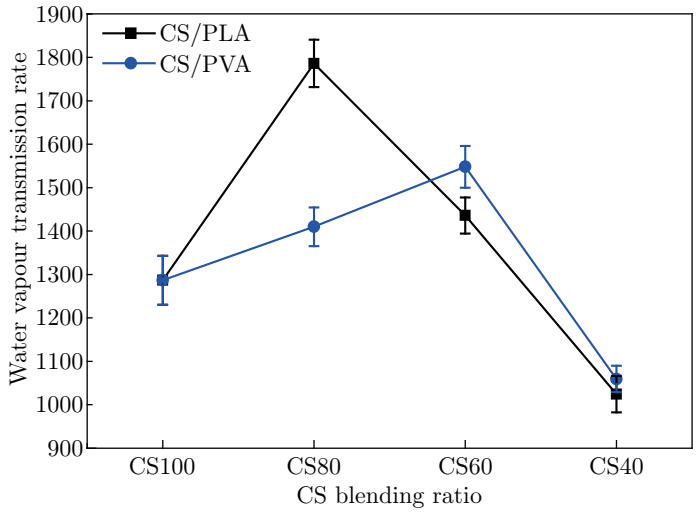


Fig. 2: The water vapor penetration rate of the CS/PLAand CS/PVA blend membranes

4.3 Porosity Rate

It can be seen from Fig. 3 that adding a certain amount of PLA or PVA both can improve the porosity of the CS blend membranes. The CS40 porosity presents the lowest porosity value

because of the high content of PLA results in phase separation of CS and PLA, in which the higher viscosity PLA solution floating in the upper layer makes the resistance force of water molecule movement larger. With the adding of PVA content, the viscosity and moisture content of blend solution reach a saturation value, resulting in a max value of porosity rate for CS80. The similar trend between the porosity rates and moisture absorption rates indicates the relation of them, *i.e.*, with the increasing of porosity rate, the moisture regain increased. Aperture formed on the blend membrane by freeze-drying process, and its pore volume per unit volume are small, but the porosity have no significant differences among other proportions of blend membranes. Therefore the weight ratio of blend membrane has a great influence on the porosity rate. From overall point of views, the high porosity of CS/PLA blend membrane, porosity is almost reached 90%. The blend membranes have better permeability effect with high porosity, which benefits to discharge the wound effusion timely. And it is also conducive to discharge cells metabolism and supply cell nutrition. Therefore cell can contact to more effective area of membrane, which play an important role in the application of medical dressings and tissue engineering and so on[10].

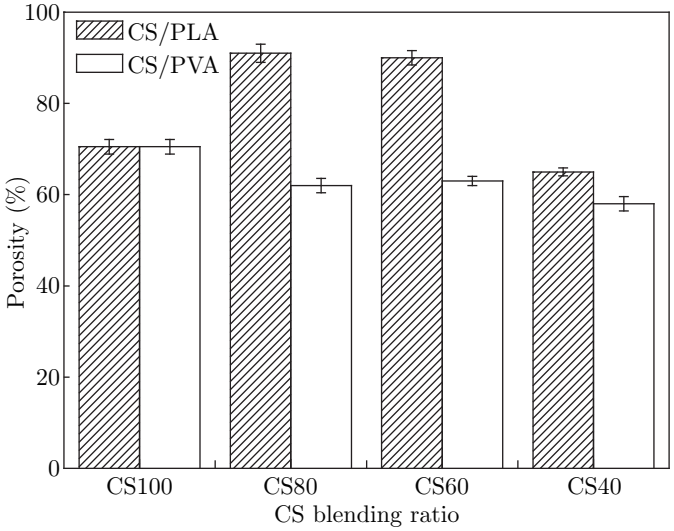


Fig. 3: The porosity of the CS/PLAand CS/PVA blend membranes

4.4 Mechanical Properties

Fig. 4 and Fig. 5 presents breaking strength and elongation of CS/PLA and CS/PVA blend membranes in different blend ratio. Adding PVA or PLA component both improves the mechanical properties of membranes apparently, the pure CSmembrane possesses the lower tensile strength and the elongation; means the frangibility of pure CS membrane is high. That the main chain of CS molecular contains lots of rigid hexatomic ring in spite of 1, 4 glycosidic linkage and there are extremely high intramolecular and intermolecular hydrogen-bond interactions cause high stiffness of molecular chain. PLA has been widely used in biomedical field, not only has it good biocompatibility and biodegradability, but also keep high mechanical properties in living things. Therefore, during improving its hydrophilicity, mechanical property should not be excessively destructed, which is the prerequisite of our modification. When the CS content decreases, the strength and elongation of the blend films first increases and then decreases, reaching the maximum value when mass ratio of CS and PLA is 3:2, which is contributed to the interaction that

change the crystal structure of blend membrane between CS and PLA molecules. The decreasing strength with the continuously adding of PLA content contributes to that the inhomogeneity of different blend ratio of CS and PLA[11,12]. If the mass fraction of PLA is too large, it would lead to the poor uniformity of the blend solution cast film, poor uniformity, structure defects, resulting in reducing the tensile strength of the blend membrane. In addition, when the PLA content increases to 60%, the blend film strength is poorer than pure CS membrane attribute to the different evaporation rate of CS and PLA in the blend solutions and not easy to control, and the stirring speed should be controlled strictly. In addition, increasing the ratio of PLA may also reduce solubility of co-solvent DMSO. The blend solution was easy to emerge phase separation. So in order to keep mechanical strength, it is necessary to choose right ratio of PLA. The amount of PLA the best maintained at less than 40%. This result was consistent with the SEM results.

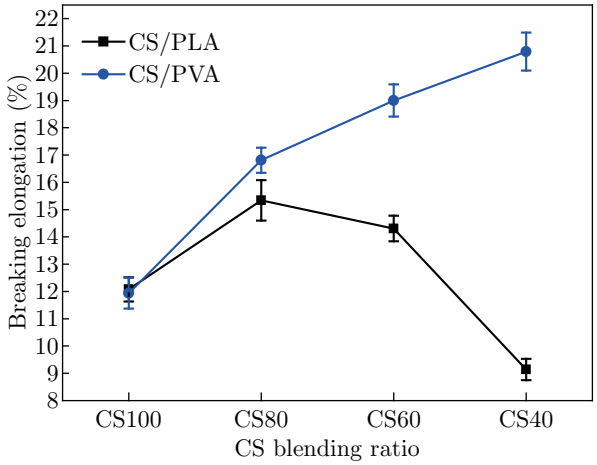


Fig. 4: The breaking elongation of the CS/PLAand CS/PVA blend membranes

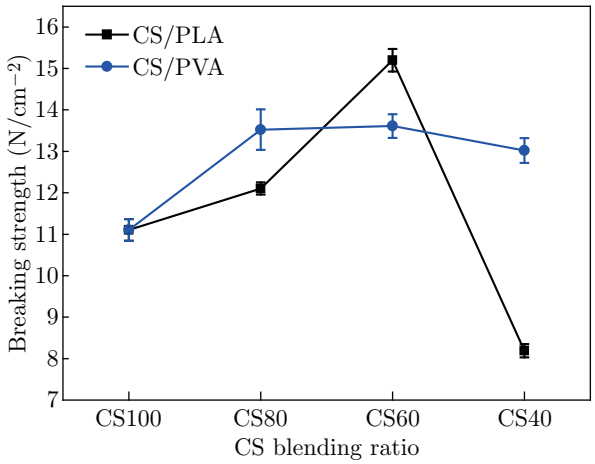


Fig. 5: The breaking strength of the CS/PLAand CS/PVA blend membranes

4.5 The Surface Morphology Analysis

Fig. 6 shows the SEM images of different proportions of CS/PLA blend membranes. In CS/PLA blend system, the surface morphology of the blend membranes has the obvious difference with

the changing of CS content. In C90, the whole surface is smooth, with some dispersed small and closed holes on the surface; In CS80, holes formed on the membrane surface are irregular, and some ripples emerge on the surface. And in the electron microscope pictures of other membrane surface appear similar the shape of the pattern. It is probably in the spraying process, due to the high temperature surpassed above the glass transition temperature of PLA, resulting in its deformation, the samples formed ripple; In CS60, the pores on the membrane surface are isolated with bad connectivity among them, and all holes are distributed in uniform pore diameter with some holes in large open shape; In CS50, holes are not obvious, with a lot of small particles on the membrane surface. Because the CS can only swell in DMSO and not be dissolved, and the great difference in polarity between them; In addition, with the increase of PLA content, the degree of phase separation of blend membranes increased, the reunion phenomenon becomes obvious. When the content of PLA increased to 50%, the degree of phase separation of blend membranes become more serious, preparation of blend membrane has been difficult to form well. Fig. 6(f) is the image of the section structure of a membrane, presenting the lamellar structure of blend membrane, which maybe cause that during the freeze-drying process, the temperature dropped to below freezing point, thus water molecules in CS solution got crystallized, resulting in phase separation of the two polymers. Phase separation process will be stop after water completely crystallized.

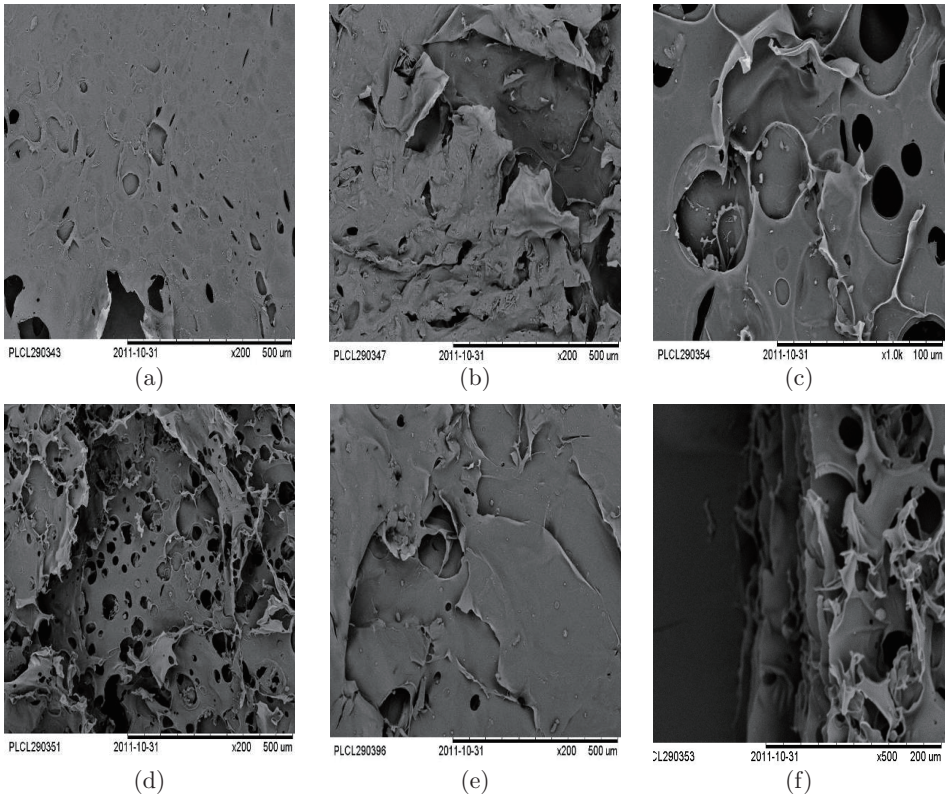


Fig. 6: SEM images of the surface of CS/ PLA blend membranes: (a) CS90; (b) CS80; (c) CS60, × 1000; (d) CS60; (e) CS50; (f) cross section

Obviously, the crystallization behavior of water will determine the final form of the morphological structure of the film hole. In the freeze-drying process, casting membrane solution was frozen layer by layer from the surface inward, thus forming a unique sheet structure. In the solution of CS water content is high, when the crystal phase separation is easy to form larger wafer, also

contributed to the formation of lamellar structure.

4.6 FTIR Spectra

Fig. 7 shows infrared spectrum of pure PLA film, while Fig. 7 shows infrared spectra of CS/PLA blend membrane. The infrared absorption of the pure PLA film has stretching vibration of C=O near 1752 cm^{-1} and stretching vibration of C-O near 1184 cm^{-1}, proving the existence of carbonyl. The wave number for the absorption peak near 1453 cm^{-1} is bending vibration peak of -CH3, proving the existence of -CH3. The absorption peak at 2945 cm^{-1} is the stretching vibration of -CH, proving the existence of -CH. And comparing with the previous reference[2], the position of the peak and intensity just has a little difference.

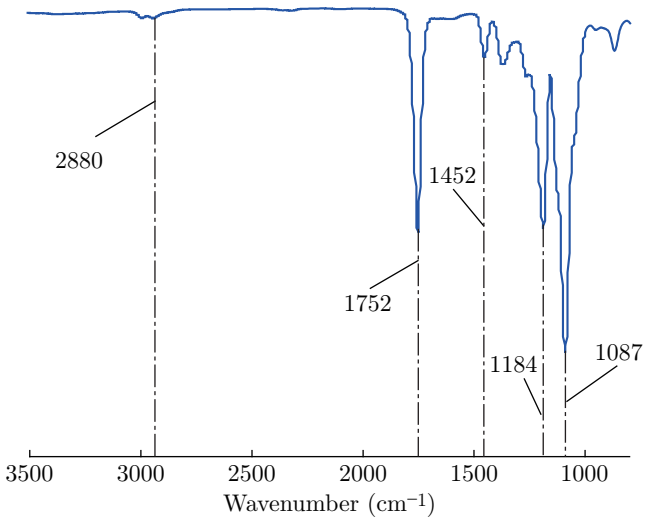


Fig. 7: FTIR curve of the PLA membrane

Infrared spectrum analysis can determine the changes before and after the formation of the position of vibration peaks and intensity of each CS/PLA blend membrane components. In order to explain the interaction between PLA and CS molecules, from the Fig. 7, it can be seen the different composition of hydrogen bonding interactions in the blend membrane. Referring to pure CS, there is a strong absorption peak of amide in the region of 1625.4-1634.6 cm^{-1}. The displacement of that peak for different samples is small, thus the peak can be used to determine CS deacetylation degree[13]. The crystallization peak of CS located at 1030 cm^{-1} move to the high range, indicating the changes of crystalline region of CS; 1084 cm^{-1}, 1134 cm^{-1}, 1184 cm^{-1} are the peak of C-O-C stretching vibration, proving the existence of ester group[14]. 3000-3600 cm^{-1} absorption peak attributes to the hydroxyl stretching vibration. Due to each hydroxyl of hydrogen bonds generated strong broad peak, from the figure, the width of the absorption peak of the blend membrane was gradually narrowed with the decrease of chitosan content, indicating that hydroxyl function enhanced. Meanwhile, the curve d appears characteristic peakat 1750 cm^{-1}, i.e. carbonyl peak of PLA, proving the existence of PLA; but the carbonyl absorption peak of PLA disappeared in curves b, c, and e, indicating that after the blending of CS and PLA solution, the hydrogen bonds between them appears, which also proves the compatibility of the two polymers.

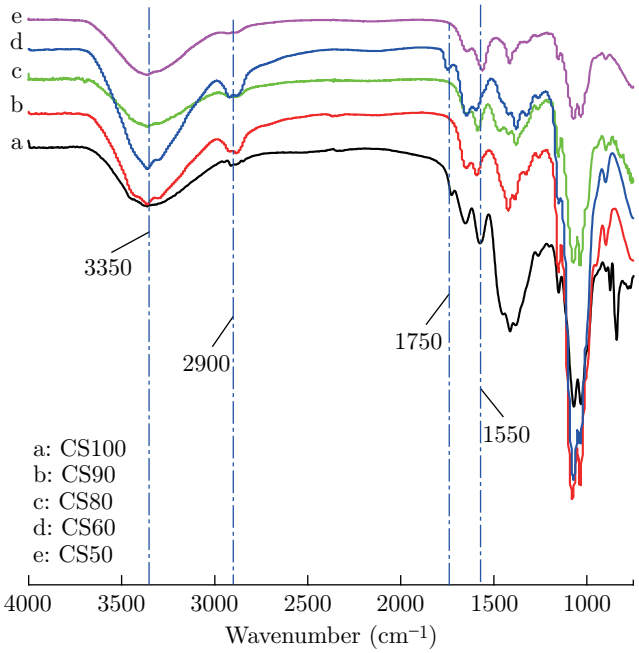


Fig. 8: FTIR curves of the CS/PLA blend membranes

4.7 DSC Analysis

From the DSC curves, the melting temperature of CS is 309.6°C due to the dehydration of sugar ring and decomposition of polymer in acetyl and deacetylation. The melting temperatures of blend porous materials are lower than that of pure CS. And with the decreases of CS content, the melting temperature of the film first decreases and then increases. The melting temperatures of CS90 and CS80 are 307.3°C and 261.9°C respectively. While the melting temperatures of CS50 and CS60 are 291.15°C and 279.1°C respectively, these indicate that the two polymer solutions are not completely separated; a certain extent interaction force exists between them. The interaction force derives from the strong hydrogen bonds generated between the carbonyl of PLA molecules and -OH and -NH_2 of CS molecules, and makes the connection among molecules of the two polymer solutions. On the one hand, because of this effect occurred in the amorphous region of PLA, inhibited the crystallization of CS and PLA phase, which made the melting point of each component decreased[15]. On the other hand, as the mass fraction of PLA increases gradually and the effect of co-solvent DMSO in the blend solution started to work, melting temperature increase, but later due to the plasticizing effect of DMSO, the melting temperature may decrease.

5 Conclusions

A series of porous membrane was prepared by freeze-drying the PLA and CS blend solution. After the performance of the series of blend films were analyzed and characterized, the main conclusions are obtained as follows:

(1) With the ratio of CS decreased, the color of the blend solution becomes shallow to transparent, the blend solution has good compatibility and the infrared curve shows the consistency of the results. It also shows that DMSO as a co-solvent plays an important role. But when the ratio

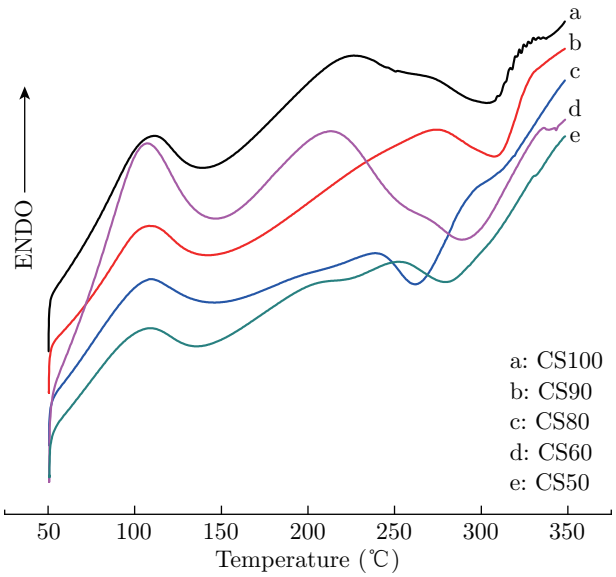


Fig. 9: DSC curves of the CS/PLA blend membranes

of CS decreased to 50%, the blend solutions started to a slight phase separation, then reduced the proportion of CS, the solution has obvious stratification phenomenon, cannot prepare blend membrane.

(2) Compared with pure chitosan, moisture absorption, water vapor transmission rate of CS/PLA and CS/PVA blend membranes are higher, which was mainly attributed to the interaction between CS and PLA or PVA, disrupting the regular structure of the original CS; After freeze-drying, the polymer blend membrane porosity has also been improved, but the weight ratio of the polymer blend membrane has a certain influence on porosity. The mechanical properties of blend films compared with each proportion of the blend films. With the proportion of CS reducing, the breaking strength and the breaking elongation increase gradually, which is related to add PVA or PLA component both improved the mechanical properties of membranes apparently, meanwhile because the addition of PLA changed the crystal structure of CS. In addition, the compatibility of two kinds of solution still needs to be further explored.

(3) The DSC curve analysis showed that with decreasing CS content, the decompose temperature of the films decreased firstly and then increased; there is some interaction force between the two. This effect occurred in the amorphous region of PLA, which inhibited the crystallization of CS and PLA phase and made the components of melting point depressed. On the other hand, because of the effect of co-solvent DMSO in the blend was at work, the melt temperature increased.

(4) The infrared spectra of CS/PLA results showed there is the formation of strong hydrogen bonding interaction between the two, which is consistent with the conclusion of DSC. Moreover, when the mass fraction of CS is greater than 50%, in the co-solvent DMSO system their compatibility is good. But to reduce the ratio of CS, the characteristic peaks of PLA appeared in the group of them, also showed that the phase separation appeared which is consistent with the conclusion of SEM.

In a word, the freeze-drying method is simple and effective for the preparation of CS based blend membrane. The polymer blend membrane material prepared has good moisture absorption,

porosity, water vapor transmission properties and so on. The research work provides theoretical and experimental basis for the research of applications of chitosan in medical dressing, artificial skin and other biomedical fields.

Acknowledgement

In this paper, we would like to give thanks to Shanghai Municipal Natural Science Foundation (14ZR1401000) and Shanghai University Students Innovation Project for providing support.

References

[1] Huang GF, Qing SB, Li SB, Huang SQ. The Advance of Polysaccharide Biomedical Materials-Chitin and Chitosan. J Polym Bull, 3, 2001 43-48

[2] Yuan J, Study on the Properties of Cellulose/chitosan Biodegradable Blend Films and Its Preparation, J. Plastics Science and Technology, 37 (2009), 43

[3] Jiang T, Chitosan, second ed, Chemical Industry Press, Beijing, 2006

[4] Yu RB, You HY, Xu XL, Li HX. Preparation and Properties of the Blend Film of PVA and Chitosan. J Mod Plast Process Appl, 13, 2001, 16-18

[5] Liu JM, Lv YC, Jia LX. A feasible study of PLA fibers application to medical use, JSH Textile: Sci Technol, 7, 2009, 37

[6] Xia M, Liu JC, Wan DY, Li SH, Chen YW, Wang LF. Advance on Modification of Environment-friendly PLA. J EngPlast Appl, 3, 2014, 22-126

[7] Guo C, Dong YS, Lin PH, Pu YP, Liu B. Study on Fabrication of Poly lactic Acid Porous. J SE Univ: NatlSci Ed, 4, 2004, 495-499

[8] Luo BH, Lu ZJ, Formation of Highly Porous Biodegradable Scaffolds for Tissue Engineering. J. Foreign Medical Sciences Biomedical Engineering, 2001, 154

[9] Li RL, Li CY, Zhang W. Micro-structure of Composite Tissue Engineering Scaffold of Chitosan and Type Collagen with Scanning Electron Microscope. J SUN YAT-SEN Univ: MedSci, 5, 2006, 557-561

[10] Ding B, Kimura E, Sato T, Fujita S, Shiratori S. Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning. J Polym, 45, 2004, 1895-1902

[11] Liu WJ, Lin ZH. Preparation and Mechanical Properties of Biodegradable Cellulose/Chitosan Blend Film. J China Plast Ind, 12, 2003, 44-46

[12] Pearson FG, Marchessault RH, Liany CY. Infrared spectra of crystalline polysaccharides V chitin. J Polym Sci, 141, 1960, 101-116

[13] Zislis T, Martin SA, Cerbas E. A scanning electron microscopic study of in vitro toxicity of ethylene-sterilized bone repair materials. J Oral Implantol, 1, 1989, 41-47

[14] Domszy JG, Roberts G, Makromol AF, Evaluation of infraxedspectropic techniques for analyzing chitosan. J Macromol Chem Phys, 8, 1985, 1671-1677

[15] Yang K, Ji P, Teng CQ, Xu YB, Yu MH, Melt PolycondensationProparation of Poly (Lactic Acid) and Its Poly(ε-Caprolactone) Chain-extension Exploration. J. Polymer Materials Science and Engineering, 21 (2005), 128-131