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Preparation and characterization of regenerated cellulose/poly (vinylidene fluoride) (PVDF) blend films

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ABSTRACT

Regenerated cellulose/poly (vinylidene fluoride) (PVDF) blend film was successfully prepared through coagulating their N,N-dimethyl acetamide (DMAC)/LiCl solution with water. The toughness of the blend films, compared with virgin regenerated cellulose film, was significantly improved when the content of PVDF in blend films was no more than 20 wt.%. The elongation at break increased from 12% to 34%, and the tensile strength was also improved from 89 to 106 MPa with the addition of PVDF till 20 wt.%. The mechanical properties of the blend films became worse when the content of PVDF in blend films was more than 20%. The oxygen permeability was firstly decreased from 2.3×10^{-10} to 0.036×10^{-10} cm^3 cm/cm^2 s Pa when the PVDF content increased from 0 to 5 wt.% in the blend films. Afterwards, the oxygen permeability would increase with the increasing of the PVDF content. The film showed some pores when the loading level of PVDF was more than 50%. The pore size of blend film became larger with the increasing of PVDF content. These phenomena were well correlated to the crystallinity, hydrogen bonds and morphologies of the blend films.

1. Introduction

In recent years, the research and development of biodegradable film has been paid more and more attention due to the serious “white pollution” of the non-biodegradable plastic film and the exhausting petroleum resource. Cellulose is the most abundant renewable material on the earth. Cellulose film has high mechanical strength, excellent hydrophilic properties (Babu & Gaikar, 2001; Nuortila & Nyström, 1996), good thermal resistance and biodegradability (Kallioinene, Pekkarinen, & Mänttäri, 2006). However, the toughness of cellulose film is poor; the elongation is less than 15% under dry condition (Zhang, Ruan, & Gao, 2002), and this limits its applications. To solve the problem, a common method of immersing the film into plasticizer solution is used (Akim, Naimark, & Vasilev, 1971; Naimark, 1978), but it was found that the plasticizer is easily lost during utilization. So cellulose blending with a number of polymers has been studied recently, e.g. poly (ethylene oxide) (Nishio, Roy, & Manley, 1987), poly (acrylonitrile) (Kondo & Shin, 1998), and starch (Lan, Li, & Zhong, 2009). These blend materials were considered to be composed of partially miscible pairs due to hydrogen bonds between the three hydroxyl groups of cellulose and functional groups of the polymers.

In our previous work, cellulose was dissolved and blended with poly (vinyl alcohol) (PVA) and thermoplastic polyurethane elastomer (TPU) (Zhang, Zhu, & Liu, 2012a,b, in press-a). It was found that the two polymers had strong hydrogen bonds with cellulose and were very compatible with cellulose. Poly (vinylidene fluoride) (PVDF) is highly miscible with oxygen-containing polymers, which is the result of the interaction between the fluorine atoms and carbonyl groups of the counter polymer (Bama, Devi, & Ramachandran, 2009; Jamil & Jamieson, 1989; Lee & Kim, 2011; Liu, Lin, & Huang, 2005; Ma, Xiong, & Lv, 2011; Moussaif, Pagnoulle, & Jerome, 2000; Nguyen, Mighri, & Deyrail, 2010; Scheinbeim & Gao, 2001; Xi, Qiu, & Li, 2006; Yang, Han, & Kim, 1994). PVDF which exhibits high flexibility and thermal stability is a semi-crystalline polymer including an amorphous phase and a crystalline phase. Besides, PVDF is an advanced material for membrane separation due to easily forming microporous structure. It has unique properties such as good processability, excellent mechanical property, and exceptional chemical stability. The electronegativity of fluorine atoms was stronger than oxygen and nitrogen atoms. So the compatibility between cellulose and PVDF may be better than that of cellulose and TPU or PVA. Meanwhile, the pore size of PVDF film for separation was also important. It was also very hard to control the porous size of PVDF film. In this article, the cellulose and PVDF blend films were prepared in DMAC/LiCl solution. And the effect on the toughness and rate of oxygen permeability of cellulose film will be evaluated with various amounts of PVDF, while the regulation function of cellulose content in blend on the pore structure of

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PVDF film was studied. The property–structure relationship of the cellulose/PVDF blend films will also be discussed in the article.

2. Experimental

2.1. Materials

The cotton linter was used as cellulose source. It was obtained from Dezhou Tianma Fiber Company, Dezhou, China. It contains over 97.6% cellulose. Its viscosity-average molecular weight was determined in DMAC/LiCl solution to be 1.05×10^5 g/mol (DP = 640) by a multi-angle light scattering (DAWN DSP, Wyatt Technology Co., Santa Barbara, USA). Poly (vinylidene fluoride) (PVDF, Mw = 400,000–600,000) was purchased from Shanghai Fluorine Chemical Technology Co., Ltd. DMAC (anhydrous, 99.8%, CP) was obtained from a Guoyao group. LiCl, AP, 97%, was purchased from Shanghai Jufeng Chemical Company.

2.2. Preparation of cellulose/PVDF blend films

According to our previous reports (Zhang et al., 2012a,b, in press-a), activation of cellulose and its dissolution were done as follows: prior to dissolution, the cellulose sample was activated by heating and stirring for about 30 min at 160 °C in DMAC solution. And then the cellulose was removed from the solution and squeezed at about 180 °C. The activated cellulose was added into DMAC/LiCl solution and stirred at 100 °C for 3 h until a gel state was formed. Transparent cellulose solution was obtained after cooling the resulting gel at room temperature for 24 h. PVDF can be dissolved at 80 °C in DMAC/LiCl solution. The solutions obtained above were then mixed according to mass ratios of cellulose to PVDF: 100/0 (RC), 97.5/2.5 (RC2.5), 95/5 (RC5), 90/10 (RC10), 80/20 (RC20), 60/40 (RC40), 50/50 (RC50), 40/60 (RC60), 20/80 (RC80) and 0/100 (PVDF), respectively. The mixture solutions were stirred vigorously for about 0.5 h at 85 °C, and then spread over a glass plate to give a 0.25 mm layer of solution by glass rod with copper wire, whose diameter was 0.25 mm. The glass plate covered with the mixture solution was coagulated in the air and then the film was detached in distilled water. The detached film was immersed in running water for over 12 h. The blend film was finally dried and stored for characterization.

2.3. Apparatus and measurements

The blend films were frozen in liquid nitrogen, snapped immediately, and then vacuum dried. Cross-section of the fractured films was coated with a thin layer of gold (about 2 nm) to observe their microstructures by using a field emission scanning electron microscope instrument (S-4800, JEOL, Japan). The tensile properties were measured on Instron 5567 tester at a crosshead speed of 5 mm/min at room temperature. The specimen gauge length was 50 mm and the specimen width was 10 mm. The crystallization pattern of the dried films was recorded on a wide-angle X-ray diffraction (XRD) instrument (D8 Advance, Bruker AXS, German) with Cu Kα radiation ($\lambda = 0.154$ nm). XRD data were collected from $2\theta = 4$–35° at a scanning rate of 2°/min. Peak fitting was performed on jade software with Gaussian function. The crystallization was determined by the method reported by Wang, Ding, and Cheng (2007). PERME VAC-V2 Gas Permeability Tester (Labthink, China) was utilized to test the oxygen permeability (OP) of the films according to standard method ASTM D3985-95. Oxygen transmission rates (*OTR*) were determined at 23 ± 1 °C and 50 ± 1% RH. The film samples were masked with aluminum foil mask with an exposure area of 38.48 cm^2. These samples were mounted in a 'diffusion cell' to form a sealed semibarrier between two chambers at ambient atmospheric pressure. During testing, one chamber containing O_2 at a specific high pressure will be purging O_2 at a setted purging rate of 100 ml/min, and the other chamber, at relatively low pressure, will receive the permeating O_2. The lower pressure chamber was initially evacuated and the transmission of the gas through the test specimen was indicated by an increase in pressure. Five replicates of each film were evaluated.

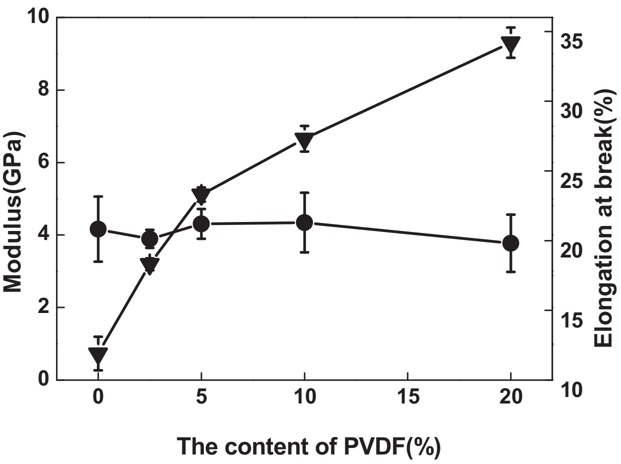

Fig. 1. The dependence of elongation at break (▼) and modulus (●) of the films with different contents of PVDF.

OP was calculated by the following equation:

$$\mathrm{OP} = \frac{OTRd}{\Delta P}$$

where d is the film thickness; ΔP is the oxygen partial pressure difference; the units for OP were cm^3 cm/cm^2 s Pa.

3. Results and discussion

3.1. The properties of blend films

The PVDF film has good ductility. The toughness of cellulose was expected to be improved by blending PVDF into cellulose. The effect of the PVDF content on the elongation at break (ε), tensile strength (σ) and modulus (E) of blend films is shown in Figs. 1 and 2 and Table 1. The elongation at break was dramatically improved from initial 12% to 34% with 20 wt.% loading of PVDF. The tensile strength was firstly increased and then decreased. The maximum strength

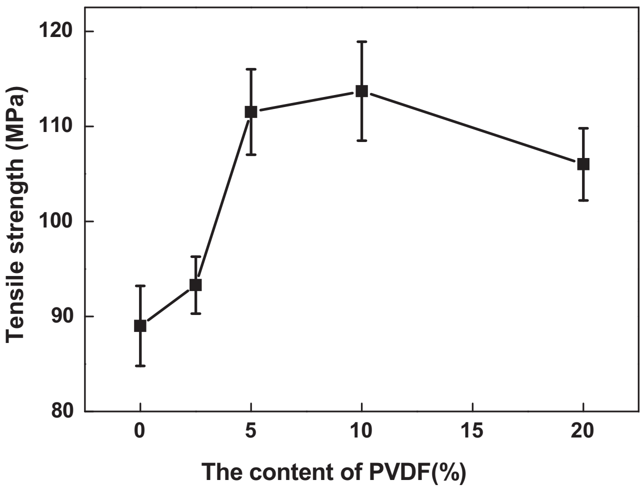

Fig. 2. The dependence of tensile strength of the films with different contents of PVDF.

Table 1
The mechanical properties, oxygen permeability and the crystallinity of the blend films.

Samples	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)	Degree of crystallinity (%)	Oxygen permeability (cm^3 cm/cm^2 s Pa)
RC	89.0	4163	12	58	2.3×10^{-10}
RC2.5	93.3	3894	18	55	0.16×10^{-10}
RC5	111.5	4305	24	54	0.036×10^{-10}
RC10	113.5	4344	27	46	0.045×10^{-10}
RC20	106.0	3772	34	40	0.15×10^{-10}
RC30	88.0	2646	26	34	25×10^{-10}
RC40	40.2	1657	11	32	750×10^{-10}
RC50	18.0	1450	9	38	–
RC60	3.2	676	9	39	–
RC70	2.4	451	9	40	–
RC80	3.0	284	15	43	–
PVDF	2.0	179	62	48	–

was 113.5 MPa with 10 wt.% PVDF loading level. It was interestingly found that the toughness and strength of the films were significantly improved when the content of PVDF was no more than 20%, while the modulus was slightly higher or kept the same. For example, the blend film with 5 wt.% or 10 wt.% PVDF showed improved toughness, tensile strength and modulus. The results were much better than those of cellulose/TPU or cellulose/PVA blend films in our previous studies (Zhang et al., 2012a,b, in press-a). The mechanical properties of the blend films with higher content of PVDF (more than 20 wt.%) all steadily decreased with the increase of PVDF content shown in Table 1.

The gas barrier properties were particularly important for packaging materials because ingress of even very small amounts of oxygen caused most protected products to deteriorate. The oxygen permeability data of the films are reported in Fig. 3 and Table 1. The results showed that the addition of PVDF had a great effect on oxygen permeability data. The oxygen permeability was firstly decreased from 2.3×10^{-10} to 0.036×10^{-10} cm^3 cm/cm^2 s Pa and then increased with the increasing of the PVDF content. The changes in oxygen permeability were explained by the strong hydrogen bond interaction between hydroxyl groups and fluorine atoms. So it can be seen that the oxygen permeability can be greatly reduced by the loading of PVDF. These results were related to the change of film microstructure, which will be determined by SEM and discussed in Section 3.2.

3.2. *The property–structure relationship of the blend films*

The toughness and strength of the films were significantly improved when the content of PVDF was no more than 20%, while the modulus was slightly higher or kept unchanged. However, for the blend films with higher content of PVDF (>20%), the mechanical properties decreased significantly. On the other hand, the oxygen permeability decreased at first, and then increased with the increasing of the PVDF content. In order to explain these phenomena, we investigated the structure changes of blend films through XRD and SEM.

As can be seen in Table 1 and Fig. 4, the crystallinity of the blend films decreased with increasing PVDF content when the PVDF content in blend films was no more than 20%. However, compared with pure cellulose film, the oxygen barrier property of the blend films was improved. This illustrated that the oxygen permeability of cellulose film was controlled by amorphous phase. The incorporation of PVDF improved the compactness of amorphous phase in blend films, which had a good effect on the improvement of oxygen barrier property. It may be due to the fact that the hydrogen bond between the hydroxyl group of cellulose and fluorine atom in PVDF was stronger than that between different hydroxyl groups of cellulose, and had better compatibility. Besides, the modulus of the blend films was kept unchanged or even slightly higher though the toughness and strength of the films significantly increased. This was also related with the more compact structure of the amorphous phase in blend films. So the improvement of toughness and oxygen barrier properties, compared with our previous work, was better than that of cellulose/TPU or cellulose/PVA (Zhang et al., 2012a,b, in press-a).

On the other hand, the characteristic diffraction of the PVDF could be seen in blend films when the PVDF content in blend films reached 40%. A slight shoulder peak marked by a circle appeared in the curves of RC40 and gradually came to an obviously sharper peak in RC50. At this case, as can be seen in Fig. 5(a)–(c), the size

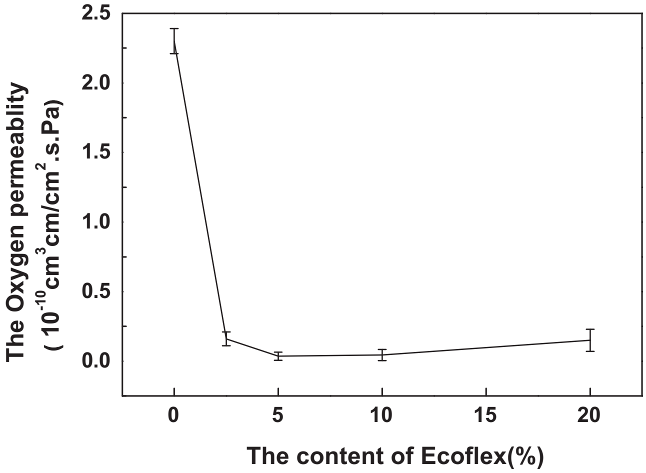

Fig. 3. Effect of the content of PVDF on the oxygen permeabilities of cellulose film.

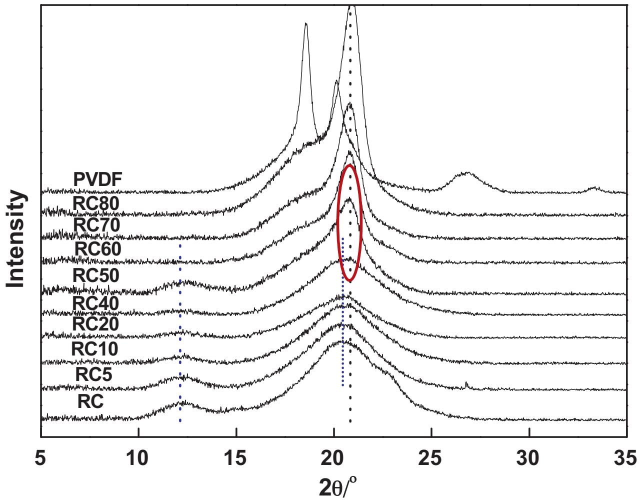

Fig. 4. XRD patterns of the films with different contents of PVDF.

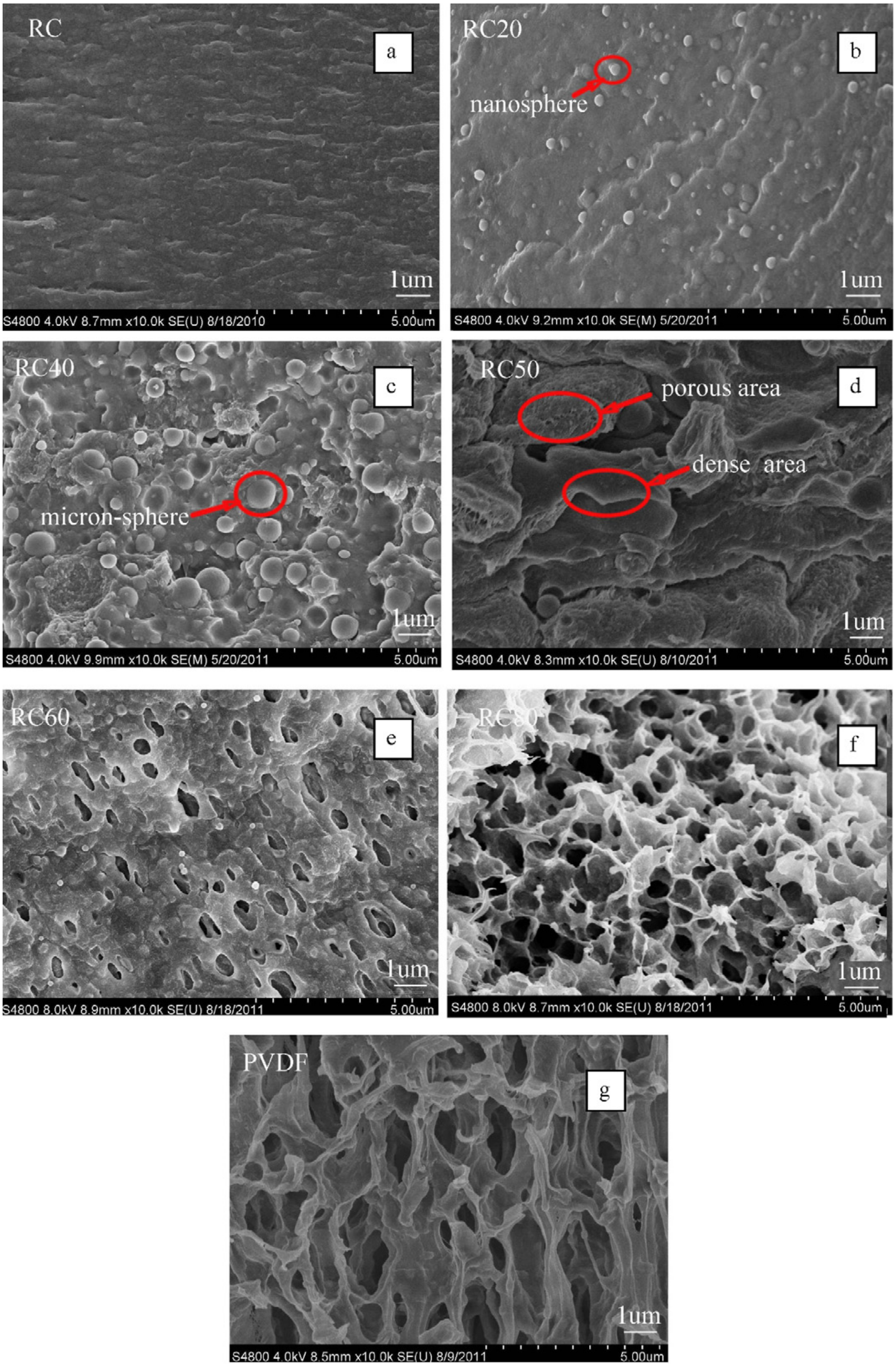

Fig. 5. The SEM of the cross section for the films with different contents of PVDF.

of the PVDF as disperse phase increased steadily. And a bicontinuous structure was formed and some small pores appeared in PVDF matrix when the PVDF content increased to 50% as shown in Fig. 5(d). The appearance of the pores can be explained by separation mechanism of regeneration film, the porous PVDF film was formed by the way of instaneous separation (Smoder, Reuvers, & Boom, 1992; Zhao, Chen, & Zhang, 2011). So the decrease of mechanical properties and oxygen barrier property of cellulose film were mostly due to the large dispersion size or porous structure of the PVDF.

Finally, when the content of PVDF increased to 60%, the characteristic diffraction peak of the cellulose disappeared in XRD curves of blend films. Only one peak at around $2\theta = 20.8^\circ$ (β-type of PVDF) could be seen. At this case, the PVDF formed a fully continuous structure. The size of pores increased with the further increasing content of PVDF as shown in Fig. 5(e)–(g). The mechanical properties became further worse with the increasing content of PVDF. And the oxygen permeability was too high to be measured, which may be induced by macro-porous structures.

To sum up, the morphology change of blend films was divided into three cases. Firstly, PVDF as a disperse phase was nano-dispersed in cellulose matrix when the PVDF content in blend films was no more than 20%. Secondly, the size of PVDF as a disperse phase was gradually growing up and a bicontinuous structure was formed when the PVDF content increased to 50%. Finally, the PVDF formed continuous phase with pores, and the pore size increased gradually with the further increase of PVDF content. In other words, addition of small amount of PVDF into cellulose can improve the toughness and strength of cellulose film, while addition of cellulose into PVDF can decrease the pore size of PVDF film. The structure observation of blend films well supported the changes of their properties.

4. Conclusion

Regenerated cellulose/PVDF blend films were successfully prepared by coagulating with water. The positive effect on the toughness of cellulose was confirmed by the results of mechanical properties when the content of PVDF in blend films was no more than 20%. The mechanical properties of the blend films with higher content of PVDF were worse due to the appearance of porous structure. It was demonstrated that cellulose could be miscible with polymers containing strong electro-negativity of atoms, and the toughness of regenerated cellulose could be improved by blending with these kinds of polymers having good toughness. The oxygen permeability of cellulose film was significantly decreased by adding less than 20 wt.% of PVDF, while the pore size of PVDF film became small with the incorporation of cellulose. These blend films showed potential application as packaging or separating materials.

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