Properties of Poly(vinyl alcohol) Plasticized by Glycerin

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Abstract—The plasticized poly(vinyl alcohol) (PVA) films were prepared by the casting method using glycerin as the plasticizer. The interaction between PVA and glycerin was analyzed by Fourier transform infrared (FTIR) spectroscopy, Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC). Thermal properties, water resistance and mechanical properties of PVA and plasticized PVA were studied respectively. It was found that the glass transition temperature and thermal decomposition temperature of modified PVA were lower than PVA. The plasticized PVA had lower tensile strength and higher elongation at break, lower degree of swelling and higher solubility than PVA.

Index Terms — Poly(vinyl alcohol); Glycerin; Plasticizers; Modified

I. INTRODUCTION

Poly(vinyl alcohol) (PVA) has excellent film forming, water-soluble, adhesion, emulsification and barrier properties, which has been used in fibers, films and adhesive agents widely[1-4]. The structure of PVA molecule has many hydroxyl groups, which can form hydrogen bonds, this hydrogen bonding gives PVA many excellent properties. But the PVA film has the defects of low elongation at break, poor decomposition temperature and high glass transition temperature. The defects affect the application of PVA widely. So PVA was studied by many researchers. Jiang X C[5-7] studied the PVA which were prepared through the melt processing by employing magnesium chloride and polyethylene glycol as the complex plasticizer, the results showed that the plasticizer can effectively destroy the hydrogen bonding between PVA molecules and decrease the crystallinity and melting point of PVA significantly. Then he used MgCl₂ as plasticizer of PVA, the results showed that the modified PVA was with lower tensile strength and higher elongation at break than PVA. Ren D C[8] used urea/triethanolamine as a mixed plasticizer to modify PVA, he found that with the mass fraction of mixture of plasticizer increasing, the modified PVA was with lower tensile strength and higher elongation at break, good light transmission rate, lower degree of swelling and higher solubility than pure PVA. Jiang T[9] studied the plasticized starch/PVA films which were prepared by casting method using magnesium nitrate as the plasticizer. It was found that magnesium nitrate could form some interaction with starch and PVA molecules, magnesium nitrate could destroy the crystals of starch. Tensile testing showed that magnesium nitrate was highly effective in modifying the mechanical properties of starch/PVA films. In summary, the thermal properties and mechanical properties of plasticized PVA were improved by destroying the hydrogen bonds of PVA molecular. In this paper, we use glycerol as the plasticizer to improve the thermal properties and mechanical properties of PVA.

II. MATERIALS AND METHODS

Materials

PVA (AR) was purchased from ShangHai Yingjia Industrial Development Co., Ltd. (Shanghai, China). The degree of polymerization is 2400. Glycerin was purchased from NanJing Chemical Reagent Co., Ltd. (Nanjing, China)[5-6].

Samples preparation

3g PVA and 1.2g PVA was dissolved in distilled water by heating in an oil bath at 95°C for 2h. Then the solution was casted into a clean glass Petri dish (diameter 12cm) and dried at 60°C in the vacuum oven to completely eliminate water. Then the dried films were stored at RH of 54% for one week before testing. Films without plasticizer addition were also prepared as control[5-6].

Testing and characterizaton

The FTIR studies were carried out using a IS10 (PE Company, USA). The spectra were acquired in the range of 4000-400 cm⁻¹ at a resolution of 4 cm⁻¹. Glass transition temperature (Tg) was determined by differential scanning calorimetry using a Diamond DSC (PE Company, USA). Samples od about 7mg were condition in aluminum pans and heated at 20k/min under an inert atmosphere of N₂(50ml/min N₂) between 40-600°C. An empty pan was used as reference. Thermogravimetric analysis was carried out in a TG209F1 (Netzsch Company, Germany) in N₂ atmosphere(50ml/min) at a heating rate of 20k/min. The samples were kept into platinum and scanned from ambient temperature to 600°C. PVC films and plasticized PVA films after drying and weighing were put in deionized water for 24h, then weighed the samples after drying with filter paper. The calculation formula of swelling ratio is DS=(Wt-Wd)/ Wo, We: the mass of PVA films after swelling balance; Wo: the dry weight of PVA films. The samples were weighted after swelling balance were put in vacuum oven at 60°C for 24h. The calculation formula of

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dissolution rate is \( S = \left( \frac{W_o - W_d}{W_o} \right) \). \( W_o \), \( W_d \): the dry weight of of PVA films after swelling balance.
Tensile strength and percentage tensile elongation at break of the films were determined at room temperature using an Instron 5567 mechanical property measurement following GB13022-91, the Chinese standard equivalent to ISO 527-4.

III. RESULTS AND DISCUSSION

The FTIR measurements
There are many hydroxyl groups on PVA chains and they can form hydrogen bonding easily. The crystalline, thermal and mechanical properties of PVA can be affected by the intensity of the hydrogen bonding in PVA. The recent studies showed that the intensity of the interaction between the plasticizer and PVA is critical for the plasticizing efficiency of the plasticizer. It is an efficiency way to study the hydrogen bonding for in the infrared region using FTIR, the vibrations of molecules can be investigated. The pure PVA and PVA plasticized with the Glycerin were obtained and shown in Fig. 1. There is no absorption band of free “-OH” at 3600cm\(^{-1}\) for PVA. This indicates the hydroxyl groups are generally associate with the intermolecular and intramolecular hydrogen bonding. It was shown in Fig.1 that the absorption band of “-OH” shift to a higher wave number after the addition of the complex plasticizer of Glycerin. The shift in the frequency is valuable as the measurement of the hydrogen bonding of the hydroxyl group. It indicates that the hydrogen banding is weakened when the frequency shifts to a higher value. From the Fig.1, the spectrum of pure PVA showed the absorption of hydroxyl at 3255.15cm\(^{-1}\), the absorption band of hydroxyl shifted to a higher value at 3271.96cm\(^{-1}\) with the addition of the complex plasticizer (PVA-P), it indicated that the addition of the Glycerin would reduce the intensity of the hydrogen bonding of PVA molecules. It is because Glycerin forms strong hydrogen bonding with PVA, which take place of the hydrogen bonding between the hydroxyl group of PVA molecules. Glycerin reduces the intensity of the hydrogen bonding in PVA, it showed that Glycerin have a plasticizing effect for PVA.

Differential scanning calorimetry
Differential scanning calorimetry was performed in order to determine the glass transition temperature (Tg) of polymeric matrix. The temperature is an important parameter in polymer characterization being able to evaluate the plasticizing effects of substance added to polymeric systems.

DSC curves of PVA and plasticized PVA are shown in Fig.2. The addition of the glycerol to PVA film shifted the Tg towards lower temperature, from 348.5°C in the PVA film to 328.5°C in the plasticized PVA. The PVA has a large number of hydrogen bonding, which makes PVA a stable state of aggregation and high degree of crystalline, so the PVA has a high glass transition temperature. The addition of glycerol destroyed the hydrogen bonding, the activity of PVA chains will be enhanced, which reduced the glass transition temperature.

Thermogravimetric analysis
Thermogravimetric curves of PVA and plasticized PVA were showed in Fig 3. We can get the decomposition temperature from the thermogravimetric curves. International Bureau of standards (ISO) defined the temperature of intersection which was between the base line and the extended line of the connection of 20% weight loss and 50% weight loss point as the decomposition. In the thermogravimetric curves of PVA and plasticized PVA, the point A,B and C, D is 20% weight loss and 50% weight loss point of PVA and plasticized PVA respectively. The point E and F is the decomposition of PVA and plasticized PVA respectively, it is 218°C and 227°C. Because plasticized PVA contains many small molecules, they will volatile when the temperature from 100°C to 600°C, the thermogravimetric curves of PVA is lower than the PVA.

![Fig.1 IR Spectra of PVA and modified PVA](image1)

![Fig.2 DSC curves of PVA and modified PVA](image2)
Swelling ratio and dissolution rate
The value of swelling ratio and dissolution rate are showed in Table 1. From Table 1 we can see that the degree of swelling PVA and modified PVA is 2.62 and 1.76, the solubility is 0.24 and 0.39 respectively. The reason why the modified PVA has lower degree of swelling and higher solubility is that hydroxyl of PVA has been destroyed.

Mechanical properties
The value of mechanical properties of PVA and modified PVA films are showed in Table 1. The elongation at break of PVA and modified PVA is 210.58% and 360.20% respectively. The tensile strength of PVA and modified PVA is 32.26 MPa and 17.12 MPa respectively. We interpreted that the change of mechanical properties arises from the degree of the crystallinity. The entanglement and interaction between PVA chains was weak and then the tensile strength decreased when the PVA was with a lower crystallinity. Because the plasticizer was with higher plasticizing efficiency, PVA would be more completely melted to form a continuous phase and thus show better mechanical properties.

Table 1
Swelling ratio, dissolution rate and mechanical performance parameters
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<tr>
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<th>PVA</th>
<th>PVA(40%)</th>
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<tr>
<td>Degree of swelling</td>
<td>2.62</td>
<td>1.76</td>
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<tr>
<td>Solubility</td>
<td>0.24</td>
<td>0.39</td>
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<tr>
<td>Elongation at break(%)</td>
<td>210.58</td>
<td>360.20</td>
</tr>
<tr>
<td>Tensile strength(MPa)</td>
<td>32.26</td>
<td>17.12</td>
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IV. CONCLUSION
The Glycerin was proved to be with a high plasticizing effect for PVA by all the results in our article. Glycerin could interact with PVA molecules and replace the hydrogen bonding within PVA molecules. The crystallization of PVA was interrupted and the intensity of the hydrogen bonding in PVA was reduced in the way. The Glycerin could improve the compatibility of PVA, and the plasticized PVA films appeared a more continuous than pure PVA films. The thermal stability and the glass transition temperature of decreased with the addition of Glycerin. The mechanical properties of PVA were improved significantly and the plasticized PVA films appeared a more tougher than pure PVA films after adding the Glycerin. It can also be expected that the Glycerin could play an important role in the polymer such as cellulose that contains many hydroxyl groups.

REFERENCES