

Development of Humidity-Sensitive Films from Oleic Acid – Modified PVA

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Abstract

Humidity-sensitive films from modified Poly (vinyl alcohol) (P*) were developed. Poly (vinyl alcohol) was modified by adding 1, 3 and 5 pph (part per hundred) of oleic acid in the presence of *p*-toluenesulfonic acid (*p*-TSA) as a catalyst. Cobalt chloride as a desiccant was also added. Effects of the amount of oleic acid in the films on properties were determined. The results from preliminary properties tests (%swelling, and %solid remaining) of the films indicated that the 5 pph of oleic acid modified poly (vinyl alcohol) provided great water resistance properties. In addition, water resistance properties of the films increased when increasing amount of oleic acid. The moisture content of the films was measured under various moisture conditions (0-95 %RH). The sheet resistance at different moisture conditions was investigated by 4 Point Probe Resistivity measurements. The sheet resistance of the films was inversely proportional to the relative humidity. The values were in the ranges of 68×10^6 to $1.5 \times 10^4 \Omega$ as the %RH varied from 0 to 95 %.

Keywords: Humidity sensor, Humidity sensitive, oleic acid, Poly (vinyl alcohol), Tung oil

Introduction

Relative humidity (RH) is a physical parameter which indicates the concentration of water vapor in ambient air. The influence of humidity is of importance in diverse areas, such as moisture food processing, sensitive products, textile technology, storage areas, computer rooms, hospitals, museums, libraries, high voltage engineering and accelerator systems [1,2]. Therefore, sensing and controlling of relative humidity is of great importance. Different types of humidity sensors, such as metal oxide sensors and catalytic, are available in industry [3]. However, they require high temperature operation and consume significant amount of power. There has been a considerable interest in exploiting organic substances. Advantage of using polymers as sensing materials, is that they can be functioned at room temperature wherein the inorganic sensors normally operate at elevated temperatures. Among them, poly (vinyl alcohol) (PVA) has favorable characteristics for a given a humidity sensor [4-6]. However, its resistance to water molecules is poor such as high moisture uptake and fast moisture transmission, originating from hydroxyl groups in the repeating unit of PVA [7]. It can cause swelling and degradation when used in high humidity conditions. Therefore, improvement in the water resistant properties of PVA was developed. Much research has been studied to improve water resistance properties of PVA using clay [8], graphene [9], and polymer-polymer blends [10]. In terms of chemical structure, hydroxyl groups in PVA can be exploited as reactive sites capable of reacting with multifunctional substances to obtain three-dimensional networks in PVA, and this enhances resistance to dissolution in water and improves the mechanical properties and thermal stability [11, 12]. PVA can be crosslinked by chemical reagents such as hexamethylenediisocyanate [13], glutaraldehyde [14], glyoxal [15], and boric acid (BA) [16, 17]. However, their toxicities made them not suitable for human and food applications. Therefore, various natural hydrophobic chemicals have been thoroughly studied to improve the water resistant property of PVA. Oleic acid, a saturated fatty acid, can alternatively be used. The long carbon chain of oleic acid provides not only a hydrophobic property but also a good crosslinker to form network structure because it has a double bond structure which is able to generate free radicals and to crosslink itself into network structure resulting in film formations. Although, the density of crosslinking can improve the water resistant property of PVA, the electrical resistivity of the received PVA films is raised as a function of amount of crosslinking [18] which is not suitable for the application of sensor. To decrease the resistivity of the

film especially at low relative humidity (RH) and, thus, to increase its humidity sensitivity, cobalt chloride (CoCl₂) as both electrolyte and desiccant can be added into the film. Here we report the use of cobalt chloride containing in oleic acid modified PVA film as for a sensing humidity. Change in electrical resistance of the modified PVA with the changing relative humidity from 0 to 95% relative humidity was investigated to be an appropriate measure of relative humidity for sensor application.

Materials and methods

2.1 Materials

Partially saponified type of PVA with the weight-average molecular weight of 120,000 g/mol and a degree of hydrolysis of 85–87 % (JP- 2 7 grade) was purchased from Japan Vam & Poval CO, LTD. Oleic acid, cobalt chloride and *p*-toluenesulfonic acid (*p*-TSA) were purchased from Carlo Erba Reagent CO, LTD.

2.2 Preparation of modified P* films

For the preparation of the P* films, PVA (60 g) was dissolved in deionized water (540 g) by stirring at 90°C for 1 h to give a PVA solution. Oleic acid at various amounts of 1, 3, and 5 pph (P1*, P3*, P5*) based on PVA solution was added to the PVA solution under stirring, and *p*-TSA was added to the resulting solution, followed by additional stirring at 90 °C. After 24 h, the solution was allowed to cool down to room temperature. Cobalt chloride as a desiccant was then added with well-stirred. Each mixture solution was coated onto a PET substrate. The coated films were dried in a room temperature for 48 h. The films thickness was maintained at about 35 ± 5 μm to aid in evaluating physical properties.

2.3 Water resistance and solid remain of P* films

The P* films were cut into a rectangular shape (2x2 cm²). Each of the specimens was weighed and immersed in water for 24 h to ensure that the films had reached the equilibrium state of swelling. The specimen was dried to constant weight in an oven. The percentage of solid remains was calculated as follows:

$$\% \text{solid remaining} = (W_2/W_1) \times 100$$

Where W₁ is the dry weight (g) before immersion in water and W₂ is the dry weight (g) after immersion in water for 24 h.

In case of swelling behavior, after the P* films were swelling in water for 24 h, the swollen films were weighted. The swelling degree was calculated as follows:

$$\% \text{swelling} = ((W_2 - W_1)/W_1) \times 100$$

Where W₁ is the dry weight (g) before immersion in water and W₂ is the swollen weight (g) after the swelling in water for 24 h

2.4 Moisture content

The P* films were cut into a rectangular shape (2x2 cm²). Before the measurement, these specimens were kept to afford constant weight in 0% RH at ambient conditions for 7 days and weighed to record as dried films. The films were later kept into a desiccator (75%RH) for 3 days before weighing to obtain the adsorbing weight. The percentage of moisture content of the films was calculated as follows:

$$\% \text{moisture content} = (W_2 - W_1/W_1) \times 100$$

Where W₁ is the dry weight (g) at 0%RH and W₂ is adsorbing weight (g) after held in a desiccator 75 %RH after kept at 3 days.

2.5 The sheet resistance of P* films

The P* films were cut into a rectangular shape (2x2 cm²). The moisture content of the films was measured under various moisture conditions (0-95 %RH). After 24 h conditions, the sheet resistance at different moisture conditions was investigated by 4 Point Probe Resistivity measurements. The sheet resistance of the films was calculated as follows:

$$\text{Sheet resistance } (R_s) = \frac{\pi \Delta V}{\ln(2) I} \quad (1)$$

Where ΔV is the change in voltage measured between the inner probes, and I is the current applied between the outer probes [19].

Results and discussion

3.1 The reaction of PVA and Oleic acid

The structure of PVA composes of hydroxyl group resulting in poor wettability resistance and poor humidity resistance. To improve these properties, PVA was modified by oleic acid by using *p*-TSA as an initiator. There are three kinds of the proposed reactions able to occur as illustrated in Figure 1: (a) esterification reaction between carboxylic groups of oleic acid and hydroxyl groups of PVA, (b) H-bonding among hydroxyl groups of PVA and/or carboxyl groups oleic acid and (c) crosslinking reaction initiating at double bond at long hydrocarbon chains of oleic acid via free radical mechanism.

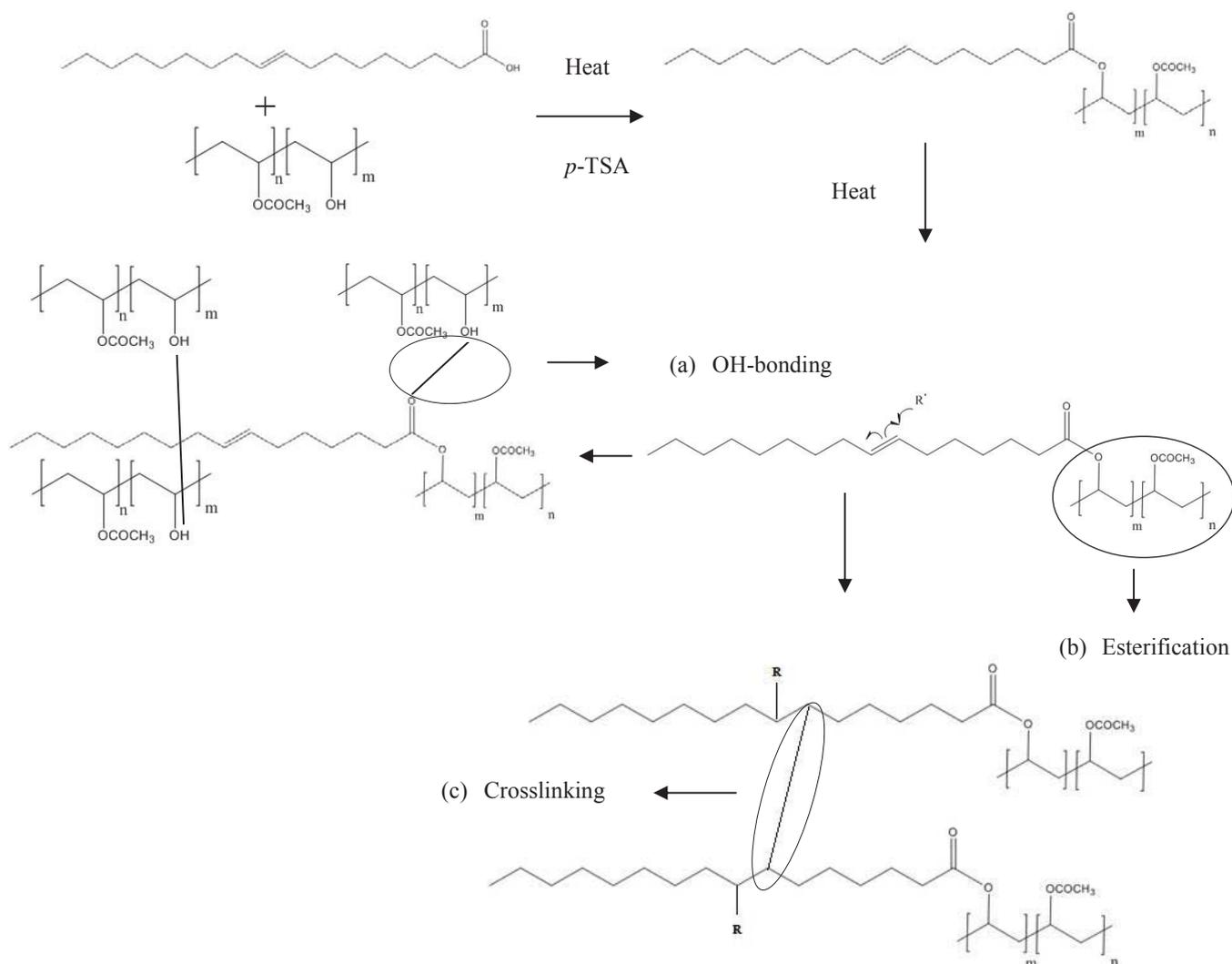


Fig.1. The proposed reactions of PVA and Oleic acid

3.2 Water resistance of PVA/oleic acid film

Time dependent swelling of P* films in water was shown in Figure 2. The percentage of swelling of all the samples reached the equilibrium value after time interval at 8 h. The increasing of oleic acid to PVA ratio caused the decrease in the percentage of swelling. Thus, P1* has higher swelling at all-time interval than others and reached the highest maximum percentage of swelling at 135% after 24 h comparing with 86 % of P3* and 47% of P5*. It was obvious that the swelling decreased when oleic acid was increased. It was due to the hydrophobic structure of oleic acid and the formation of crosslinking structure within the film. Thus, the addition of oleic acid could improve the water resistance of the film.

Table 1 shows the solid remains of P1*, P3*, and P5*. It should be noted that pure PVA film cannot withstand the water and, hence, easily swelling and dissolving in water (0% solid remaining). The presence of oleic acid in the film dramatically increased the % solid remain values compared with those of pure PVA film. The % solid remains of P1*, P3* and P5* were at 89.0, 94.5 and 95.6%, respectively. The higher the amount of oleic acid in the film, the higher % solid remains was obtained.

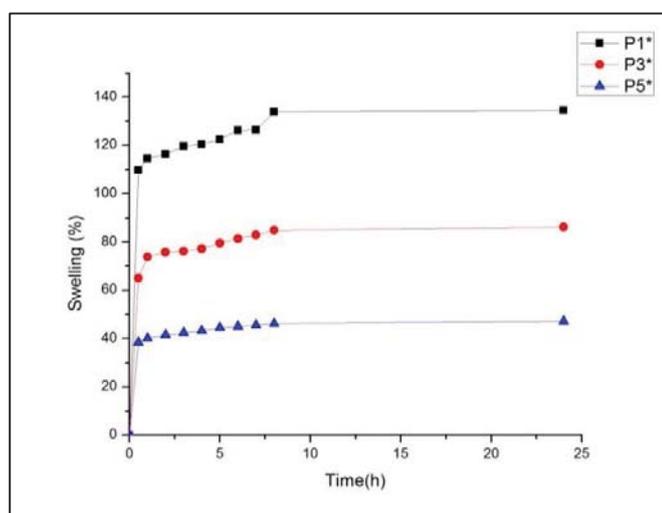


Fig.2. Time dependent swelling of P1*, P3* and P5*

Table 1 The % solid remains of P1*, P3*, and P5*.

Sample	%Solid remain
P1*	89.0
P3*	94.5
P5*	95.6

3.4 Moisture content

The moisture contents of the films are shown in Fig.3. The addition of oleic acid from 1 to 5 pph in the films resulted in the slightly decrease in the moisture content. P1* gained the moisture content at 8.9% after condition for 72 h comparing with 7.3% of P3* and 5.1% of P5* at the same time interval. To increase the capability of moisture absorption in order to the usage in humidity sensor application, the addition of CoCl₂ to the P* film was applied as it is such a desiccant. The results of the increase of water vapor absorption demonstrated in Fig. 4. The moisture uptake were increased from approximately 8.9% for P1* to 14.5% for P1*Co, 7.3% for P3* to 13.0% for P3*Co and 5.1% for P5* to 12.0% for P5*Co

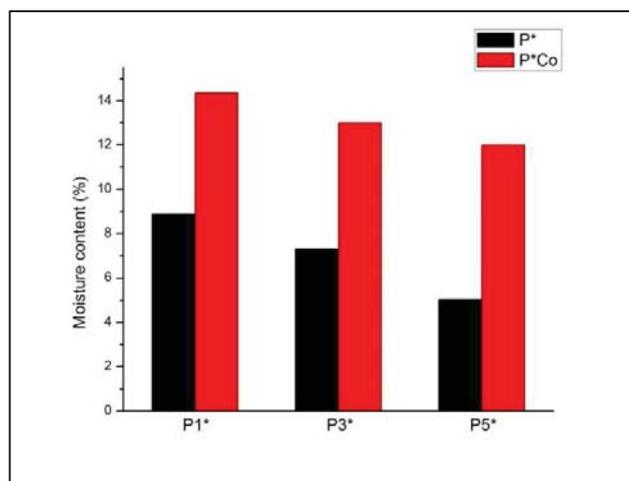


Fig.3. Moisture contents of P* and P*Co films

3.5 Humidity sensing properties of P* films

The sheet resistances (R) of the films are shown in Fig.4. The starting of sheet resistance values, conditioned at 0%RH, differed from approximately $68 \times 10^6 \Omega$ for the P5* to $22.65 \times 10^6 \Omega$ for the P3* and $11.33 \times 10^6 \Omega$ for the P1*. At various condition of %RH before the measurement, the resistance was decreased as a function of %RH. For example, the resistances of P5* reduced from $68 \times 10^6 \Omega$ at 0%RH to $3.82 \times 10^6 \Omega$ at 50%RH and to $1.65 \times 10^6 \Omega$ at 95%RH. This is because the hydroxyl groups in PVA were continuously connected via water molecules, and multilayer hydrogen bonds were constructed.

The effects of the addition of CoCl_2 to the P* films on the humidity-sensing characteristics are shown in Fig. 4 (P1*Co, P3*Co and P5*Co). The resistance tended to decrease at lower %RH values. Obviously, the sensitivity of P* films was much improved with the addition of CoCl_2 . For example, for the P5*, and P5Co*, the correlative resistances were reduced from approximately 13.4×10^6 to $6.79 \times 10^5 \Omega$ at 50%RH, respectively.

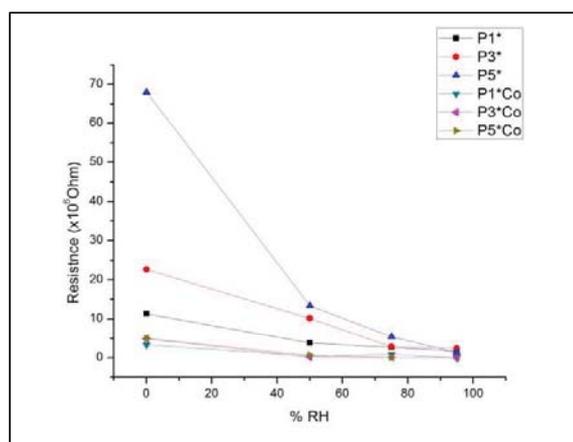


Fig.4. Humidity sensing properties of P* films

4. Conclusion

The P* films for humidity sensitive application were successfully prepared. Water resistance properties including percentage of swelling, solid remain, moisture content and sheet resistance of films were investigated. The films were formed by esterification reaction, hydrogen bonding and crosslinking. The increase of oleic acid from 1 to 5 pph in the films affected the improving of water resistance and sheet resistance of the P* films. The

addition of CoCl₂ into the P* film increased the water vapor absorption resulting in the decrease in sheet resistance of films especially at lower %RH values.

Acknowledgements

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