

The Plasticizing Mechanism and Effect of Aluminium Chloride and Glycerin on Poly(vinyl alcohol) Films

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ABSTRACT: Poly(Vinyl Alcohol) (PVA) films were prepared with $AlCl_3 \cdot 6H_2O$ /glycerin and $AlCl_3 \cdot 6H_2O$ /poly glycerin as two kinds of complex plasticizer. The micromorphology of pure PVA film and PVA films plasticized with complex plasticizer was observed by Scanning Electron Microscope (SEM). The interaction between complex plasticizer and PVA molecules was investigated by Fourier Transform Infrared (FT-IR) spectroscopy. The influence of complex plasticizer on crystalline, thermal and mechanical properties of PVA films was studied by X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), ThermoGravimetric Analysis (TGA), and tensile tests, respectively. The results showed that both $AlCl_3 \cdot 6H_2O$ /glycerin and $AlCl_3 \cdot 6H_2O$ /poly glycerin complex plasticizers could interact with PVA molecular and then effectively destroy the crystals of PVA. PVA films plasticized with $AlCl_3 \cdot 6H_2O$ /glycerin and $AlCl_3 \cdot 6H_2O$ /poly glycerin complex plasticizers became soft and ductile, with lower tensile strength and higher elongation at break compared with pure PVA films. This is an important cause of plasticization of $AlCl_3 \cdot 6H_2O$ /glycerin and $AlCl_3 \cdot 6H_2O$ /poly glycerin on PVA films.

KEYWORDS: Poly(vinyl alcohol); Films; Glycerin; Aluminium chloride; X-ray diffraction.

INTRODUCTION

PolyVinyl Alcohol (PVA) is one of the important water soluble polymers from an industrial viewpoint, which is widely used in many applications such as films, hydro gels, adhesives and paper coating agents, because it is a potential material having excellent mechanical, optical, electrical and thermal property [1-7]. The property of PVA is usually improved by adding plasticizers and thermal stabilizers [8-13]. Plasticizers could effectively improve the mechanical and thermal properties of PVA by adding them in PVA matrix [14]. There are many researchers have studied the plasticization of PVA with

many different plasticizer such as glycerin, polyethylene glycol and some organic compounds which could change the mechanical and thermal properties of PVA by forming strong hydrogen bonding with the hydroxyl groups of PVA, the hydrogen bonding between the PVA and plasticizer can replace the intermolecular hydrogen bonding and then improve the flexibility of PVA films [15-18].

Recently some researchers have paid more attention on the effect of various metal salts and rare-earth salts on the thermal, optical, crystalline and electrical of PVA.

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X.C. Jiang did many works about the PVA films plasticized with different metals salts as plasticizer [25-27]. They have proved that the metals salts had an obvious effect on the mechanical, thermal and optical properties on PVA. The plasticizers include different types of different types of metal ions such as Mg^{2+} , Ca^{2+} and so on and rare-earth ions such as Ho^{3+} , Er^{3+} , Sm^{3+} , Eu^{3+} and La^{3+} [19-16].

The aim of this article is to illustrate the plasticizing effect of complex plasticizer of $AlCl_3 \cdot 6H_2O$ /glycerin and $AlCl_3 \cdot 6H_2O$ /polyglycerin on PVA. The effect of complex plasticizer of $AlCl_3 \cdot 6H_2O$ /glycerin and $AlCl_3 \cdot 6H_2O$ /polyglycerin on the mechanical, crystalline and thermal properties of PVA were studied.

EXPERIMENTAL SECTION

Materials

PVA (DP=2400) was provided by ShangHai Yingjia Industrial Development Co., Ltd, Analytical grades of Glycerin, Polyglycerin (DP=2) and Aluminium chloride were kindly supplied by Nanjing Chemical Reagent Co., China.

Sample preparation.

PVA films were prepared by the casting method. 3g PVA and 2g complex plasticizer (the mass ratio of $MnCl_2 \cdot 4H_2O$ and glycerin/ Polyglycerin is 3:1) were dissolved in 120g distill water at 95°C and stirred for 2h, then 5wt% PVA aqueous solutions were prepared, the solution were casted onto the Petri dishes and dried at room temperature for one week to eliminate water. The PVA films without complex plasticizer were prepared in the same way. All the films were stored at relative humidity of 54% for one week before testing.

FT-IR studies were carried out using a Nicolet iS10 FT-IR (Nicolet Instrument Crop., America). The spectra were acquired in the range of 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1} . Tensile modulus, tensile strength, and elongation at break were determined according GB/T 1040.1-2006 (China) under ambient conditions, using E43.104 Universal Testing Machine (MTS Instrument Crop., China). The reported values were the average of at least.

TGA was carried out in a TG 209F1 TGA thermal analysis instruments (Netzsch Instrument Crop., Germany) in N_2 atmosphere (50mL/min) at a heating rate

of 10°C/min. The samples was put into platinum pans and scanned from ambient temperature to 600°C.

DSC was performed by a Diamond DSC differential scanning calorimeter (PE Instrument Crop., America). Slices of PVA and modified PVA films with total of 6mg were weighted and sealed in aluminum pans. The temperature of pans is from -60°C to 80°C at a heating rate of 10°C/min under a flow of nitrogen.

The cross section of films was observed on a 3400-I SEM (Hitachi Instrument Crop., Japan). The samples were first freeze fractured by liquid nitrogen. The fracture surfaces were vacuumed coated with gold and examined with the acceleration voltage of 20kV.

X-ray diffraction patterns were recorded in the reflection mode in the angular range of 5-50° (2theta) at ambient temperature by a D8 FOCUS diffractometer (Bruker Instrument Crop., Germany). The radiation from the anode, operating at 50KV and 35mA, monochromized with a nickel foil, the measurements were performed at a scanning speed of 2theta =0.06°/s.

RESULTS AND DISCUSSION

FT-IR

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 common plasticizers for PVA such as glycerol and polyethylene glycol can form the hydrogen bonding with PVA molecules. In the interactions, the intensity of the intermolecular and intermolecular hydrogen bonding between PVA would be reduced. 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 FT IR, the vibrations of molecules can be investigated. The pure PVA and PVA plasticized with $AlCl_3 \cdot 6H_2O$ /glycerin (PVA-1) and $AlCl_3 \cdot 6H_2O$ /polyglycerin (PVA-2) were obtained and shown in Fig. 1. There is no absorption band of free “-OH” at 3600 cm^{-1} for PVA. This indicates the hydroxyl groups generally associate with the intermolecular and intermolecular hydrogen bonding. It was shown in Fig.1 that the absorption band of “-OH” shift to a higher wave number after the addition of $AlCl_3 \cdot 6H_2O$ /glycerin and $AlCl_3 \cdot 6H_2O$ /polyglycerin.

Table 1: Mechanical properties of PVA, PVA-1 and PVA-2.

Sample	PVA	PVA-1	PVA-2
Tensile strength(MPa)	30.18	20.24	23.22
Elongation at break(%)	372.34	698.78	702.13
Young's	892.12	49.91	30.44

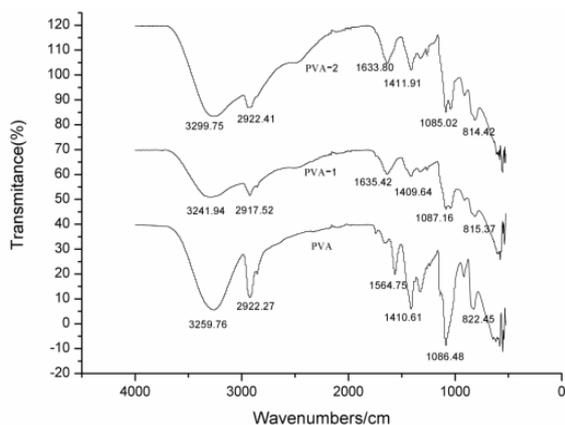


Fig. 1: FT-IR spectra of PVA.

The shift in the frequency is valuable as the measurement of the hydrogen bonding of the hydroxyl group. It indicates that the hydrogen bonding 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 3259.75cm^{-1} , the absorption band of hydroxyl shifted to a higher value at 3241.94cm^{-1} and 3299.75cm^{-1} with the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin, it indicated that the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin would reduce the intensity of the hydrogen of bonding of PVA molecules. It is because AlCl_3 can form strong interaction with PVA molecules, glycerin and polyglycern can form strong hydrogen bonding with PVA, which takes place of the hydrogen bonding between the hydroxyl groups of PVA molecules. The commonly used plasticizers for PVA are organic compounds such as glycerol, urea and caprolactam which only form hydrogen bonding with PVA molecules, the work in this article, the glycerin forms hydrogen bonding with PVA molecules and AlCl_3 can form strong interaction with PVA molecules, they both reduce the intensity of the hydrogen bonding in PVA, it showed that $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin have a plasticizing effect for PVA.

Mechanical properties

The tensile strength, elongation at break and Young's modulus of PVA films, PVA-1 films and PVA-2 films were tested using E43.104 Universal Testing Machine, the mechanical properties were shown in Table 1. From the Table 1, we can see that the plasticized PVA shows different mechanical properties when compared with pure PVA, with a concurrent decrease in the tensile strength and increasing in the elongation at break with decreasing in Young's modulus. It is accordance with the common rule that the plasticizer can increase the elongation at break and decrease the tensile strength Young's modulus. 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 and Young's modulus decreased when the PVA was with a lower crystallinity. Because the complex plasticizer was with higher plasticizing efficiency, PVA would be more completely melted to form a continuous phase and thus show better mechanical properties.

TGA

The thermal ability of pure PVA films and PVA plasticized with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin films were investigated by the TGA. The TGA curves of pure PVA films, PVA-1 films and PVA-2 films are shown in the Fig.2, From the Fig.2, there is a two-step mechanism for the thermal degradation of PVA, the thermal ability of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin plasticized PVA is lower than pure PVA, the decomposition temperature (T_d) is determined as the temperature of 5% thermal weight loss, the T_d values of pure PVA, PVA-1 and PVA-2 is 195°C , 115°C and 136°C were analyzed. The thermal weight loss rate value increased from 14% to 18% at 200°C , it indicated that the thermal degradation of PVA-P is easier than PVA at 200°C . The thermal degradation of PVA is initiated from the amorphous phase and extends to

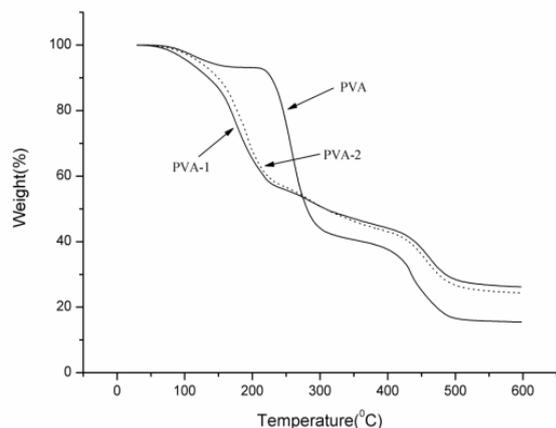


Fig. 2: TGA curves of PVA.

the crystalline region after the melting. The thermal stability of PVA is determined by the intensity of hydrogen bonding, the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin destroyed the crystals of PVA and decreased the degree of crystallinity of PVA. The PVA-2 showed a lower thermal stability than PVA, because the amorphous PVA was easily to start the thermal degradation. We can notice that the residue rate of PVA at 600°C could significantly improve with addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin, because the residue rate of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin at 600°C is higher than that of PVA. Previous some studies show that the high value of residue rate may imply the good flame retardancy of the material. It shows that the $\text{AlCl}_3 \cdot 4\text{H}_2\text{O}$ in complex plasticizer can be used as a retardant plasticizer for PVA.

DSC

The influence of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin on tg of PVA was determined by DSC measurement. The DSC measurement was carried out from -60°C to 80°C at a heating rate of 20°C/min. The obtained DSC curves are shown in Fig. 3. From the Fig.3, with the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin the tg decreased from 21.56°C to -4.85°C (t_{g1}) and -4.21°C (t_{g2}), the decrease of tg indicated that the chain mobility of PVA decreased. The reason is that $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin could interact with PVA molecular hydrogen bonding within the PVA molecules is interrupted.

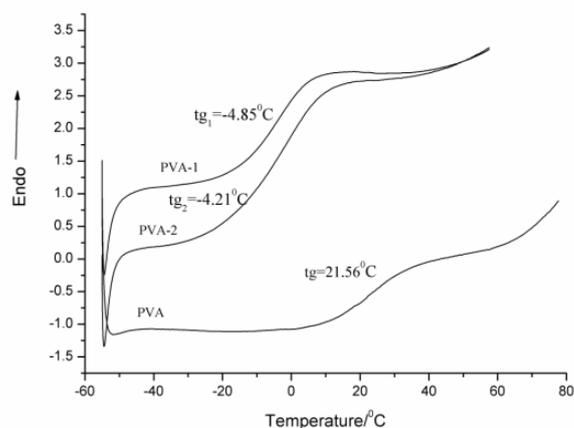


Fig. 3: DSC curves of PVA.

SEM

PVA and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin molecules could associate with each other by intermolecular and intramolecular hydrogen bonding. It can be seen with naked eyes that PVA films would become more homogeneous and ductile with the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin. Fig.4, Fig.5 and Fig.6 show the SEM figures of the cross section of pure PVA films and PVA films plasticized with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin. It was observed from Fig.5 and Fig.6 that with the high temperature, pressure, and the action of complex plasticizer, PVA granules were physically broke up small fragments and molten.

PVA form a homogeneous phase with the addition of plasticizers and no AlCl_3 chloride crystals were observed. This indicated that $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin could effectively improve the compatibility of PVA. The improvement of the compatibility of PVA should be attributed to that $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin could effectively destroy the crystals of PVA. The entanglements and interaction of PVA molecules would be enhanced when the crystals were destroyed. The mechanical properties of PVA films would be greatly enhanced when the compatibility of PVA was improvement.

XRD

The X-ray diffraction patterns of pure PVA and plasticized PVA films are shown in Fig.7. The pure PVA

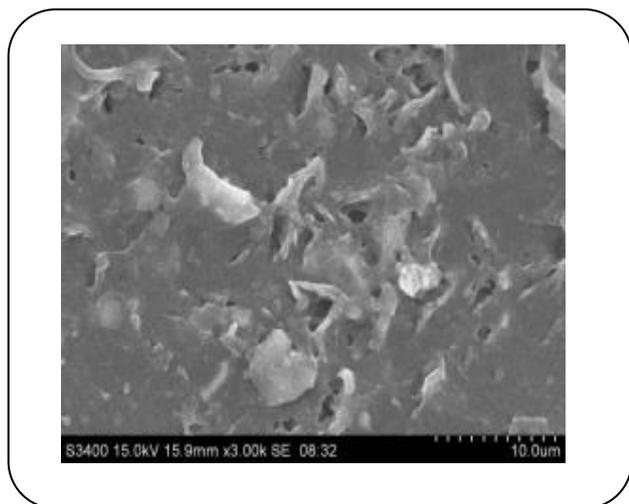


Fig. 4: SEM micrographs of PVA film.

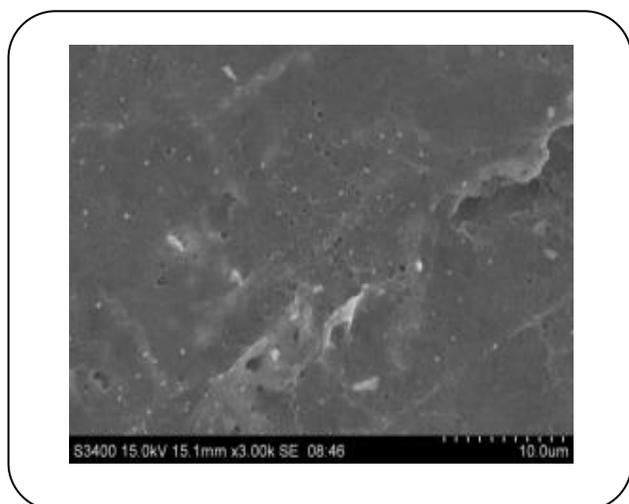


Fig. 5: SEM micrographs of PVA-1 film.

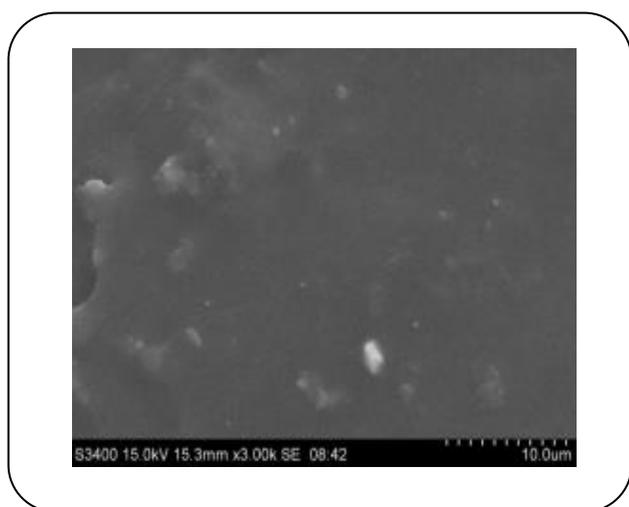


Fig. 6: SEM micrographs of PVA-2 film.

films exhibited the diffuse characteristic pattern of an amorphous phase with the main halo of the typical peak at $2\theta = 19.8^\circ$. Comparing the pure PVA with that plasticized PVA, the diffraction peaks of plasticized PVA film almost disappeared with the addition of complex plasticizer. This indicated that the addition of complex plasticizer could effectively destroy the crystals of PVA. This is because that $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin could form strong interaction with PVA molecules and this interaction would interrupt the intermolecular hydrogen bonding in PVA crystals. With the crystals of PVA destroyed, PVA molecules could form more interaction with each other. The disappearance of the intensity of diffraction peak indicated that the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin could effectively decrease the degree of crystallinity of PVA films.

CONCLUSIONS

The complex plasticizer $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin were proved to be with a high plasticizing effect for PVA by all the results in our article. Both of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin 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 complex plasticizer $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin were proved to be with a high plasticizing effect for PVA by all the results in our article. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin 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 complex plasticizer $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin 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 $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin. The mechanical properties of PVA were improved significantly and the plasticized PVA films appeared a tougher than pure PVA films after adding the complex plasticizer. It can also be expected that the complex

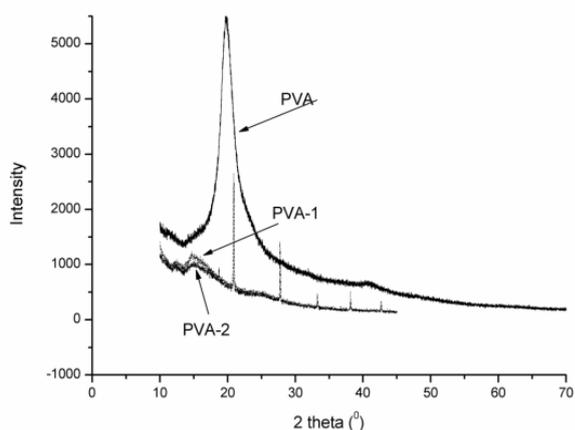


Fig. 7: XRD curves of pure PVA.

plasticizer $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /glycerin and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /polyglycerin could play an important role in the polymer such as cellulose that contain many hydroxyl groups.

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