

Preparation and Characterization of Chitosan/Poly (vinyl alcohol)/Gelatin Ternary Blend Films

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ABSTRACT

The chitosan/poly (vinyl alcohol)/gelatin (CS/PVA/GA) ternary blend films were prepared by solution blend method in this study. The thermal properties of the CS/PVA/GA blend films were examined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The melting point of the CS/PVA/GA blend film is increased when the amount of GA in the blend film is increased based upon the DSC thermal analysis. XRD analyses exhibits that the intensity of diffraction peak at 19° which stands for the crystalline of PVA becomes significantly flat and broad with increasing the amount of GA in the CS/PVA/GA ternary blend film. Although CS, PVA, and GA are hydrophilic biodegradable polymers, the results of water contact angle measurement are still as high as 83°, 68°, and 66°, respectively. When the amount of GA is increased in the CS/PVA/GA ternary blend film, the water contact angle of the CS/PVA/GA ternary blend film is increased with the exceptions on GA5 and GA6. It indicates there is a minimum water contact angle for the CS/PVA/GA ternary blend film occurred at 60wt% GA (i. e. GA6).

Keywords: chitosan, poly (vinyl alcohol), gelatin, solution blend, thermal analysis

INTRODUCTION

Chitin, next to cellulose, is the second common polysaccharide on the earth. Chitin, the source material of chitosan, is prepared from the shells of crabs, shrimps, other arthropods, fungi, yeasts, squid pens...and so on [1]. Chitosan, a deacetylated product of chitin, is a high molecular weight heteropolysaccharide with composed mainly or fully of β - (1,4)-2-deoxy-2-amino-D-glucopyranose and partially or none of β -(1,4)-2-deoxy-2-acetamido-D-glucopyranose units [2]. Unlike chitin, chitosan is readily soluble in various acidic solutions, such as formic and acetic acids.

Both chitosan and chitin have good biocompatibility, biodegradation, and various biofunctionalities [3-6]. Therefore, many efforts have been devoted to produce new biofunctional materials from chitin and chitosan, such as the applications in cotton, nonwoven fabric, sponge, film, and gel forms [7]. However, chitosan films are brittle and not suitable for use in the dry state.

PVA is a water-soluble synthetic polymer. Due to the characteristics of easy preparation, good biodegradability, excellent chemical resistance, and good mechanical properties, PVA has been used on many biomaterial applications [8]. For example, PVA membranes have been used in the artificial pancreas [9,10], hemodialysis [11], and implantable biomaterials [12,13]. Since chitosan contains hydroxyl and amine groups, it has the potential to be miscible with PVA due to the formation of hydrogen bonds [14,12]. Therefore, poly (vinyl alcohol) (PVA) has

been blended with chitosan to enhance the physical properties of chitosan films by adopting the solution blend method in our previous research [15].

The blending of two or more polymers has gradually become an important technique to improve the cost-performance ratio on commercial products [16]. Several researchers have studied on the CS/PVA binary blend film, but the study of CS/PVA/GA ternary blend film is still rare. Therefore, the CS/PVA/GA ternary blend system becomes the main focus on this study. The CS/PVA/GA ternary blend films with various blend ratios are prepared by using the solution blend method. Our previous study illustrated if the weight ratio of CS/PVA is equal to 1, the mechanical properties of CS/PVA binary blend film is better than those of other weight ratios. Therefore, the weight ratio of CS/PVA is kept to 1 and then the binary mixture is blended with various amounts of gelatin (GA) solution in this study. Thermal properties and chemical structure of CS/PVA/GA ternary blend films are examined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), X-ray diffractometer (XRD), and contact angle instrument.

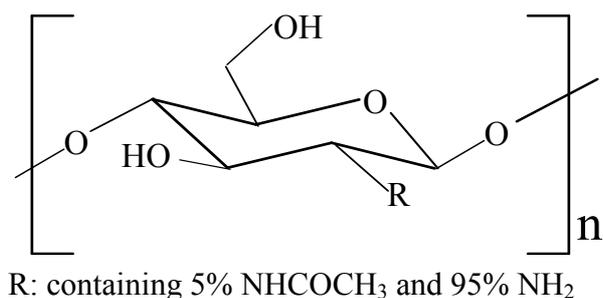
EXPERIMENTAL

Materials

Chitosan (CS) with 95% deacetylation (prepared from β -chitin) was supplied by Ohka Enterprises Co., Ltd., Taiwan. The molecular weight of chitosan is about 200,000. Acetic acid was also purchased from Union Chemical Works Ltd., Taiwan. PVA was purchased from Merck Ltd., Germany. The molecular weight of PVA is about 72,000. Gelatin (GA) was purchased from CICA Chemical Ltd., Japan. The molecular weight of gelatin is about 40,000.

Preparation of CS/PVA/GA Ternary Blend films

2.5 g CS powder (chemical structure is shown as Scheme 1) was added into a 100ml 0.1M acetic acid and the mixture was stirred to form a 2.5wt% clear CS solution. Meanwhile, 2.5 g PVA powder was charged into 100 ml 80°C purified water while stirring to form a 2.5wt% clear PVA solution. Then, CS solution and PVA solution were blended together to form a homogenous CS/PVA solution. 2.5 g GA powder was charged into 100 ml purified water and stirred to form a 2.5wt% GA solution. Different weight percentages (as indicated in Table 1) of CS/PVA and GA solutions were homogeneously blended to form a ternary solution. Then the ternary solutions were poured into the PP petri dishes. After 48-hour setting, these CS/PVA/GA ternary blend solutions were de-bubbled and then transferred into a 60°C oven for about 24-hour drying. After that, these blend films were vacuum dried for 24 hours at 80°C in order to remove the residues of water and acetic acid.



Scheme 1. The chemical structure of chitosan with 95% degree of deacetylation.

DSC Analysis

A differential scanning calorimeter (DSC; Perkin Elmer, model: DSC 7, USA) was used to examine the thermal property of the CS/PVA/GA ternary blend film with a constant heating rate of $5^\circ\text{C}/\text{min}$ under a nitrogen flow. The sample was two-stage heated. Firstly, the sample was heated from 50°C to 220°C and then cooled to room temperature in order to release the internal stress of the sample. Secondly, the sample was reheated from 50°C to 250°C with a heating rate $5^\circ\text{C}/\text{min}$. The results were recorded and analyzed.

TGA Analysis

A thermogravimetric analyzer (TGA; Perkin Elmer, model: TGA 7, USA) was conducted to measure the thermal weight loss of the CS/PVA/GA ternary blend film in the temperature ranged from 50°C to 700°C with a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen stream. The weight losses at different stages were analyzed.

DMA Analysis

The CS/PVA/GA ternary blend film was cut into pieces with dimensions of 20mm long, 4mm wide, and 0.009mm thick. A dynamic mechanical analyzer (DMA; Perkin Elmer, model: DMA 7e, USA) was conducted to measure the thermal dynamic mechanical properties of the CS/PVA/GA ternary blend films. The sample was also two-stage heated. Firstly, the sample was heated from 0°C to 120°C with a heating rate $5^\circ\text{C}/\text{min}$ and then cooled to 0°C in order to release the internal stress of the sample. Secondly, the sample was heated from 0°C to 200°C with the heating rate $2^\circ\text{C}/\text{min}$, amplitude 10μ , and tension 105%. The results were recorded and analyzed.

XRD Analysis

X-ray diffraction patterns of these CS/PVA/GA ternary blend films were obtained by using an X-ray diffractometer (XRD; Rigaku Company, model: DMAX-2200, Japan). The working voltage and current were 40kV and 30mA,

respectively. A CuK α radiation with a wavelength of 0.154 nm was used. The scanning rate was 2°/min in the range from 5° to 35° (2 θ).

Contact Angle Measurement

Contact angle measurement of CS/PVA/GA ternary blend films were performed by following the sessile drop method [17] with a contact angle instrument equipped with an Image Analysis Attachment (First Ten Angstroms, Model FTA 100, USA). The probe liquids used were deionized distilled water. Uniform drops of liquids (\approx 2 micro-liter/drop) were carefully deposited on the blend film surface by using an assembly consisting of a micrometer syringe. Measurements were consistently conducted at the condition of relative humidity 70% and temperature 24°C. Contact angle measurements were recorded within 5–10 seconds. Each reported result of contact angle measurement is an average of at least three separate drops that were tested in different locations in a given blend film. The volume of the drops was kept constant (\approx 2 microliter/drop) since variations in the volume of the drops can lead to inconsistent contact angle measurements [18].

RESULTS AND CONCLUSIONS

DSC Analysis

Two-stage heating process was conducted for the DSC analysis. The first-stage heating is used to decrease the water content in the blend films and release the stress of the blend films. Since chitosan contains -NH₂ and -OH functional groups, the hydrogen bonding force is strongly formed among moleculars. It is difficult to identify the T_g of chitosan since this compound is semicrystalline. DSC curves of CS/PVA/GA ternary blend films are shown on the Figure 1. The endothermic peak in Figure 1 is the melting point of CS/PVA/GA ternary blend film. Figure 2 exhibits that the melting point of CS/PVA/GA ternary blend film is increased when the amount of GA solution in the ternary blend film is increased. This is resulted from the strong intermolecular attraction (hydrogen bonding) formed among CS, PVA, and GA molecules. It indicates that GA can improve the compatibility between CS and PVA.

TGA Analysis

TGA and DTG curves of chitosan with 95% degree of deacetylation are shown on Figure 3. Here, ΔY is the weight loss due to the thermal degradation of chitosan and T_{onset} stands for the thermal degradation onset temperature of the chitosan. Figure 4 shows TGA curves of CS, PVA, and GA. Two weight losses are observed in the CS TGA curve. The weight loss at 50-150°C is due to the moisture vaporization. The other weight loss at 200-300°C is due to the degradation of

chitosan molecule. There are also two significant weight losses are observed in the GA TGA curve. One weight loss at 50-150°C is due to the moisture vaporization, and the other at 250-320°C is due to the thermal degradation of GA molecule. Meanwhile, three weight losses are observed in the PVA TGA curve. The first weight loss at 50-150°C is due to the moisture vaporization. The second weight loss at 200-300°C is due to the thermal degradation of PVA molecule. And, the third weight loss at 400-450°C is due to the by-product generation of PVA during the TGA thermal degradation process. According to Hay's report [19], thermal degradation led to the production of aldehyde and alkene end-groups in the molten state. And, this effect could lead to the formation of a vinyl ester by the rearrangement.

Figure 5 shows TGA curves of GA0, GA5, and GA10, respectively. Since the GA5 film is prepared by 5 g GA solution with 5 g CS/PVA solution, the GA5 TGA curve on Figures 5 contains weight losses resulted from CS, PVA, and GA. There are total three weight losses are observed in the GA5 TGA curve. The first weight loss (ΔY_1) at 50-150°C is due to the moisture vaporization. The second weight loss (ΔY_2) at 250-400°C is due to the thermal degradation of CS, PVA, and GA. And, the third weight loss (ΔY_3) at 400-450°C is due to the by-product generation of PVA during the TGA thermal degradation process as mentioned by Hay's report [19].

Figures 6 and 7 illustrate the influence of amount of GA solution on the weight losses ΔY_2 and ΔY_3 in CS/PVA/GA ternary blend films. Figure 6 shows that ΔY_2 is increased when the amount of GA solution is increased with the exception on the GA10 film. Figure 7 exhibits that ΔY_3 is decreased when the amount of GA solution is increased. Since ΔY_3 is resulted from the by-product generation of PVA during the TGA thermal degradation process, no ΔY_3 is observed on the TGA curve of GA10 (10 g GA solution blended with 0 g CS/PVA solution) film. It implies that ΔY_3 is resulted from the existence of PVA in the ternary blend film [10].

DMA Analysis

Figure 8 shows the DMA curves of GA0, GA5, and GA10. Since the partial miscibility between PVA and CS, two Tgs (i.e. two significant α relaxation peaks) are found in the DMA curve of the GA0 film (0 g GA solution blend with 10 g CS/PVA solution) as shown in Figure 8. The first one is seen at about 70°C. This is resulted from the amorphous fraction of PVA. The second one is observed at about 140°C. This Tg is resulted from the amorphous structure of CS. For the DMA curve of GA5, it is still observed two Tgs. The first one is seen at about 75°C. This is also resulted from the amorphous fraction of PVA. The second one is observed at about 168°C. This Tg is represented for the amorphous structure that is resulted from the of CS. The influence of GA content on the Tg of the CS/PVA/GA ternary blend film is illustrated in Figure 9. It shows that the Tg of CS/PVA/GA ternary blend film is increased when the amount of GA is increased up to 60wt%. The maximum Tg value is around 172°C when the weight content of GA solution is 60 wt% in the CS/PVA/GA ternary blend film (i.e. 6 g GA solution blended with 4 g

CS/PVA solution).

XRD Analysis

XRD results of GA0, GA2, GA6, and GA10 are shown in Figure 10. The GA0 film dried from acetic acid shows two diffraction peaks at about 19° and 22.5° , which are characteristics of the crystalline peak of PVA and the hydrated crystalline structure of chitosan [20], respectively. As increasing the amount of GA in the CS/PVA/GA ternary blend film, the intensity of diffraction peak at 19° for PVA becomes the flatter and the broader. The peak of the hydrated crystalline structure of chitosan at 22.5° has the same tendency as that at 19° . It illustrates that the existence of GA decreases the crystalline of PVA and CS due to the significant hydrogen bonding interaction among CS, PVA, and GA molecules. In other word, the addition of GA improves the compatibility between CS and PVA.

Contact Angle Measurements

Figure 11 (a), (b), and (c) show the photo images of water drops on the surface of GA10, GA5, and GA0 films, respectively. According to the sessile drop method, the water contact angle of the GA0 film (58°) is smaller than that of the GA10 film (66°). It implies that GA0 is more hydrophilic than GA10. Although CS, PVA, and GA are hydrophilic biodegradable polymers, their water contact angles are still as high as 83° , 68° , and 66° , respectively. This behavior is likely to be associated with the hydrophobic backbone of the polymer chains [21].

When the amount of GA is increased in the CS/PVA/GA ternary blend film, the water contact angle of the CS/PVA/GA ternary blend film is increased with the exception on GA5 and GA6. It indicates there is a minimum water contact angle occurred at about 60wt% GA (i.e. GA6). The water contact angle for GA6 is 55° . This behavior is primarily due to the reorientation of polar functional groups toward to the top surface of CS/PVA/GA ternary blend films. Polar group reorientation could be especially important for polymers with asymmetric repeating units [22].

CONCLUSIONS

The thermal properties of CS/PVA/GA ternary blend films are studied. Results indicate the melting point of the CS/PVA/GA ternary blend film is increased when the amount of GA in the ternary blend film is increased. Two weight losses are observed in TGA curves of CS and GA and three in the PVA TGA curve. It is found that the second weight loss (ΔY_2) is increased when the amount of GA in the blend film is increased. However, the third weight loss (ΔY_3) is decreased when the amount of GA in the ternary blend film is increased. And, ΔY_3 is resulted from the existence of PVA in the ternary blend film. From DMA results, it shows that the Tg of CS/PVA/GA ternary blend film is increased when the amount of GA is increased up to 60wt% (i.e. GA6). It illustrates that the existence of GA decreases the crystalline of PVA and CS as shown in the XRD spectra. This is because the significant hydrogen bonding interaction occurs among CS, PVA, and GA molecules. In other word, the

addition of GA improves the compatibility between CS and PVA. From the water contact angle measurement, it indicates a minimum water contact angle is existed when the blend film contains about 60wt% GA.

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Table1. Abbreviation for CS/PVA/GA ternary blend film and blend ratio for CS/PVA and GA solution

| Abbreviation | Blend Ratio |
|--------------|--|
| GA0 | (GA solution 0 g + CS/PVA solution 10 g) |
| GA2 | (GA solution 2 g + CS/PVA solution 8 g) |
| GA4 | (GA solution 4 g + CS/PVA solution 6 g) |
| GA5 | (GA solution 5 g + CS/PVA solution 5 g) |
| GA6 | (GA solution 6 g + CS/PVA solution 4 g) |
| GA8 | (GA solution 8 g + CS/PVA solution 2 g) |
| GA10 | (GA solution 10 g + CS/PVA solution 0 g) |

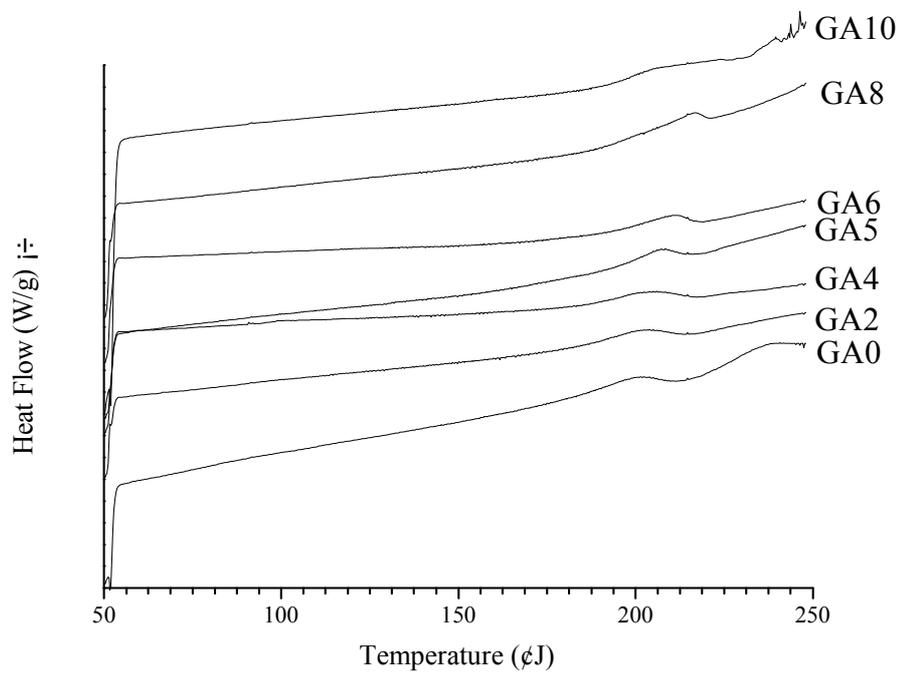


Figure 1. DSC analyses of CS/PVA/GA ternary blend films.

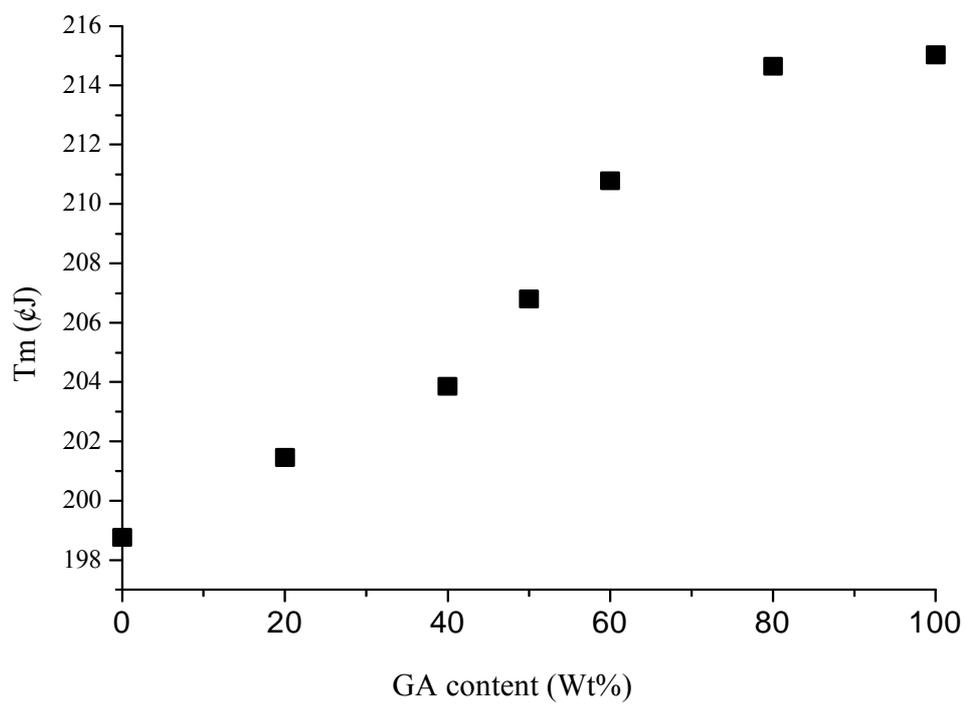


Figure 2. Influence of GA content on the melting temperature (T_m) of CS/PVA/GA ternary blend films.

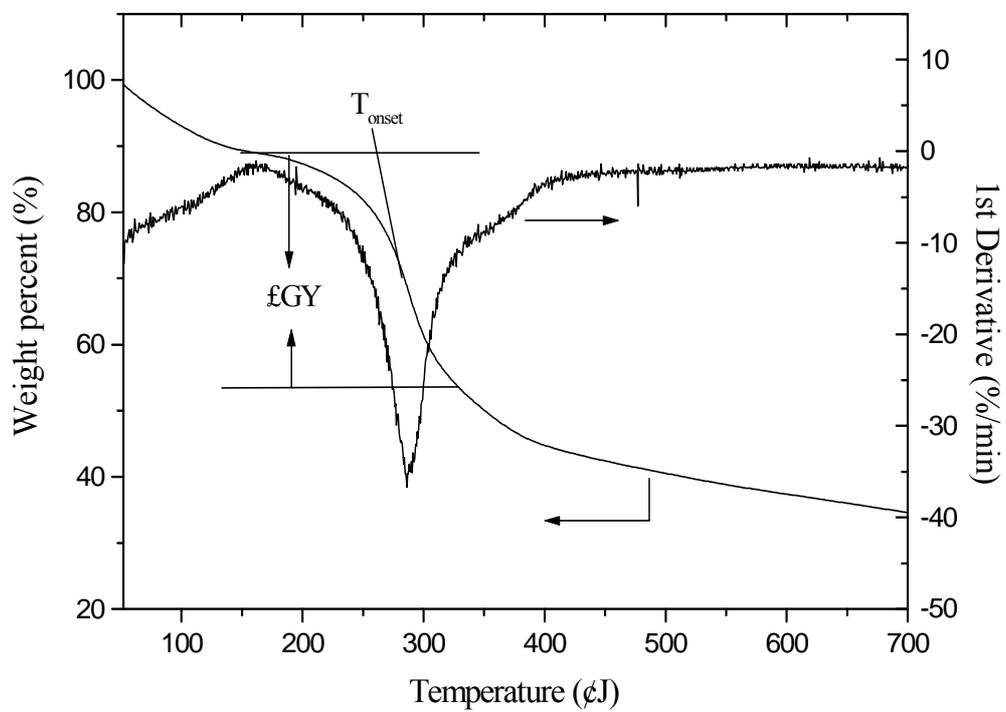


Figure 3. The TGA curve of chitosan (CS) with 95% degree of deacetylation.

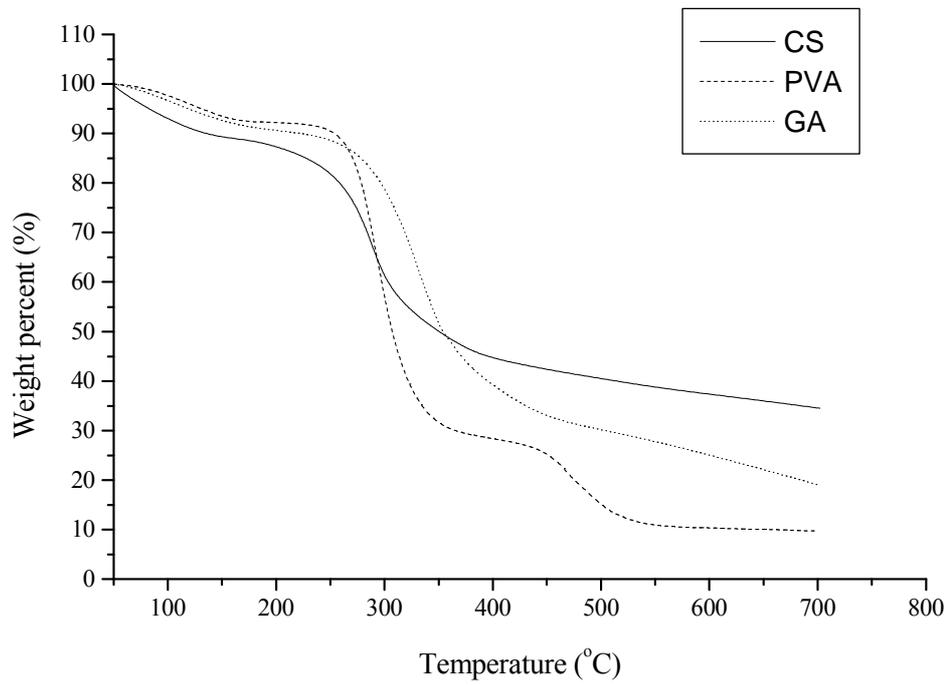


Figure 4. TGA curves of CS, PVA, and GA.

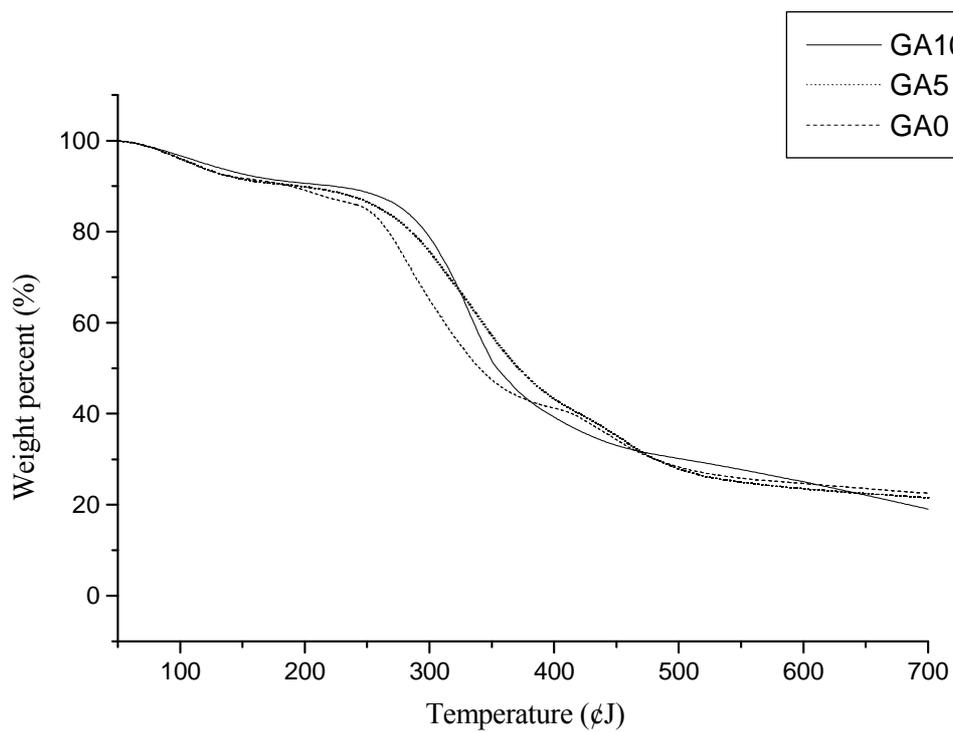


Figure 5. TGA curves of GA0, GA5, and GA10 films.

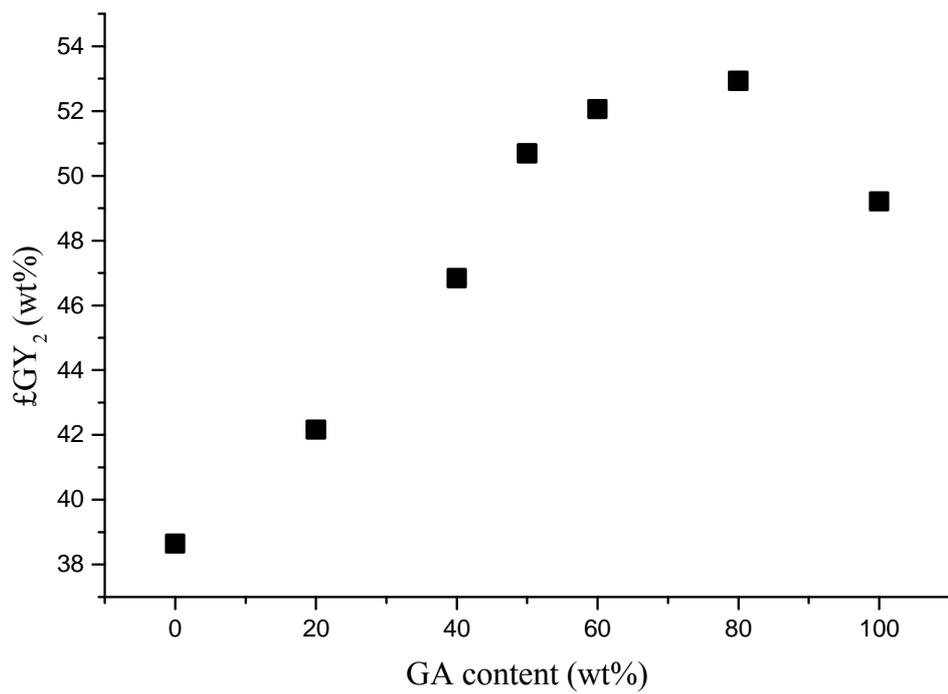


Figure 6. Influence of GA content on the second weight loss (ΔY_2) of CS/PVA/GA ternary blend films.

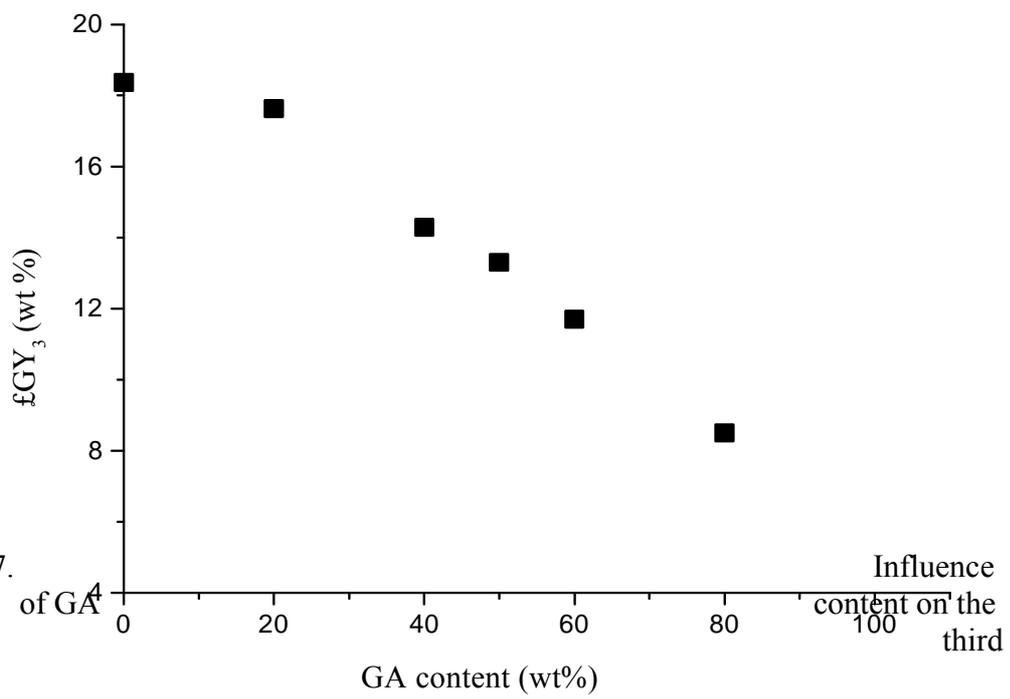


Figure 7.

of GA

Influence
content on the
third

GA content (wt%)
weight loss (ΔY_3) of CS/PVA/GA ternary blend films.

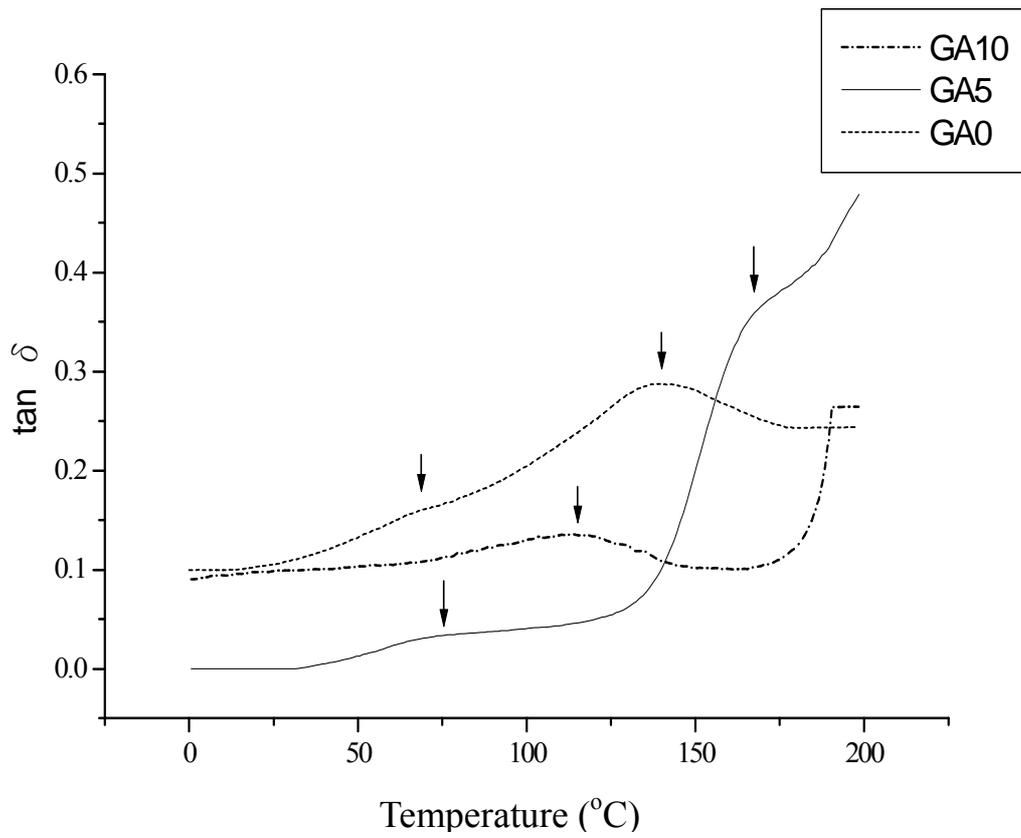


Figure 8. DMA curves of CS/PVA/GA ternary blend films, GA0, GA5, and GA10 (tan δ vs. Temperature).

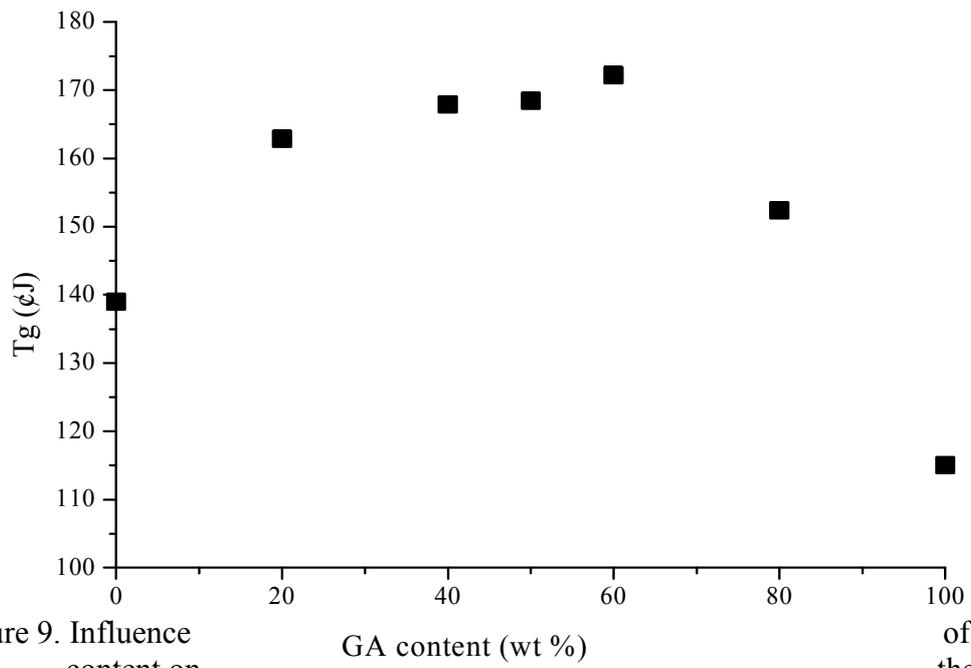


Figure 9. Influence of GA content on transition temperature (T_g) of CS/PVA/GA ternary blend films.

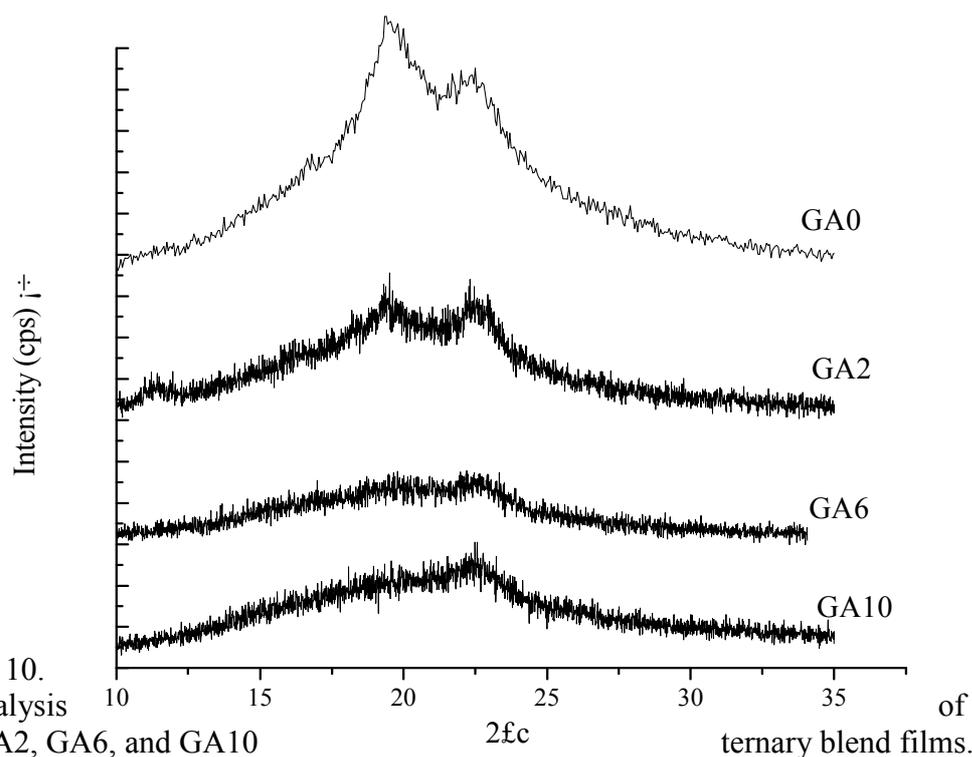


Figure 10.
XRD analysis
GA0, GA2, GA6, and GA10 of
ternary blend films.

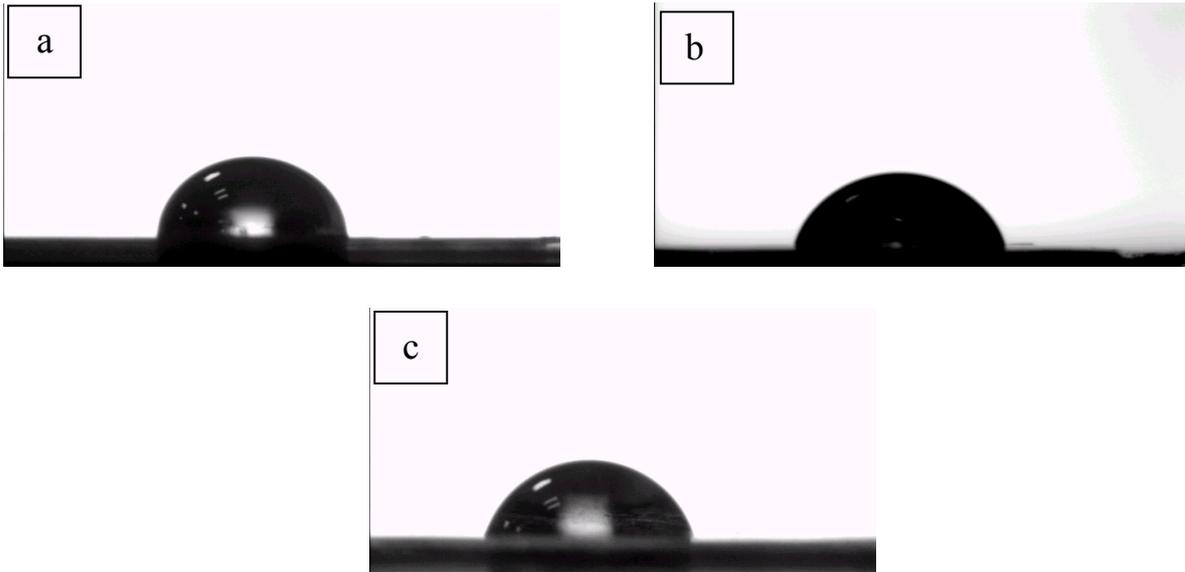


Figure 11. Photo images of water drops on the (a) GA10 film, water contact angle = 66° (b) GA5 ternary blend film, water contact angle = 57° and (c) GA0 blend film, water contact angle = 58° .