Carbohydrate Polymers 90 (2012) 1595–1600

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Effect of gelatinization and additives on morphology and thermal behavior of corn starch/PVA blend films

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ARTICLE INFO

Article history:
Received 11 May 2012
Received in revised form 8 July 2012
Accepted 10 July 2012
Available online 16 July 2012

Keywords:
Polyvinyl alcohol
Starch
Gelatinization
Additive
Morphology
Thermal behavior

ABSTRACT

The blend films of ungelatinized and gelatinized starch/polyvinyl alcohol (PVA) were prepared with a solution casting method by the introduction of additives (glycerol/urea) or not. The phase morphologies and thermal behaviors of the blends were carefully analyzed. A droplet phase was observed in the blends containing ungelatinized starch and a laminated phase was observed in the blends containing gelatinized starch. For both ungelatinized and gelatinized starch/PVA blends, the melting temperature (T_m) (210–230 °C) of PVA was detected, and the T_m of gelatinized starch/PVA blends was higher than that of the ungelatinized starch/PVA blends. Blend films containing 16.8 wt% of glycerol or urea exhibited a decreased T_m. The introduction of additives (glycerol or urea) reduced the decomposition onset temperature of the blend films. These various morphologies and thermal behaviors could be attributed to the different hydrogen bonding interaction characteristics between starch and polyvinyl alcohol at different conditions.

1. Introduction

Polyvinyl alcohol (PVA) is a synthetic water soluble polymer which is produced by hydrolysis of polyvinyl acetate (Tang & Alavi, 2011). It is a biodegradable polymer as it goes through biodegradation by enzymes and microorganism in natural environment, which has resulted in its wide use in biodegradable packaging field (Chen, Imam, Gordon, & Greene, 1997; Jayasekara, Harding, Bowater, Christie, & Lonergan, 2003). However, the low rate of biodegradation and high cost are two major constraints while using packaging films made of pure PVA (Mao, Imam, Gordon, Cinelli, & Chiellini, 2000; Jayasekara et al., 2003). These drawbacks can be overcome by blending PVA with starch, which is a completely biodegradable, cheap, renewable and easily available material (Liu, Xie, Yu, Chen, & Li, 2009; Yu, Dean, & Li, 2006).

Since 1980s, the starch/PVA blend has been studied primarily for producing films by means of solution casting because PVA is easily degraded during the melting processing (Tang & Alavi, 2011). Starch/PVA blend films have been proven to have better tensile strength and elongation than unadulterated starch films, and both blend ratio and PVA molecular weight can be adjusted to create desired mechanical properties (Chen, Cao, Chang, & Huneault, 2008). On the one hand, both starch and PVA are polar substances having hydroxyl groups (—OH) in their chemical structure, these highly polar hydroxyl groups tend to form intermolecular and intramolecular hydrogen bonds, improving the integrity of starch/PVA blends accordingly (Sin, Rahman, Rahmat, & Khan, 2010; Sin, Rahman, Rahmat, & Mokhtar, 2011). On the other hand, starch/PVA blends are assumed to be biodegradable since both components are biodegradable in various microbial environments (Ishigaki, Kawagoshi, Ike, & Fujita, 1999).

For almost any application, the ordered granular structure of starch is disrupted by heating with a plasticizer or gelatinization agent (Chen et al., 2011; Liu et al., 2011). This process is known as gelatinization which has a remarkable influence on starch-based polymers (Forssell, Mikkilä, Moates, & Parker, 1997; Pushpadass, Bhandari, & Hanna, 2010; Zeng et al., 2011). A number of researchers have investigated the effects of blending both gelatinized and ungelatinized starch with biodegradable aliphatic polyesters (Dean, Yu, Bateman, & Wu, 2007; Dubois & Narayan, 2003). For example, Dean et al. (2007) investigated ungelatinized and gelatinized starch/polycaprolactone (PCL) blends, and light microscopy indicated that blends with gelatinized starch had better interfacial adhesion. Furthermore, in order to decrease the melting temperature of PVA and increase the flexibility and workability of starch and PVA, a number of plasticizers, e.g. water, glycerol and urea have been essayed (Frost et al., 2011; Liu et al., 2009). For instance, the mixture of glycerol and urea was used as

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0144-8617/$ – see front matter.
http://dx.doi.org/10.1016/j.carbpol.2012.07.036

Table 1
Composition of polyvinyl alcohol/starch blends prepared by film casting.

Sample	Composition (wt%)			
	Starch	Polyvinyl alcohol	Glycerol	Urea
STARCH	100	–	–	–
PVA	–	100	–	–
PVA–GS	50	50	–	–
PVA–GGS	41.6	41.6	16.8	–
PVA–UGS	41.6	41.6	–	16.8
PVA–NS	50	50	–	–

a complex plasticizer for the thermoplastic starch/PVA extruded blends (Zhou, Cui, Jia, & Xie, 2009). Results showed that the complex of glycerol and urea could form more stable and stronger hydrogen bonds with water and starch/PVA molecules than the single plasticizer such as glycerol. Besides, the studies made by the same group also investigated the physical bonding interaction of cassava starch/PVA blends (Rahman, Sin, Rahmat, & Samad, 2010; Sin, Rahman, Rahmat, & Khan, 2010; Sin et al., 2011; Sin, Rahman, Rahmat, & Samad, 2010; Sin, Rahmat, Rahman, Sun, & Samad, 2010). Results showed that the interaction between PVA and cassava starch molecules is extensively strong which is predominantly attributed to the presence of hydrogen bonds between PVA and starch molecules.

Since starch gelatinization is the basis of converting starch to be thermoplastic and additives have been evaluated and used in various formulations of starch/PVA blend films prepared by casting solution (Liu et al., 2009; Moad, 2011; Zeleznak & Hoseney, 1987), it is necessary to present their effects on the morphology and thermal behavior of the blends. This study outlines different phase morphologies of starch/polyvinyl alcohol blends with an emphasis on the starch phase being pregelatinized during its blending with polyvinyl alcohol. The effects of ungelatinized and gelatinized starch and the relationships between the resulting morphologies and thermal properties of these blends are reported respectively. In addition, preliminary data on the effect of additives (glycerol and urea) on morphologies and thermal properties of starch/polyvinyl alcohol blends are also presented. A conceptual model is established to explain the relationship between the interaction characteristics and the resulting morphologies and thermal behaviors of these blend films.

2. Materials and methods

2.1. Materials

Corn starch was purchased from Ningxia Tian Hao Starch Co. Ltd. Fully hydrolyzed polyvinyl alcohol 1799 (viscosity 21–29 cps, ash <0.2%) was manufactured by Chengdu Ke Long Co. Ltd. Urea and glycerol were of analytical grade and purchased from commercial sources in Mianyang, China.

2.2. Methods

The formulation of starch/PVA blends is listed in Table 1. In order to investigate the effect of additives (glycerol or urea), the blend ratio of starch/PVA was fixed at 50/50 in weight and the additive content was 16.8 wt% (based on the total weight of the blend). PVA-series represent the polyvinyl alcohol/corn starch blends with different components. PVA–GS, PVA–GGS and PVA–UGS series represent the gelatinized starch/polyvinyl alcohol blends with no additives, the additives of glycerol and urea respectively, and the descriptor PVA–NS represents ungelatinized starch/polyvinyl alcohol blend.

Samples PVA–GS, PVA–GGS and PVA–UGS were prepared by dissolving PVA in distilled water and heating in a water bath at 97 ± 2 °C for 30 min until PVA particles were completely dissolved. Then the corn starch and glycerol or urea were added, and the mixture was heated at 97 ± 2 °C for another 30 min (Sin, Rahman, Rahmat, & Khan, 2010). In order to comparatively study the blends of gelatinized starch/polyvinyl alcohol and ungelatinized starch/polyvinyl alcohol, sample PVA–NS was prepared by dissolving polyvinyl alcohol in distilled water as described above, and then gradually cooled down to 50 ± 2 °C, then corn starch particles were added and kept at 50 ± 2 °C for another 30 min. Under this condition there was no gelatinization present for corn starch. Meanwhile, sample of neat PVA or corn starch (STARCH) was heated at 97 ± 2 °C, respectively, in 400 g of distilled water for 1 h. The mixtures were then casted onto Petri dishes with similar weight and dried at 65 °C to constant weight.

2.3. Scanning electron microscopy (SEM) observations

Cross-sections were obtained by cracking the films in liquid nitrogen and their morphologies were studied by a scanning electron microscopy (S440 Leica Cambridge LTD.).

2.4. Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) analyses were carried out using a DSC Q200 apparatus of TA Instruments under a nitrogen gas atmosphere. A sample for DSC was weighed (about 6 mg) on a small aluminum pan, followed by sealing the pan. For all the samples, a heating scan program from 20 to 250 °C at 10 °C/min was used.

2.5. Thermogravimetric analysis

Thermogravimetry experiments were performed using a TGA Q500 apparatus of TA Instruments. The sample weight was about 5 mg. Samples were heated from 20 to 650 °C at a heating rate of 10 °C/min. All the TGA scans were carried out under a nitrogen atmosphere.

3. Results and discussion

3.1. Cross-sectional morphologies of PVA/starch blends

It is well known for polymer blends that the morphology control of the respective phases is a key factor in achieving the desired material properties (Xie, Halley, & Avérous, 2011). In fact, the apparent morphology can be easily observed with aids of the Scanning Electron Microscope (SEM). Fig. 1 shows the cross-sectional images of gelatinized starch (STARCH), pure PVA, gelatinized starch/PVA blends (PVA–GS, PVA–GGS, PVA–UGS) and ungelatinized starch/PVA blends (PVA–NS), respectively. The phase morphologies of these films can be depicted as continuous (Fig. 1(a) and (b)), laminated (Fig. 1(c), (d) and (e)) and droplet (Fig. 1(f)) forms. As expected, the neat gelatinized starch and polyvinyl alcohol films show a singular dispersed phase (Fig. 1(a) and (b)) as the sole component in these films is starch or polyvinyl alcohol, respectively. A clearly laminated phase separation was observed in the gelatinized starch/PVA blend films (PVA–GS; PVA–GGS; PVA–UGS) as shown in Fig. 1(c), (d) and (e). This is due to the fact that when the content of starch in the blends is beyond a certain threshold, the samples' miscibility deteriorates. Previous studies have shown that the tensile strength, elongation at break, and transparency of starch–polyvinyl alcohol composites decreased rapidly with the increased starch content (up to 40 wt%) (Chen et al.,

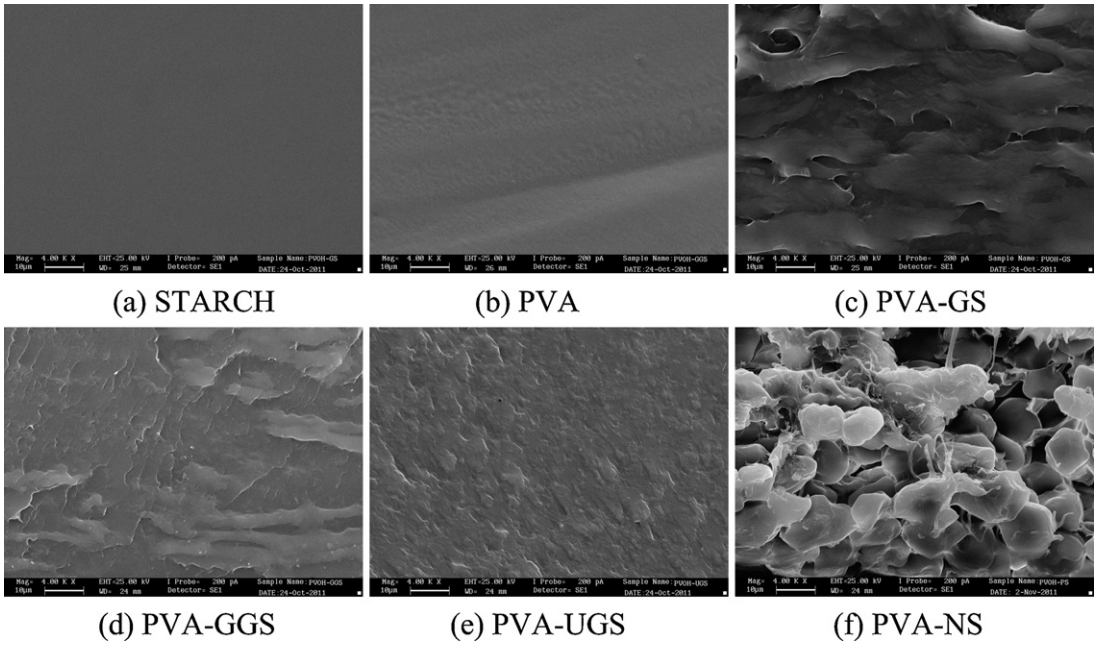

Fig. 1. SEM images of polyvinyl alcohol/starch blends with different weight ratios: (a) STARCH; (b) PVA; (c) PVA–GS(50/50); (d) PVA–GGS(50/50) with glycerol(16.8%, w/w total weight); (e) PVA–UGS(50/50) with urea(16.8%, w/w total weight); and (f) PVA–NS(50/50).

2008). They attributed this property deterioration to the relatively poor compatibility between starch and PVA. In this study, the weight percentages of starch in all blend films are 41.6 wt% (PVA–GGS and PVA–UGS) and 50 wt% (PVA–GS), and at such high starch contents, a low level degree of continuity was exhibited throughout the blend films. However, if comparing the Fig. 1(c), (d) and (e), the introduction of 16.8 wt% additives of total blend weight does lead to significant effects on the morphologies of gelatinized starch/polyvinyl alcohol blend films. It can be noted that the uniformity of the gelatinized starch/polyvinyl alcohol blend films morphologies follows the order: PVA–UGS > PVA–GGS > PVA–GS, which corresponds well with the intensity of newly formed hydrogen bonds between starch, polyvinyl alcohol and glycerol/urea (which will be discussed later in Section 3.2). This is also consistent with several previous studies involving polyvinyl alcohol–starch systems in which a higher compatibility was achieved by plasticizer strategy (Frost et al., 2011; Han, Chen, & Hu, 2009; Tudorachi, Casaval, Rusu, & Pruteanu, 2000).

Regarding ungelatinized starch/polyvinyl alcohol blend films (Fig. 1(f)), the exposures of starch granules are visible under SEM. Through the pre-experiment, we identified that full gelatinization of corn starch conditioning are: excess water (>60%) and should be above 60 °C. If the temperature range is too low, complete gelatinization of corn starch will not occur. During film cast processing of PVA–NS, the temperature was kept at 50 ± 2 °C, and the starch granules underwent swelling merely, resulting in the well dispersion of starch granules in the polyvinyl alcohol matrix.

3.2. Thermal interactions of PVA/starch blends

The effects of gelatinization and additives on thermal interactions of PVA/starch blends were evaluated by DSC. Fig. 2 shows the DSC thermograms of various starch/PVA blend films. Onset temperature (T_O), melting temperature (T_m) and enthalpy of melting (ΔH) were extracted from DSC thermograms and tabulated in Table 2.

It can be observed in Fig. 2 that there are no discernible changes of the thermograms for the gelatinized starch (STARCH), which indicates that the neat starch film is actually in amorphous phase, consistent with the previous study involving polyvinyl alcohol–cassava starch system (Sin, Rahman, Rahmat, & Khan, 2010). Unplasticized polyvinyl alcohol degrades at about 180 °C by eliminating water to form conjugated double bonds, while the T_m of PVA ranges from about 180 to 240 °C depending on its degree of hydrolysis (Tang & Alavi, 2011). In this study, the T_m (210–230 °C) of polyvinyl alcohol was detected for all blends.

Table 2 lists the detailed data describing the thermograms in Fig. 2. It can be noted in Table 2 that, the T_m of polyvinyl alcohol is slightly affected by blending with gelatinized or ungelatinized starch. Concretely, the T_m of polyvinyl alcohol blending with gelatinized starch is higher than that blending with ungelatinized starch as substantiated by DSC results. It is because starch can be gelatinized with polyvinyl alcohol and form stronger hydrogen bonding interactions at an elevated preparation temperature. It is well-accepted that starch gelatinization is helpful to destroy the crystalline structure of starch granular (Chen et al., 2011; Paes, Yakimets, & Mitchell, 2008; Qiao, Tang, & Sun, 2011). For the sample of PVA–GS, similar gelatinization processing

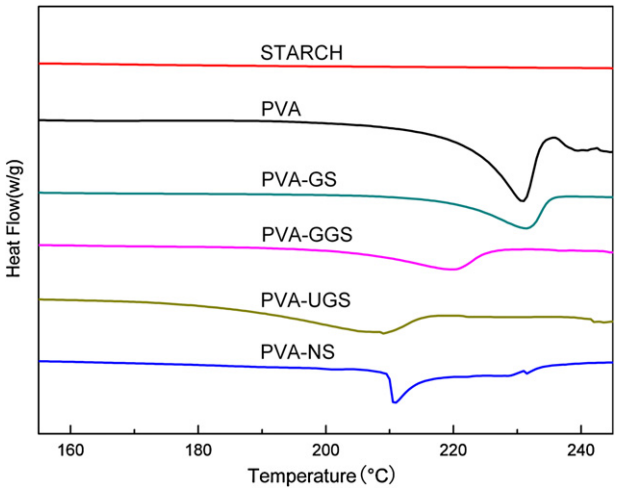

Fig. 2. DSC thermograms of various PVA/starch blend films.

Table 2
Onset temperature (T_O), melting temperature (T_m) and enthalpy (ΔH) of various PVA/starch blend films.

Sample	STARCH	PVA	PVA–GS	PVA–GGS	PVA–UGS	PVA–NS
T_O (°C)	–	222.82	219.61	203.59	186.17	209.91
T_m (°C)	–	230.79	231.32	219.86	208.96	210.75
ΔH (J/g)	–	55.65	36.80	31.58	39.96	15.09

at elevated temperature (97 ± 2 °C) leads to breakage of intramolecular *H-bonds* in starch, which increases the number of free hydroxyl groups accordingly (Sarazin, Li, Orts, & Favis, 2008). These increased free hydroxyl groups in the blends facilitate more interactions between starch and PVA molecules, causing the T_m of PVA increased. On the other hand, as confirmed by Scanning Electron Microscopy observations (Fig. 1(c)), in the PVA–GS blend films, starch can develop to be a continuous phase rather than be present as a particular filler. Thus, the physical entanglement of polymer chains is more powerful, which increases synergistic interactions between PVA and starch, resulting in the T_m of PVA increased as well. For the relatively lower T_m of polyvinyl alcohol in the PVA–NS system, besides the above reasons, another possible reason is as follows: the crystal structure of polyvinyl alcohol is destroyed when blended with ungelatinized starch (shows an unbroken granular form). The observed higher value of ΔH for PVA–GS blend film (Table 2) confirms this reasoning.

Native starches are non-plastic due to the intra- and intermolecular hydrogen bonds in starch molecules (Averous & Boquillon, 2004; Li, Sarazin, & Favis, 2008). PVA is also not considered as a thermoplastic because its melting temperature exceeds the degradation temperature for fully hydrolyzed grades (Tang & Alavi, 2011). Various plasticizers and additives have been evaluated and developed to decrease the melting temperature of PVA and starch (Ma & Yu, 2004; Talja, Helén, Roos, & Jouppila, 2008). Glycerol and urea were the conventional plasticizers used in these blends. As showed in the DSC curves (Fig. 2), the melting range peak of starch/polyvinyl alcohol blend films is weakened with the presence of 16.8 wt% glycerol or urea. The weakening of melting range peak with the adding of plasticizers can be due to decreased crystallization of PVA molecules. As plasticizers can form hydrogen bonds with both PVA and starch, it is hard for polyvinyl alcohol chains to move and rearrange during the drying process of casting solutions. Consequently, hydrogen bonds between glycerol/urea and polyvinyl alcohol molecules effectively suppress the recrystallization of polyvinyl alcohol in the blend films. A similar reasoning was offered by Mao et al. (2000), since hydrogen bonding between glycerol and polyvinyl alcohol molecules hindered the formation of crystallites in the plasticized films.

Moreover, the T_m of PVA–UGS was lower than that of PVA–GGS (Fig. 2). This evolution can be ascribed to the stability and intensity of hydrogen bonds, which is newly formed between glycerol/urea, starch and polyvinyl alcohol. According to Ma, Yu, and Wang (2007), the interaction between starch and urea is stronger than that between starch and polyols such as glycerol and sorbitol. In this study, considering that PVA mainly consists of hydroxyl functional groups as starch, it can be proposed that urea can form stronger interaction with starch and polyvinyl alcohol than glycerol. Accordingly, the more stable and stronger the hydrogen bonds are, the more likely the correlative T_m of blend films shifts to a low temperature. On the other hand, regarding to the enthalpy (ΔH), it can be noted in Table 2 that PVA–UGS has a higher ΔH than PVA–GGS, although PVA–UGS has a relative lower T_m. The reason may be that when urea is introduced into the blending system containing starch and PVA, the higher stability and intensity of hydrogen bonds newly formed between urea, starch and polyvinyl alcohol is strong enough to produce synergistic effect towards higher energy stability hierarchy (Sin, Rahman, Rahmat, & Khan, 2010).

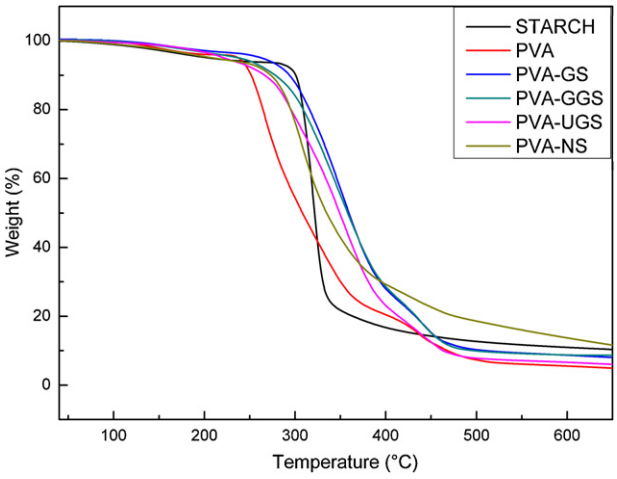

Fig. 3. TGA curves for various PVA/starch blend films.

3.3. Thermal stability of PVA/starch blends

Fig. 3 shows the weight remains versus temperature as measured by TGA for various PVA/starch blend films. The behavior of the mass loss curves was similar for several films. Three distinct regions can be seen in these thermogravimetric curves, as discussed by previous authors (Galdeano et al., 2009; Saiah, Sreekumar, Leblanc, & Saiter, 2009). The initial weight loss is generally due to the loss of volatiles (water, glycerol and urea) in the blend system (75–200 °C); the second stage is the main degradation zone of both the starch and the polyvinyl alcohol (predominantly due to dehydration of hydroxyl groups and the subsequent formation of low molecular weight unsaturated and aliphatic carbon species (Sin et al., 2011) (300–500 °C), and the final stage is generally carbonization (Shi et al., 2011) (above 500 °C).

Further analysis of the weight loss in these systems is illustrated in Fig. 4. Fig. 4 shows the percentage of weight loss at 200 °C,

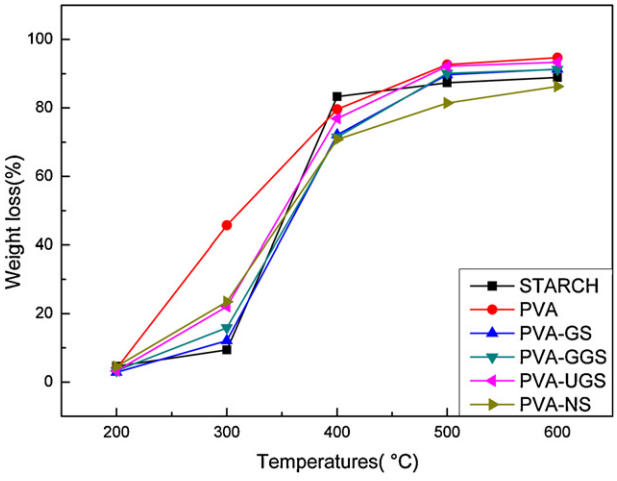

Fig. 4. Percentage weight loss at different temperatures during the thermal scanning of PVA/starch blend films.

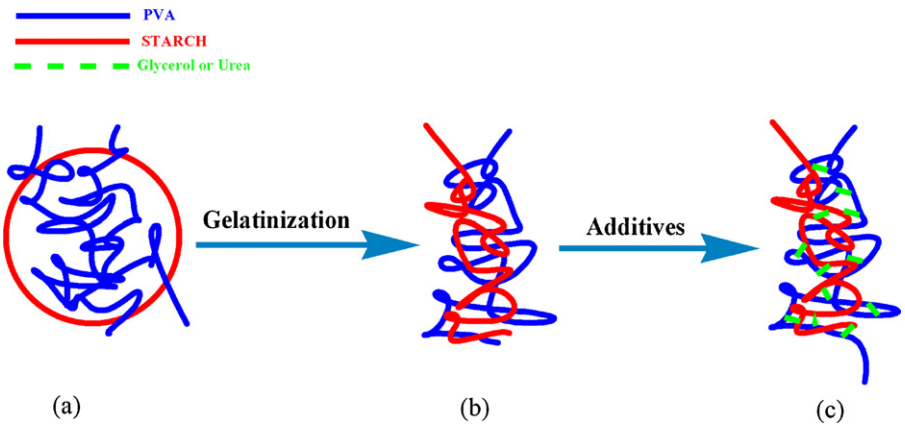

Fig. 5. Schematic presentation of preferential interactions between starch and polyvinyl alcohol in various PVA/starch blend films.

300 °C, 400 °C, 500 °C and final weight loss at 600 °C taken from the TGA curves for respective PVA/starch blends. The PVA/starch blends show a decrease in weight loss when compared with neat polyvinyl alcohol at 300 °C. This is partly due to the blending of PVA and starch is synergistically compatible and contributes towards high-energy stability hierarchy (Sin et al., 2011). It also indicates that starch is more thermally stable than PVA, which may be due to the presence of thermal resistive cyclic hemiacetal in starch structure (Liu, Yu, Liu, Chen, & Li, 2008).

The weight loss over the first 300 °C for sample PVA–NS is larger than that for PVA–GS, this may be expected as the starch particle dispersed in the PVA continuous phase resulted in phase separation and this weight loss would predominantly be the decomposition of PVA. However, after scanning up to 400 °C the weight loss for the PVA–NS was less than that for PVA–GS. The destruction of the fine starch particle in PVA–GS and the formation of a continuous phase in the blend system can explain this behavior. These phenomena correspond well with the afore-mentioned DSC results. More interestingly, after scanning up to 600 °C the ash concentration for neat polyvinyl alcohol was kept at approximately 5% of the original weight, which was lower than PVA/starch blends (7–10%). This might be associated with the chemical structure of starch, which is prone to form a thermal resistance layer and, therefore, yield a high degree of residual carbon at these kinds of temperatures (Liu et al., 2010).

Previous studies have suggested that the difference in the decomposition onset and mass loss at onset temperature was mainly due to the different volatility of several plasticizers in thermoplastic starch (Ma, Yu, & Wan, 2006). As shown in Fig. 4, the sequence of weight loss at 300 °C is PVA–UGS > PVA–GGS > PVA–GS, which is in accordance with volatility of additives. In addition, it is necessary to notice that in the view of mass loss at 300 °C (as shown in Fig. 4), though the T_m of PVA/starch blends decreases with adding additives (glycerol or urea), the thermal stability of the blends decreases as well.

3.4. Modeling of preferred interactions in various PVA/starch blends

In this section, a conceptual model was developed for preference of these interactions and the obviously different characteristics of intercalations were explained on the basis of this model.

As mentioned in early part of this work, hydrogen bonding interaction of starch and PVA is favorable, and especially blends of PVA–UGS have the highest strength of interactions followed by PVA–GGS, PVA–GS and PVA–NS. The hypothesis of preference and intensity of hydrogen bonding interactions can be used to explain the trend of evolution. In various PVA/starch blend films, three types of hydrogen bonding interactions take place at the molecular level as shown in Fig. 5, (1) hydrogen bonding between hydroxyl groups of ungelatinized starch and PVA, (2) hydrogen bonding between hydroxyl groups of PVA and gelatinized starch and (3) hydrogen bonding between functional groups (—OH or —CO—NH—) of starch, PVA and additives (glycerol/urea). As confirmed by scanning electron microscopy observations (Fig. 1), in the PVA–NS system, starch is distributed as spherical particles in the polyvinyl alcohol matrix. So, it is imaginable that hydroxyl groups are insufficient for the formation of hydrogen bonds and the interaction intensity is low as most of hydroxyl groups embed internal structure of starch granules. When the casting solutions were prepared at a higher temperature, such as 97 ± 2 °C used in this study, the starch granules collapse eventually. As a result, the number of free hydroxyl groups in this system increased, which immensely contribute to the interaction between polyvinyl alcohol and gelatinized starch. Also, the interaction intensity is radically enhanced with the adding of additives, such as glycerol or urea. These increased interactions between polyvinyl alcohol and starch are attributed to the newly formed high intensity hydrogen bonds between glycerol/urea, starch and polyvinyl alcohol. As a result, the interactions between additive, starch and polyvinyl alcohol in PVA–UGS are relatively higher than that in PVA–GGS.

Based on the conceptual model, it is apparent from this work that gelatinization and the presence of additives have a significant effect on the interactions between starch and polyvinyl alcohol which are responsible for the morphology, thermal interaction and thermal stability of PVA/starch blends.

4. Conclusion

The ungelatinized and gelatinized starch/polyvinyl alcohol blend films were prepared with the adding of additives (glycerol/urea) or not and their phase morphologies and thermal behaviors were analyzed in detail.

The droplet phase was observed for blends containing ungelatinized starch (as observed by SEM) and the laminated phase was observed for blends containing gelatinized starch. With the addition of glycerol or urea, increased homogeneity of the blend films were attained. For both the ungelatinized and gelatinized starch/polyvinyl alcohol blends the melting temperature T_m (210–230 °C) of PVA were detected, and the T_m of PVA/ungelatinized starch blends was higher than that of PVA/ungelatinized starch blends. Samples with 16.8 wt% of glycerol or urea exhibited a decreased T_m. Thermogravimetric analysis results showed that the weight loss over the first 300 °C for ungelatinized starch/PVA blends was higher than that for gelatinized starch/PVA blends and when it scanned up to 400 °C the reverse

phenomenon occurs. Besides, the addition of glycerol or urea reduced the decomposition onset temperature and mass loss at 300 °C of the blend films.

The conceptual model of hydrogen bonding interaction between starch and polyvinyl alcohol could be used to explain the resulting morphologies and thermal behaviors of these blend films.

Acknowledgements

This work was supported by the National Science & Technology Pillar Program during the Eleventh Five-Year Plan Period (Grant No. 2007BAE42B04). Experiments were conducted at Engineering Research Center of Biomass Materials, Ministry of Education, Southwest University of Science and Technology, Mianyang, China. Thanks for the support of the analysis and testing center of Southwest University of Science and Technology.

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