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Short communication

Detection of synergistic interactions of polyvinyl alcohol–*cassava* starch blends through DSC

Lee Tin Sin *, W.A.W.A. Rahman, A.R. Rahmat, M.I. Khan

Polymer Engineering Department, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

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ABSTRACT

The synergistic interaction of polyvinyl alcohol (PVOH) and *cassava* starch was studied by differential scanning calorimetry (DSC) method. Film of the PVOH–*cassava* starch blends were prepared by solution cast method. Originally, *cassava* starch film did not show presence of any endothermic peaks in DSC thermogram. However, after adding PVOH to *cassava* starch, the PVOH–*cassava* starch blend films showed obvious endothermic peaks with onset and end-point temperatures higher than neat PVOH film. In addition, the PVOH–*cassava* starch blends have experimental enthalpy of melting higher than theoretical values. This evidence shows that the interactions between PVOH and *cassava* starch molecules are extensively strong. Due to the synergistic interactions of PVOH and *cassava* starch, it is postulated that incorporation of 65–75 wt.% of PVOH in *cassava* starch blend has physical bonding equivalent to neat PVOH.

1. Introduction

Polyvinyl alcohol (PVOH) is highly recognized as a biodegradable polymer. It is readily consumed by microorganisms and enzymes when exposed to natural environment (Chiellini, Corti, & Solaro, 1999; Spiridon, Popescu, Bodârlău, & Vasile, 2008). PVOH is suitable to be used as biodegradable packaging materials to reduce accumulation of synthetic petroleum-based polymer solid wastes. Besides, PVOH can also be utilized as biocompatible tissue scaffolding materials to promote growth of transplanted cell and it will degrade after the formation of new tissues (Sinha et al., 2007). The hydrophilic characteristic of PVOH is desirable to produce hydrogel for pharmaceutical applications typically as drug delivery medium. PVOH hydrogel has high degree of swelling with low selectivity of drugs and bioactive agents (Constantin et al., 2004). Based on the application facts, PVOH has created great impact of application innovations in domestic and specialty industries. However, the price of PVOH is quite expensive. In order to make PVOH more economical to use, PVOH can be blended with native starches to reduce the materials costs. Most of the starches are available in abundance at cheap prices where sources can be derived from *cassava*, pea, rice, maize, potatoes etc. Starch possesses similar functionality as PVOH which is biocompatible and consumable by microorganisms as well. Starch is built up of amylose and amylopectin structures. These structures are originally formed from D-glucose unit with hydroxyl groups (–OH) which are directed outside of the ring (Imam, Gordon, & Greene, 1996). When PVOH and starch are blended together, the presence of hydroxyl groups (–OH) tend to form strong hydrogen bonding among the molecules and subsequently lead to synergistic stability and better system integrity (He, Zhu, & Inoue, 2004; Rahmat, Rahman, Lee, & Yussuf, 2009). Both PVOH and starch disperse homogenously in solution casted film under the observation of Scanning Electron Microscope (Tudorachi, Cascaval, Rusu, & Pruteanu, 2000).

This paper aims at investigating the physical bonding interaction of PVOH–*cassava* starch blend using differential scanning calorimetry (DSC) method. The reactive interactions of PVOH–*cassava* starch can be determined through changes in enthalpy of melting (ΔH_m). The enthalpy of melting increases upon presence of intermolecular interaction between the blending components (Hourston & Song, 2006). This is because more energy is required to break the bonding and freeing the polymer chains out from its rigid/crystal structures to reach melting state. The reactive interactions of PVOH and starch have been studied through the increment of mechanical properties of PVOH–starch blending products. Siddaramaiah, Raj, and Somashekar (2003) reported that PVOH when blended with starch would improve blending properties. When 10 wt.% starch was added to PVOH, tensile strength increased from 268 to 279 kg/cm^2. Similarly, percentage elongation at break also increased from 200% to 230%. Mao, Imam, Gordon, Cinelli, and Chiellini (2000) used PVOH as reinforcing agent for thermoplastic starch to overcome the problem of brittleness. It is reported that addition of 10 wt.% of PVOH to starch–glycerol brought a 2.2 MPa increment in tensile strength while 37% increased was recorded in percentage of elongation.

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* Corresponding author. Tel.: +60 7 5535841; fax: +60 7 5581463.
E-mail address: direct.tinsin@gmail.com (L.T. Sin).

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Table 1
Onset and end-point melting temperature, experimental (ΔH_m) and theoretical (ΔH_{mi}) enthalpy of melting of solution casted samples.

Sample	W28	W37	W46	W55	PV	CST
PVOH:*cassava* starch (wt.%)	20:80	30:70	40:60	50:50	100:0	0:100
Onset (°C)	218.04	216.39	216.22	215.70	214.03	–
SD	2.08	0.35	0.31	0.16	1.53	–
End-point (°C)	230.99	229.43	229.71	229.50	229.47	–
SD	1.65	0.41	0.22	0.37	0.39	–
ΔH_m (J/g)	7.74	13.45	19.57	28.96	42.56	–
ΔH_{mi} (J/g)	8.51	12.77	17.02	21.28	–	–

SD = standard deviation.

2. Experimental

Fully hydrolysed PVOH grade BF-17H (viscosity 25–30 cps, hydrolysis 99.4–99.8 mol%, ash <0.7%) manufactured by Chang Chung Petrochemical Co., Ltd. was used in this study. Native *cassava* starch was purchased from Thailand-Cap Kapal ABC. PVOH, *cassava* starch and distilled water were used as received. Blends of PVOH–*cassava* starch were prepared with different composition of starch from 20 to 50 wt.% as shown in Table 1. Samples W28, W37, W46 and W55 were prepared by dissolving PVOH powder in distilled water and heating in water bath at 97 ± 2 °C for 30 min until PVOH particles completely dissolved in the solution. After the PVOH was fully dissolved, starch was then added and the mixture was again heated at 97 ± 2 °C for 30 min. Meanwhile, samples of neat PVOH (PV) and *cassava* starch (CST) were heated, respectively, in 400g of distilled water for 1 h. A motor driven stirrer (set at 800 rpm) was used to dissolve and gelatinize the mixtures. The mixtures were then casted at similar weight on *Petri* dishes and dried in oven at 65 °C to constant weight. DSC analysis was done by Perkin Elmer DSC 7. Samples were weighted into standard aluminum pans. A sealed empty pan was used as reference material while nitrogen gas was purged at 20 ml/min during experiments. Each sample was heated to 50 °C and scanning was carried out with temperature ranging from 50 to 250 °C at scanning rate of 10 °C/min.

3. Results and discussion

Fig. 1 shows DSC thermograms of solution casted samples W28, W37, W46, W55, PV, and CST. The thermal scans were conducted from 50 to 250 °C. The particular thermal scanning range was selected to include the melting point of PVOH at 230 °C, but lower than 250 °C to avoid dehydration of hydroxyl groups. When samples are heated up to the melting stage, extra energy is required by its components to vibrate and break up the bonds out of the rigid/crystal arrangement. In general, melting stage can be detected via present of endothermic peak in DSC thermograms. As noticed, samples containing PVOH (W28, W37, W46, and W55) have obvious endothermic peaks. While CST consisted of merely *cassava* starch did not show endothermic peak which indicates that the solution casted CST was actually in amorphous phase. Narrow melting range of PVOH–starch samples indicate the existing of strong intermolecular interactions among the molecules. These intermolecular interactions may be attributed predominantly to the presence of hydrogen bonds between PVOH and starch molecules.

Onset temperature, end-point temperature and enthalpy of melting (ΔH_m) were extracted from DSC thermograms and tabulated in Table 1. Onset is the temperature when sample begin to melt, while end-point is the temperature when melting stage complete. As the amount of PVOH in the blend increase from 20 to 50 wt.%, the onset and end-point temperatures decrease. This is due to the fact that beyond a certain threshold of PVOH in the blend, the samples behave towards PVOH thermal properties. In other words, the PVOH begins to pre-dominate the blend. When comparison is made between CST and W28, it was found that incorporation 20 wt.% of PVOH has significantly changed the onset and end-point temperatures of neat *cassava* starch (represented by CST), whereby *cassava* starch did not show any presence of melting stage. If there were no interactions between the PVOH and *cassava* starch, then the incorporation of PVOH into *cassava* starch would have reduced the onset and end-point temperatures of the blends. However, the actual situation is that sample W28 showed endothermic peaks together with onset and end-point temperatures higher than neat PVOH (represented by PV). In this case, it might be explained that the unique helical structure of starch with many hydroxyl groups directed outside of the ring have interacted and formed strong physical bonding with PVOH. When PVOH is introduced into blending system containing starch, the open chain hydroxyl groups of PVOH will interact freely with the hydroxyl groups of starch. Thus the interaction between PVOH and starch is strong enough to produce synergistic effect towards higher energy stability hierarchy.

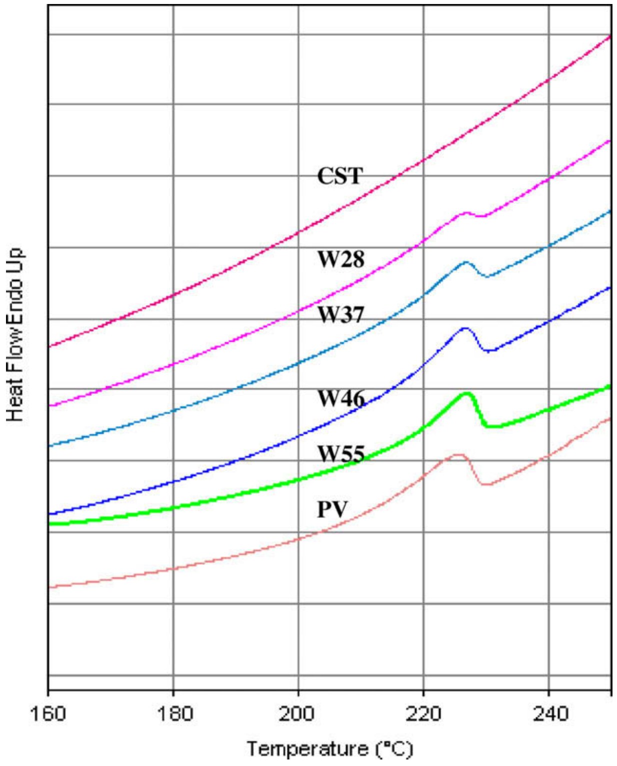

Fig. 1. DSC thermograms of solution casted PVOH and *cassava* starch films.

The enthalpy of melting (ΔH_m) also provides complementary information about physical bonding of the blending (Bernhard Wunderlich, 2006). Based on the ΔH_m of PV, it is possible to justify the following:

(a) When ΔH_m is larger than theoretical enthalpy of melting (ΔH_{mi}), it means that there is extra physical bonding formation between PVOH and *cassava* starch as compared to neat PVOH. The blending interaction is strong and preferable.

(b) However, when ΔH_m is lower than ΔH_{mi}, interaction of PVOH with *cassava* starch is limited. As a result, addition of PVOH to *cassava* starch would produce weak interaction as compared to neat PVOH. Hence, the blending interaction is considered to be weak.

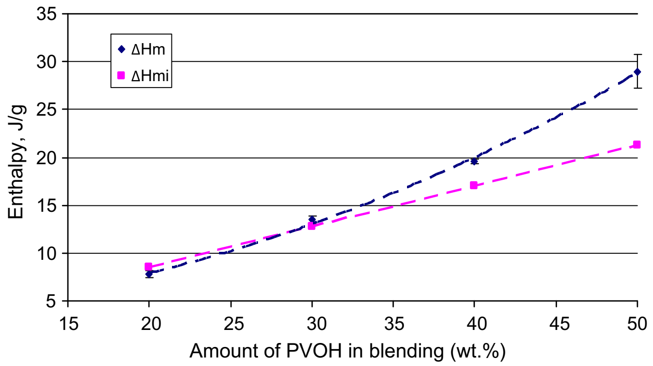

Fig. 2. Plot of experimental (ΔH_m) and theoretical (ΔH_{mi}) enthalpy of melting of solution casted PVOH and *cassava* starch films.

The results of ΔH_m and ΔH_{mi} are plotted in Fig. 2. ΔH_{mi} was taken as the basis to evaluate the extent of interaction between PVOH and *cassava* starch. ΔH_{mi} was calculated based on the ΔH_m of PV and multiplied with the percentage of PVOH of each sample. For example, W28 contains 20 wt.% of PVOH, thus the $\Delta H_{mi} = 0.2\ \Delta H_{m,PV}$. From the analysis of thermograms, CST did not exhibit melting stage. Thus, CST was assumed not to interact among starch molecules and therefore has no impact on ΔH_m. On the other hand, starch molecules would interact intensively with PVOH molecules to increase ΔH_m. The theoretical ΔH_{mi} increases proportionally with percentage of PVOH in the blends. However, the experimental values of ΔH_m did not follow the trend. Initially, W28 has ΔH_m lower than ΔH_{mi}. As the amount of PVOH increased, ΔH_m of W37, W46, and W55 started to deviate far from ΔH_{mi}. When 20 wt.% of PVOH was added, starch portion tend to weaken the interaction of PVOH, but at the same time starch molecules interact extensively with PVOH as well. Hence, $\Delta H_{m,W28}$ was just slightly lower than ΔH_{mi}. The interaction between PVOH–starch accelerated rapidly at 30 wt.% and above of PVOH where ΔH_m of W37, W46, and W55 increased more than ΔH_{mi}. These outcomes indicate that the interaction between PVOH and starch are reactive to induce synergistic effects. It is postulated that at 65–75 wt.%, the ΔH_m will be equivalent to ΔH_{mi} which means that the physical bonding of PVOH–starch is as good as neat PVOH. Thus, the overall material cost of PVOH–starch can be cut down around 30% without sacrificing the properties of the neat PVOH when replaced by PVOH–starch composite.

4. Conclusion

Thermal analysis of PVOH–*cassava* starch blends was conducted by using DSC method. The following findings were obtained:

(1) Blending of PVOH and *cassava* starch is synergistically compatible.

(2) Solution cast *cassava* starch film did not exhibit presence of melting stage. Addition of 20 wt.% PVOH in *cassava* starch showed endothermic peak with onset and end-point temperatures higher than neat PVOH.

(3) The PVOH–*cassava* starch blends containing 30 wt.% or above of PVOH have experimental ΔH_m higher than theoretical ΔH_{mi} indicating strong physical bonding between PVOH and *cassava* starch.

(4) It is postulated that 65–75 wt.% of PVOH in *cassava* starch blend has physical bonding equivalent to that of neat PVOH. Thus, the material cost of PVOH can be reduced significantly without sacrificing of its properties.

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