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Short communication

Determination of thermal stability and activation energy of polyvinyl alcohol–*cassava* starch blends

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ABSTRACT

The thermal degradation and activation energy of polyvinyl alcohol (PVOH) blends with *cassava* starch (CSV) were investigated by thermogravimetry method. Neat PVOH, CSV and PVOH–CSV specimens were prepared by solution casting method. Thermogravimetry is able to provide a clear description about the thermal resistance of PVOH–starch by comparing the onset degradation temperatures and activation energies of neat PVOH, CSV and PVOH–CSV blends (20–50 wt.% of PVOH). The results showed that neat CSV has better thermal resistance than neat PVOH. This is probably due to the presence of cyclic hemiacetal structure in starch is sustainable to thermal attacks. PVOH–CSV blend exhibits enhancement in thermal stability at 40–50 wt.% of PVOH. The activation energies of 40 and 50 wt.% of PVOH loading in CSV are 149.64 and 175.49 kJ/mol, which are 5.47% and 23.69% higher than CSV, respectively. In short, blending of *cassava* starch with PVOH significantly improved the thermal stability of PVOH.

1. Introduction

Polyvinyl alcohol (PVOH)–starch blends have been recognized as potential biodegradable polymeric materials for biomedical and environmental-friendly packaging applications (Chen, Imam, Gordon, & Grèene, 1997; Liu, Feng, & Yi, 1999; Rahmat, Rahman, Lee, & Yussuf, 2009). PVOH–starch hydrogel is compatible with living cells and able to promote tissues growth (Zhai, Yoshii, Kume, & Hashim, 2002). PVOH–starch packaging materials are consumable by microorganisms when disposed without leaving harmful substances to the natural environment (Chen et al., 1997; Mao, Imam, Gordon, Cinelli, & Chiellini, 2000). PVOH possesses good mechanical properties, water soluble and highly crystalline. In contrast, native starch is built up of D-glucose repeating units in amylose and amylopectin structures (Wade, 1999). Native starch does not possess good mechanical strength but is available abundantly at cheap cost, globally. When PVOH and starch are blended together, the presence of hydroxyl groups (–OH) tends to form hydrogen bonding among the molecules and subsequently leads to localized stability and better system integrity (Sin, Rahman, Rahmat, & Samad, 2010a). In the recent work, Sin, Rahman, Rahmat, and Khan (2010b) postulated that blending of 25–35 wt.% of *cassava* starch in PVOH blend has physical bonding equivalent to neat PVOH. PVOH–starch blend was also reported compatible with higher physicomechanical properties (Mao et al., 2000; Siddaramaiah, Raj, & Somashekar, 2004).

This paper aims at investigating the thermal degradation kinetics of PVOH–*cassava* starch blends using thermogravimetry (TG) method as disclosed by Ozawa (1965) and Flynn and Wall (1966). This thermal kinetics strategy has been well applied by international standard testing method (British Standard Institutions, 2005). Up to date, very few studies about the thermal stability of PVOH–starch have been conducted. Although, a thorough study of thermal degradation of neat PVOH and starch have been carried out separately by Holland and Hay (2001) and Stojanović, Katsikas, Popović, Javanović, and Jeremić (2005). This is unlikely to predict the direct interaction of PVOH–starch composite system because every polymer blend system has different thermal stabilities. The interpretations of TG data of polymer blends are important to provide information about the composition of materials, thermal induced reaction kinetics, and radical formations (Conesa, Marcilla, Font, & Caballero, 1996). When TG is coupled with infrared spectroscopy (IR) and mass spectrometry (MS), it will further help to understand the polymer degradation mechanism such as main-chain scission, side group scission, elimination and depolymerization through detection of volatile products evolution with an accompanying of mass changes (Price, Hourston, & Dumont, 2000). In this study, the reported thermal stability of PVOH–starch is important to provide an understanding about the extent of molecular stability in PVOH–starch as well as providing preliminary information about the stability of PVOH–starch blend.

2. Experimental

Fully hydrolyzed PVOH grade BF-17H (viscosity 25–30 cps, hydrolysis 99.4–99.8 mole%, ash <0.7%) manufactured by Chang

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Table 1
Composition of PVOH–CSV in preparation of cast film samples.

Sample	PVOH:CSV (wt.%)	PVOH (g)	CSV (g)
W28	20:80	2	8
W37	30:70	3	7
W46	40:60	4	6
W55	50:50	5	5
PV	100:0	10	0
ST	0:100	0	10

Chung Petrochemical Co., Ltd. was used. Native *cassava* starch (CSV) was obtained from Thailand – Cap Kapal ABC. PVOH, CSV and distilled water were used as received. PVOH–CSV blends were prepared according to Table 1. Samples W28, W37, W46 and W55 were prepared by dissolving PVOH powder in distilled water and heated in a water bath at 97 ± 2 °C for 30 min until PVOH particles disappeared. Fully hydrolyzed PVOH requires at least 90 °C to dissolve in water (Kuraray, 2003). After that, 200 g of distilled water was added to refill the vaporized water during the first heating. CSV was also added at this stage. The mixture was then heated at 97 ± 2 °C for 30 min again. Meanwhile, for samples PV and ST, neat PVOH and CSV, respectively was heated in 400 g of distilled water for 1 h. A motor driven stirrer was set at 800 rpm to help the mixtures to fully dissolve and gelatinize. The mixtures were cast at similar weight on *petri* dishes and dried in vacuum oven at 65 °C to achieve constant weight. All the samples were immediately sealed in polyethylene bags and conditioning under room temperature 25 °C at 65% relative humidity. The TG analysis was conducted according to BS ISO 11358-2 (British Standard Institutions, 2005). Sample of 10 ± 0.1 mg was put on the platinum pan. The data were collected from 30 to 800 °C at the heating rates of 20, 25, 30, 35, and 40 °C/min under dry nitrogen purging at 20 ml/min using Perkin-Elmer TGA 7.

3. Results and discussion

Fig. 1 shows TG mass loss curves for cast film with 20 wt.% of PVOH (W28) at the heating rates of 20, 30, and 40 °C/min. When heating rate increases, the degradation kinetics are higher and thus the activation energy can be determined through Arrhenius plot as shown in Fig. 2. Fig. 3 shows the mass loss curves for various percentages blending of PVOH–CSV. The results showed that the overall degradation can be divided into three stages (Stage 1 – below 200 °C, Stage 2 – 200–500 °C, and Stage 3 – above 500 °C). In stage 1, vaporization of volatiles in ST and PV occurred. ST has the greatest mass loss at this stage because starch absorbs moistures (Gordon, Imam, & Greene, 1996). Thus, the moisture content of ST was totally released during this stage. Meanwhile, PVOH released moistures and hydrolysis residue volatiles such as methanol and methyl acetate (Marten & Zvanut, 1992) at this stage. Upon reaching stage 2, PV tended to degrade more rapidly than ST. As reported by Tubbs and Ting (1973), the decomposition of PVOH can be divided into two stages. The initial decomposition began at 200 °C which mainly involved dehydration of hydroxyl groups, followed by the formation of volatile organic compounds as well as generation of conjugated unsaturated polyene structures. The scissioning of carbon–carbon bonds at elevated temperature produced volatile organic compound and subsequently led to the formation of carbonyl end functional groups products. When temperature reached 450 °C, second stages degradation would predominate by producing small quantities of hydrocarbon related products such as alkenes, alkanes and aromatics. Finally at stage 3, only a small amount of inert carbonaceous residues was left behind (Tubbs & Ting, 1973). Both PV and ST have the similar trends of degradation. This is because starch mainly consists of hydroxyl functional groups as PVOH. However, ST tends to exhibit higher onset degradation temperature and activation energy as compared to PV due to the presence of thermal resistive cyclic hemiacetal in starch structure. The five-or-six membered cyclic ring has good stability of its chemical structure (Wade, 1999). The cyclic form of D-glucose unit arrangement has dense structure with good shielding effect. Therefore, higher energy is required to break the bonding. When the amount of starch increased in the blends, the onset degradation temperatures were higher at stage 2. The onset degradation of the PVOH–CSV blending did not fall somewhere in between PV and ST but tended to be higher than them. This might be explained

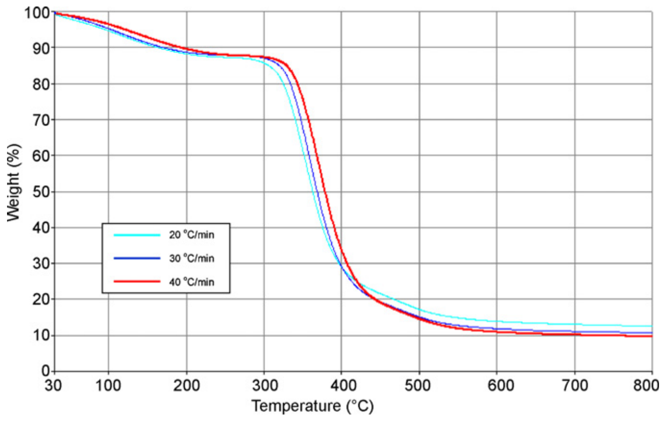

Fig. 1. Thermogravimetry curves of W28 at heating rates 20, 30, and 40 °C/min.

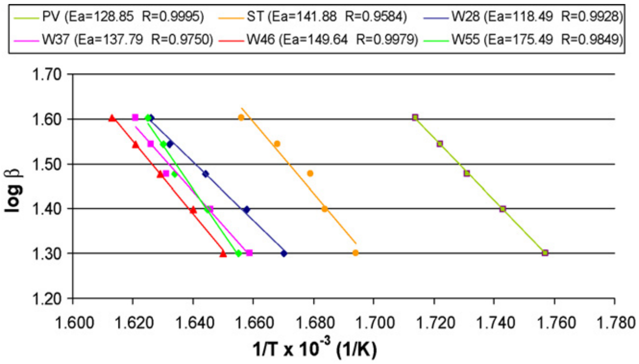

Fig. 2. Logarithm of the heating rates, log β against the reciprocal of absolute temperature, $1/T$ for 20 wt.% mass loss. Activation energy, E_a (kJ/mol) is calculated from the slope ($-0.4567\ E_a/R_c$). R_c is the gas constant 8.314 J/mol K and R is the regression of the linear graphs.

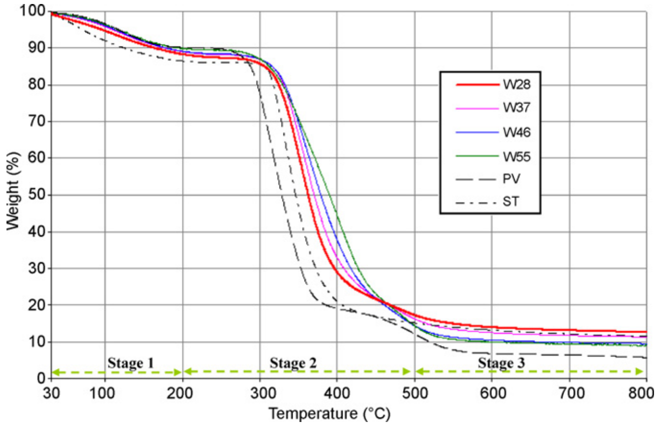

Fig. 3. Thermogravimetry curves of solution cast samples recorded at a heating rate of 20 °C/min.

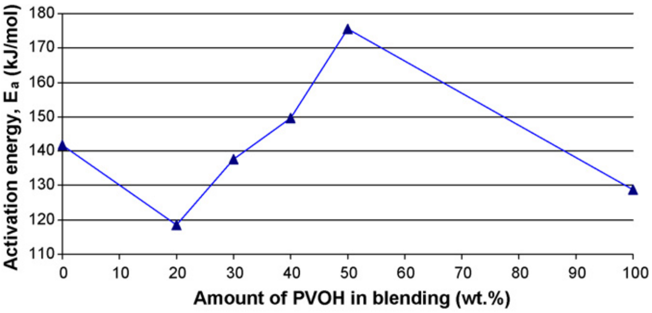

Fig. 4. Plot of activation energy (E_a) to the amount of PVOH in *cassava* starch blend films.

as blending of PVOH and CSV is synergistically compatible and contribute towards high-energy stability hierarchy. When reaching stage 3, all mass losses became stabilized above 600 °C and this indicated that inert carbonaceous residues were formed at this stage. W28 has higher carbonaceous residues as compared to ST indicated that PVOH and CSV were well interacted with each other to withstand thermal attacks. However, this effect became insignificant as the amount of starch increased. W46 and W55 have percentage of residues at combination fraction of PV and ST.

The activation kinetic analysis was opted to 20% mass loss as shown in Fig. 2. It is the onset severe degradation of the samples. W55 has the highest activation energy among the blends as shown in Fig. 4. ST has higher activation energy than PV, W28 and W37. Again, it showed that cyclic hemiacetal structures rendered thermal stability to ST. However, at small amount of PVOH loading such as W28, PVOH caused a reduction of 16.49% of activation energy as compared to ST because low loading of PVOH disrupted the cyclic hemiacetal from performing shielding effect. Thus, less energy was required to break the bonding. At 40 and 50 wt.% of PVOH loading, the activation energy was higher than ST at 5.47% and 23.69%, respectively. In short, blending of CSV with PVOH has significantly improved the thermal stability of PVOH. W46 and W55 have the best thermal stability among the PVOH–CSV blends.

4. Conclusions

Thermogravimetry analysis has provided a clear description about the thermal stability of PVOH–CSV blending. The following findings were obtained:

1. The thermal degradation of PVOH, CSV and PVOH–CSV can be divided into three stages – Stage 1 is vaporization of volatiles, Stage 2 is rapid decomposition/dehydration of hydroxyl groups and Stage 3 is formation of carbonaceous residues.
2. Neat PVOH and CSV have similar trends of degradation because both PVOH and CSV molecules contain similar hydroxyl functional groups.
3. ST has higher activation energy and onset temperature than PV, indicating that CSV has better thermal stability than neat PVOH. The cyclic hemiacetal structure of starch plays an important role in contributing thermal stability of CSV.
4. Blending of 40 and 50 wt.% PVOH (W46 and W55) with CSV have the highest activation energies (E_a) among the samples. This indicated that high loading of PVOH with CSV was synergistically compatible.

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