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Thermal behaviour and interactions of *cassava* starch filled with glycerol plasticized polyvinyl alcohol blends

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ABSTRACT

Thermal behaviour and interactions of glycerol plasticized polyvinyl alcohol (PVOH)–*cassava* starch (CSS) blended films were analysed using thermogravimetry and differential scanning calorimetry methods. The outcomes showed that addition of glycerol has reduced the onset and end-point melting temperatures of the blended films. Samples with 30 and 40 wt.% of PVOH–glycerol blended with CSS exhibited experimental enthalpy of melting (ΔH_m) lower than theoretical enthalpy of melting (ΔH_{mi}). Meanwhile, the thermogravimetry degradation of the PVOH–glycerol–*cassava* starch can be divided into three phases, whereby phase 1 is the vaporization of volatiles, phase 2 is the rapid decomposition/dehydration and elimination of degradants and phase 3 is the formation of carbonaceous residues. These samples have thermogravimetry degradation activation energy (E_a) higher than their original components. For instance, 20 wt.% of PVOH–glycerol blended with CSS has a E_a which is 6.36 and 4.07 times higher than glycerol plasticized PVOH and CSS, respectively. Blending of PVOH–glycerol and CSS are favorable to produce biodegradable compounds resist to thermal attacks.

1. Introduction

Polyvinyl alcohol (PVOH)–starch composite is recognized as a potential biodegradable polymeric material (Chen, Imam, Gordon, & Grèene, 1997; Liu, Feng, & Yi, 1999; Tang, Zhou, Xiong, & Tang, 2008; Zhai, Yoshii, Kume, & Hashim, 2002). This composite is suitable to be used as biodegradable packaging materials because it can be fully consumed by microorganisms without leaving away harmful pollutants in the environment (Mao, Imam, Gordon, Cinelli, & Chiellini, 2000). Besides that, it can also be used as promising hydrogel and tissue culture scaffolding materials in biomedical and pharmaceutical applications (Constantin et al., 2004; Sinha et al., 2007; Xiao & Yang, 2006). It is biocompatible and able to induce surrounding growth of tissues for transplanted cell to attach (Gomes, Godinho, Tchalamov, Cunha, & Reis, 2002). According to a recent work conducted by Lee, Rahman, Rahmat, and Khan (2010a), the blending of PVOH with *cassava* starch (CSS) produced synergistic increments of the enthalpy of melting of PVOH–CSS blends. The hydroxyl groups of the PVOH and starch form extensive hydrogen bonds among the molecules and subsequently lead to tremendous blending system interactions (Siddaramaiah, Raj, & Somashekar, 2004). In previous works, PVOH–starch blends were reported to be compatible due to their good physico-mechanical properties (Chiellini, Corti, D'Antone, & Solaro, 2003; Mao et al., 2000). In another study, Ramaraj (2007) highlighted that starch blended with PVOH has a higher tensile strength than the theoretical values. For instance, when 50 wt.% of PVOH is added to starch, the experimental tensile strength (8.02 MPa) is 1.44 MPa higher than the theoretical tensile strength (6.58 MPa). This indicates that the PVOH and starch are reactively compatible. Similarly, Chiellini, Cinelli, Ilieva, Imam, and Lawton (2009) have found that PVOH can be used as a reinforcing agent to enhance the maximum force yield of the foam articles. It has also been proven that the presence of PVOH in thermoplastic starch could improve flexibility and water resistance of finished foam trays (Cinelli, Chiellini, Lawton, and Imam, 2006). Moreover, the observation using scanning electron microscope (SEM) showed that the incorporation of PVOH could build up strong foam structures within a weak starch matrix (Chiellini, Cinelli, Ilieva, Imam, & Lawton, 2009).

Previous studies have reported that PVOH–starch blends can be well processed by adding glycerol (Fishman, Coffin, Onwulata, & Willet, 2006; Mao et al., 2000). Glycerol is used to plasticize and gelatinize the PVOH–starch blends for better system integrity (Garg & Jana, 2007). This is due to the solubility parameter of glycerol (21.1 $\text{MPa}^{1/2}$) (Belmares et al., 2004), PVOH (22.5 $\text{MPa}^{1/2}$) (Moolman, Meunier, Labuschagne, & Truter, 2005) and starch (23.4 $\text{MPa}^{1/2}$) (Liu et al., 1999) are very close to each others. Hence, glycerol can effectively plasticize the PVOH–starch compounds (Liu et al., 1999; Forssell, Hulleman, Myllärinen, Moates, & Parker, 1999). In this study, differential scanning calorimetry

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Table 1
Composition of PVOH–glycerol–CSS in preparation of cast films.

Sample	PVOH:CSS (wt.%)	PVOH (g)	CSS (g)	Glycerol (g)
WG28	20:80	2	8	0.857
WG37	30:70	3	7	1.286
WG46	40:60	4	6	1.714
WG55	50:50	5	5	2.143
PVG	100:0	10	0	4.286
STG	0:100	0	10	4.286

(DSC) was used to determine the changes of enthalpy of melting (ΔH_m). The ΔH_m increases when intermolecular interactions are present among the blending components. Higher energy is required to break the bonding and free the polymer chains from the rigid/crystal structures. Besides that, the degradation kinetics of PVOH–glycerol–CSS was studied using thermogravimetry (TG) method (Flynn & Wall, 1966; Ozawa, 1965). At present, there is a lack of study on the thermal stability of PVOH–glycerol–CSS blending system. Although a thorough study on thermal degradation of neat PVOH, corn starch and glycerol have been carried out by Holland and Hay (2001), Stojanović, Katsikas, Popović, Javanović, and Jeremić (2005), and Dou, Dupont, Williams, Chen, and Ding (2009), respectively, these data would not be able to predict the PVOH–glycerol–CSS reactive blending as every polymer blending system has different thermal stabilities and extensive interactions among the polymer chains. TG is able to provide remarkable “fingerprint” in terms of temperature range, extent and kinetics decomposition and thus become the means to distinguish properties of the various polymers blends (Price, Hourston, & Dumont, 2000). Hence, this paper aims to characterize the thermal behaviour of PVOH–glycerol–CSS blends because the incorporation of starch would change the inherent thermal properties of PVOH–glycerol. It is forecasted that favorable interactions of starch and PVOH–glycerol would be exhibited when these PVOH–glycerol–CSS blends produce higher enthalpy of melting and degradation activation energy. Such an outcome would be a useful guide means to produce high quality starch based biodegradable compounds.

2. Experimental

2.1. Materials

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., China. was used. The native *cassava* starch (CSS) was obtained from Thailand-Cap Kapal ABC and the glycerol with 99.5% purity was supplied by Fischer Scientific, United States. These PVOH, CSS, glycerol and distilled water were used as received.

2.2. Methods

The solution cast samples of PVOH–glycerol–CSS were prepared as shown in Table 1. Samples WG28, WG37, WG46 and WG55 were prepared by dissolving PVOH and glycerol in distilled water and heated in a water bath at 97 ± 2 °C for 30 min until PVOH particles dissolved. Fully hydrolysed PVOH requires at least 90 °C to be dissolved in water (Kuraray Specialities, 2003). The amount of glycerol is based on the following equation:

$$30\ \text{wt.\%}\ \text{glycerol} = \frac{M_{\text{glycerol}}}{M_{\text{glycerol}} + M_i} \times 100\% \quad (1)$$

where M_{glycerol} is the mass of glycerol, M_i is the pre-determined mass of PVOH for preparation of WG28, WG37, WG46, WG55 and PVG; or pre-determined mass of CSS for preparation of STG. After the PVOH has fully dissolved, CSS was then added and the mixture was again heated at 97 ± 2 °C for 30 min. Meanwhile for preparation of samples of PVG and STG, neat PVOH or CSS together with glycerol were heated in 400 g 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 cast with similar weights of 20 g on *Petri* dishes and dried in an oven at 65 °C to achieve constant weight. All the samples were immediately sealed in polyethylene bags and stored under room temperature 25 °C at 65% relative humidity for conditioning purpose (average moisture content 10%). A DSC analysis was carried out using Perkin-Elmer United States-DSC7. The samples were weighed and placed in standard aluminum pans. A sealed empty pan was used as the reference while nitrogen gas was being purged at 20 ml/min during these experiments. Each sample was heated to 50 °C and scanned at temperatures ranging from 50 to 250 °C at 10 °C/min. Meanwhile, a TG analysis was also being conducted according to BS ISO 11358-2 (British Standard Institution, 2005) whereby 10 ± 0.1 mg of sample was put on a platinum pan. The TG data was collected from 30 to 800 °C at heating rates of 20, 25, 30, 35, and 40 °C/min with nitrogen purging at 20 ml/min using Perkin-Elmer United States-TGA7.

3. Results and discussion

3.1. Differential scanning calorimetry analysis

Fig. 1 shows DSC thermograms of solution cast PVOH–glycerol–CSS samples. The onset temperature, end-point temperature and enthalpy of melting (ΔH_m) data extracted from the DSC thermograms are presented in Table 2. Onset is the temperature when samples begin to melt, while end-point is the temperature when the melting stage ends. All these samples have broad melting ranges with the exception of STG did not show any presence of endothermic peaks throughout the heating process. When the amount of PVOH–glycerol increased from WG28 to WG46, the onset and end-point temperature decreased. This is because the glycerol has disrupted the rigidity arrangements of PVOH and CSS. Basically, glycerol promotes internal lubrication and flexible chain sliding. In fact as reported in some literatures (Fishman et al., 2006; Lin & Ku, 2008; Mao et al., 2000), the addition of glycerol in PVOH is necessary, especially in conventional plastic processing techniques

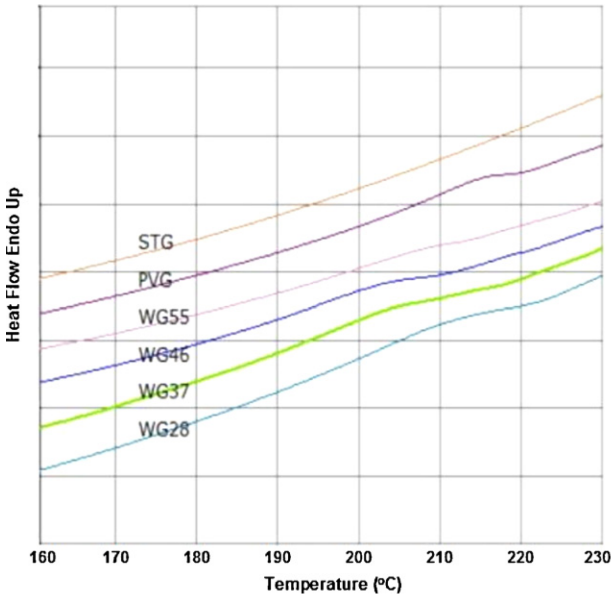

Fig. 1. DSC thermograms of solution cast PVOH–glycerol–CSS blends.

Table 2
Onset and end-point melting temperatures, experimental enthalpy of melting (ΔH_m) and theoretical enthalpy of melting (ΔH_{mi}) of solution cast samples.

	WG28	WG37	WG46	WG55	PVG
Onset (°C)	207.20	196.52	193.03	197.07	194.90
SD	1.25	2.05	3.19	2.29	4.67
End-point (°C)	219.36	214.83	210.16	216.00	215.58
SD	1.16	0.69	2.12	2.73	5.97
ΔH_m (J/g)	3.36	3.56	5.51	7.15	14.19
SD	0.28	0.28	0.42	0.47	0.35
ΔH_{mi} (J/g)	2.84	4.26	5.68	7.10	–

SD = standard deviation.

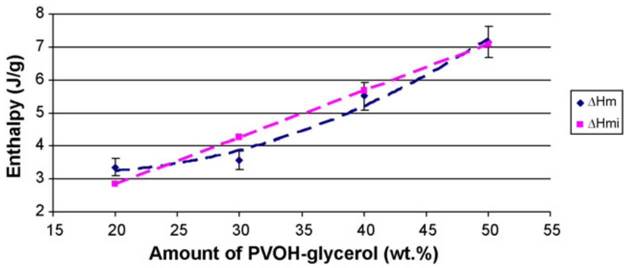

Fig. 2. Plot of experimental enthalpy of melting (ΔH_m) and theoretical enthalpy of melting (ΔH_{mi}) of solution cast PVOH–glycerol–CSS blends.

such as injection moulding and screw extrusion. This is needed to reduce the processing temperatures and compounds viscosities. PVOH is different from the commodity thermoplastics such as polyethylene and polystyrene which have degradation temperatures away from their melting temperatures (>50 °C) (Kholodovych & Welsh, 2007). Both polyethylene and polypropylene are very unlikely to undergo thermal degradation when melt processed. In contrast, PVOH without the addition of plasticizer possesses a melting point that is very close to its degradation temperature. PVOH tends to degrade during melt processing stage by having noticeable yellowish outputs (Wang, Schertiz, & Pomplun, 2001). Besides that, it was also found that the onset and end-point temperatures of WG55 were higher than WG37 and WG46. This might be due to the rigid structure of PVOH has acted as a reinforcing agent to enhance the weak structure of CSS. Thus, a higher amount of plasticizer is required to reduce the melting point of WG55 blend.

In spite of that, the enthalpy of melting (ΔH_m) analysis has provided complementary information about the physical bonding of polymers blends (Wunderlich, 2006) such as hydrogen bonds, van der Waals forces and crystallization. Based on the ΔH_m of PVG, it is possible to conclude the following:

(a) When experimental ΔH_m is larger than the theoretical ΔH_{mi}, it means that there are extra physical bonding formations between PVOH and CSS. The particular amount of glycerol has not weakened the interactions between PVOH and CSS. The blending interaction for this combination is strong.
(b) When experimental ΔH_m is lower than the theoretical ΔH_{mi}, it means that addition of glycerol has weakened the physical bonding between PVOH and CSS. The blending interaction for this combination is weak.

The results of ΔH_m and ΔH_{mi} are plotted in Fig. 2. ΔH_m was calculated based on the ΔH_m of PVG and multiplied with the percentage of PVOH for each sample. For instance, WG28 contains 20 wt.% of PVOH, thus the $\Delta H_{mi,\mathrm{WG28}} = 0.2\Delta H_{m,\mathrm{PVG}}$. Since CSS did not exhibit a melting stage, thus CSS is assumed not to have any influence on intramolecularity (among starch molecules) but affects intermolecularly (between PVOH and starch molecules) towards ΔH_m. The theoretical ΔH_{mi} increases proportional to the percentage of PVOH–glycerol in the blends. However, the experimental ΔH_m results have deviated from the expectation. Initially, WG28 has higher ΔH_m than ΔH_{mi}, but when the amount of PVOH–glycerol increases, the ΔH_m of WG37 and WG46 are lower than ΔH_{mi} and finally back to trend at WG55. These outcomes indicate that when a small quantity of glycerol is added, the plasticizing effects of glycerol are very limited and do not disrupt the physical bonding interactions between PVOH and CSS. The interactions of PVOH and CSS are strong enough to withstand external molecules from disrupting the blending structure. In contrast, the physical interactions are weakened when the amount of PVOH–glycerol is increased due to the large quantities of glycerol have gelatinized CSS. Thus, CSS has lost its rigidity to interact directly with PVOH. However, when the amounts of CSS in the blends are reduced and start to be dominated by PVOH, the blending will be inclined nearer to PVOH characteristics. Finally, the ΔH_m of WG55 increases approaching ΔH_{mi}. The strong physical bonding between PVOH–CSS is induced by the formation of hydrogen bonds between hydroxyl groups (Lee, Rahman, Rahmat, & Samad, 2010b). The extensive formations of hydrogen bonding will subsequent build up a stronger crystalline structure in the blend.

3.2. Thermogravimetry analysis (TG)

Fig. 3 shows the TG mass loss curves for WG55 with heating rates of 20, 30 and 40 °C/min, respectively. The temperatures at 20% mass loss for each sample are tabulated in Table 3. The TG degradation kinetics is related to these heating rates and thus activation energy can be determined through the Arrhenius plot in Fig. 4. Generally, the overall degradation of PVOH–glycerol–CSS blend can be divided into three phases as shown in Fig. 5 (phase 1 below 200 °C; phase 2 200–500 °C; and phase 3 above 500 °C). Initially, the vaporization of volatiles occurred in phase 1. The extent of this volatiles release (including moisture) is determined by the physical interactions of the blending components. Although PVG and STG have

Table 3
Temperatures at 20% weight loss in thermogravimetry test at heating rates of 20, 25, 30, 35 and 40 °C/min.

Heating rate (°C/min)	WG28 (°C)	WG37 (°C)	WG46 (°C)	WG55 (°C)	PVG (°C)	STG (°C)
20	327.10	299.16	280.36	267.11	204.67	297.40
SD	0.08	3.68	2.76	0.75	2.45	0.51
25	329.76	310.65	285.75	274.28	211.82	307.67
SD	0.09	0.96	1.88	1.10	1.44	1.17
30	332.22	317.47	288.95	282.33	217.50	320.65
SD	0.08	1.49	2.82	0.64	0.76	0.61
35	334.63	323.66	292.47	287.89	225.70	327.51
SD	0.08	1.18	1.71	1.31	1.78	0.73
40	337.59	330.30	296.59	295.61	233.35	334.62
SD	0.10	1.81	2.66	0.57	1.41	0.69

SD = standard deviation.

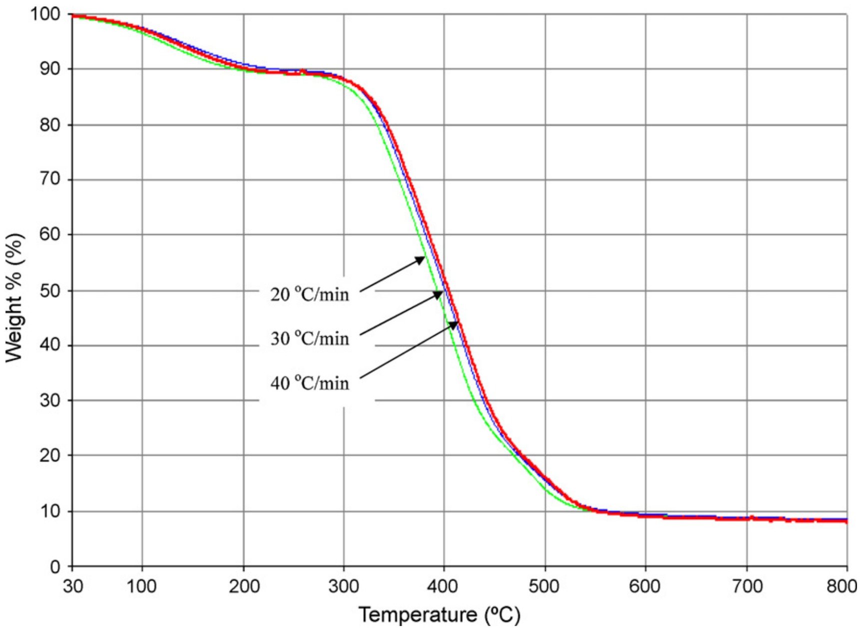

Fig. 3. Thermogravimetry curves of WG55 at heating rates of 20, 30 and 40 °C/min.

similar amounts of glycerol, but PVG tends to degrade more rapidly than STG. Seemingly, PVOH has lowered the boiling point of glycerol. Pure glycerol has a boiling point of 290 °C (Acros Organics, 2006) but in this case, the PVOH has disrupted the genuine bonding among these glycerol molecules causing a lower energy needed to vaporize the glycerol. In contrast, starch possesses hydrophilic nature with helical structure of all hydroxyl groups that are directed outside of the ring (Imam, Gordon, & Greene, 1996). This structure promotes direct interactions of starch and glycerol by forming hydrogen bonds and subsequently lowers the volatility of glycerol in CSS. Among the PVOH–glycerol–CSS samples, WG28 has the lowest mass loss in phase 1 followed by WG37, WG46 and WG55.

Prior to reaching phase 2, severe degradation has occurred which involving main-chain scission, side group scission, depolymerization and elimination of degradants (Price et al., 2000). The PVG has degraded more rapidly than STG. According to Tubbs and Ting (1973), the decomposition of PVOH occurred in two stages and began at 200 °C. The decomposition mainly involves dehydration of the hydroxyl groups. This is followed by the formation of volatile organic compounds which subsequently produced conjugated unsaturated polyene structures. The formation of these volatile organic compounds was due to the scissioning of carbon-carbon bonds which led to the generation of carbonyl end functional groups products. On the other hand, at temperature as high as 450 °C, the second stage degradation would start to dominate by producing small amounts of hydrocarbon products (alkenes, alkanes and aromatics) and finally leaving carbonaceous residues (Tubbs & Ting, 1973) at phase 3. The glycerol content was fully released in phase 2 when the temperature exceeded the boiling point. Both STG and PVG have similar trends of degradation because starch in STG also consists of hydroxyl functional groups. However, the onset degradation temperature and activation energy of STG were higher than PVG. This could be due to starch is originally built up of thermally stable cyclic hemiacetal structure. Cyclic hemiacetal structure has the highest stability in five-or-six membered rings (Wade, 1999). Cyclic-D-glucose arrangement has a compact and closed structure with good shielding effects. As a result, higher energy is required to break the bonding. When

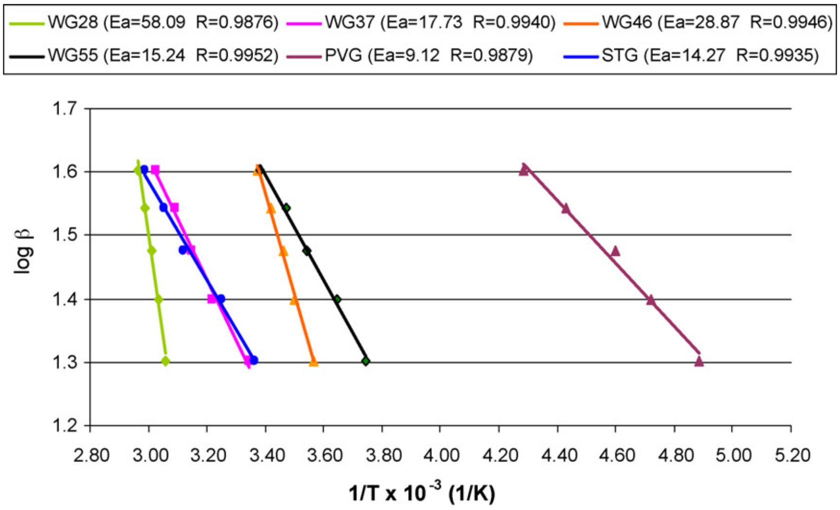

Fig. 4. Logarithm of the heating rate, log β against the reciprocal of absolute temperature, $1/T$ for 20 wt.% mass loss. Activation energy, E_a (kJ/mol) is calculated from the slope ($-0.4567E_a/R_c$). R_c is the gas constant 8.314 J/mol K and R is the regression of the linear graphs.

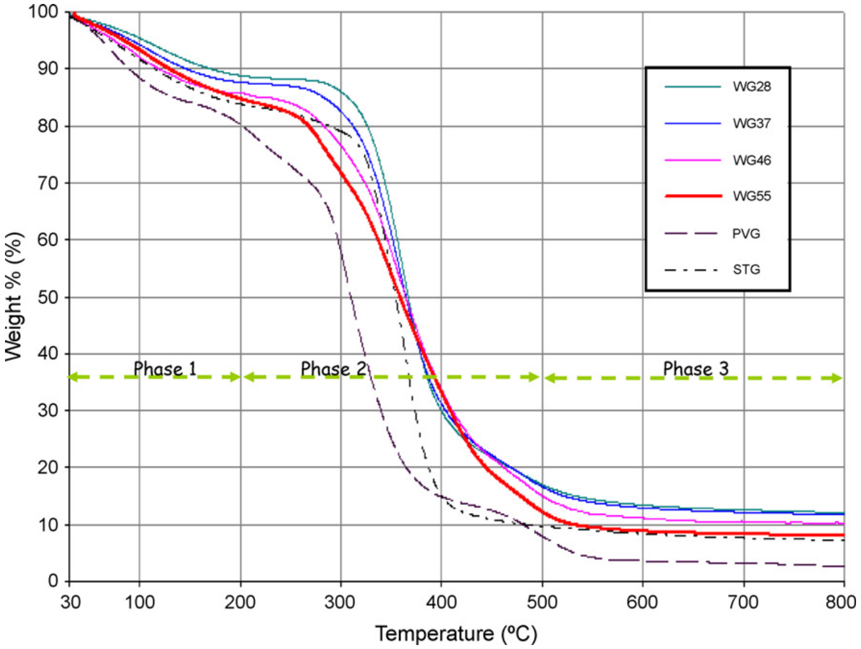

Fig. 5. Thermogravimetry curves of solution cast samples recorded at heating rate of 20 °C/min.

the amount of CSS is increased in the blending, the degradation temperatures at 20% mass loss increase as well. It was interesting to discover that after the glycerol was fully vaporized (>350 °C), the mass of WG28, WG37, WG46 and WG55 did not remain in between PVG and STG but tended to be higher than them. This can be explained that the PVOH–CSS compound is synergistically compatible and thus contributes towards a higher energy stability hierarchy. Furthermore in phase 3, all the mass losses have become constant at temperature above 600 °C and this feature indicated that stable carbonaceous residues were formed at this level. WG28 and WG37 have higher carbonaceous residues as compared to original components—PVG and STG. This shows that PVOH and CSS have reacted during the heating process by forming substances which are resistible to thermal attacks. However, this thermal resistance effect has become insignificant when the amount of starch is increased and thus WG55 has percentage of residue approaching STG.

A TG kinetics analysis was opted to 20% mass loss as shown in Fig. 4. The plot was generated according to the data in Table 3 using the Arrhenius relationship (British Standard Institution, 2005). All samples have activation energy (E_a) deviated away from its original components: PVOH (150 kJ/mol) (Holland & Hay, 2001), starch (167 kJ/mol) (Stojanović et al., 2005) and glycerol (61 kJ/mol) (Dou, Dupont, Williams, Chen, & Ding, 2009). The large deviations showed that the additional of irregular components in polymers blends would definitely change the genuine interactions of pure components. WG28 had the lowest amount of glycerol among the samples but possessed the highest activation energy. Meanwhile, STG has produced higher activation energy than PVG. Generally, the blending of PVOH–glycerol and CSS is preferable due to the thermal stability of the blends is higher than PVG and STG. The amount of glycerol added to PVOH–CSS has greatly influenced the thermal degradation and stability of the blends.

4. Conclusions

Thermogravimetry and differential scanning calorimetry analyses have provided clear descriptions about the thermal behaviour and interactions of glycerol plasticized PVOH–CSS blends. In this study, the following findings were obtained:

1. When the amount of PVOH–glycerol increases, the onset and end-point melting temperatures decrease. This is because glycerol promotes internal lubrication and disrupts rigidity arrangements of PVOH and CSS.
2. When a small quantity of glycerol is added, the plasticizing effects of glycerol are very limited and do not disrupt the physical bonding interactions between PVOH and CSS. A low amount of PVOH–glycerol (WG28) produces an experimental ΔH_m higher than the theoretical ΔH_{mi}. However, when the amount of CSS in the blends reduces and starts to be dominated by PVOH, the blending will be inclined nearer to PVOH properties. A high amount of PVOH–glycerol (WG55) has ΔH_m approaching ΔH_{mi}.
3. A TG degradation of PVOH–glycerol–CSS can be divided in three phases: phase 1 is the vaporization of volatiles, phase 2 is the rapid decomposition/dehydration and elimination degradants and phase 3 is the formation of carbonaceous residues.
4. All samples have shown E_a higher than its original components. TG has showed that WG28 has an activation energy which is 6.36 and 4.07 times higher than PVG and STG, respectively. Blending of PVOH–glycerol and CSS are preferable to produce starch based biodegradable compounds resist to thermal attacks.

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