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Short communication

Rheology and thermal transition state of polyvinyl alcohol–*cassava* starch blends

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ABSTRACT

This communication focuses to unveil the molten behaviour of biodegradable polyvinyl alcohol (PVOH) blending with native *cassava* starch (CSS). Different percentages of CSS were blended with glycerol plasticized PVOH (PPV) to study the shear rate–viscosity at 190 °C and the thermal transition state at 200 bar (20.265 MPa). The outcomes showed that the viscosities of PPV–CSS compounds reduced as the PPV composition increased. This indicates that the addition of PPV helps to improve the processability of thermoplastic starch compound. On the other hand, a higher percentage of CSS would disrupt the transition of specific volumes at the molten stage (160–180 °C) of PPV–CSS compounds. The transition was lowered due to the loss of crystallinity in PPV. It is postulated that injection moulding of PPV–CSS blends has lower volume shrinkage than PPV due to lower thermal transition and crystallinity of the compounds.

1. Introduction

The disposal of plastic wastes has been a serious issue since decades ago. Most of the commodity plastic materials such as polyethylene, polypropylene, polystyrene, and polyvinyl chloride are derived from petroleum sources. These polymers bring thousands of convenience to mankind. However, these materials are non-degradable when disposed in natural environment. Many researchers have presented alternatives to produce plastic products from natural polymeric materials such as proteins, lipids, oils and starches (Avérous, 2008). Considerable attentions have been given to utilize starch for production of biodegradable polymer blends. This is because starch is abundance and available at cheap prices (Susan, 2005).

This communication aims to report the blending of polyvinyl alcohol (PVOH) which caused changes in the rheological and thermal transition state of native *cassava* starch (CSS). The studies on rheological and thermal transition are very important to ensure PVOH–starch compound can readily replace commodity thermoplastics in domestic applications, so that these compounds can be easily processed by the existing technology and equipments. Similar to starch, PVOH is also a biodegradable polymer, but it is derived from source of petroleum. Blending of starch with low viscosity polymers such as PVOH and poly(ethylene-*co*-vinyl alcohol) is necessary to overcome inherent poor processability of native starch that is typical in blow moulding process where the modified thermoplastic starch lacks of good extensional flow properties (Stenhouse, Ratto, & Schneider, 1997). Previous researchers have found that thermoplastic starch possesses very complex thermal processing behaviour which is mainly due to multiple chemical and physical reactions – e.g. granule expansion, gelatinization, decomposition, melting and crystallization (Liu, Xie, Yu, Chen, & Li, 2009). Both starch and PVOH have huge hydroxyl (–OH) functional groups that interact extensively via hydrogen bonding (Rahmat, Rahman, Sin, & Yussuf, 2009; Sin, Rahman, Rahmat, & Samad, 2010). PVOH reinforces the weak structure of starch as well as enhance the thermal processability when it is subjected to high shear effects (Fishman, Coffin, Onwulata, & Willett, 2006). Moreover, the addition of plasticizers such as glycerol, sorbitol and urea can overcome the brittleness problem through the formation of a more stable and flexible hydrogen bonding. Blending different types of polymers, processing aids and plasticizers would cause significant changes in rheological and thermal transition of starch compounds (Forsell, Mikkila, Moates, & Parker, 1997). Chakravorty (2002) highlighted that the pressure–volume–temperature (PVT) behaviours of polymer contribute mainly to the volumetric shrinkage in injection moulding products. The internal stresses induced by the shrinkage will cause undesired product defects such as warpage and sink marks. Therefore, the objective of this communication is to unveil processability behaviour of PVOH–starch compound.

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Table 1
Compositions of glycerol plasticized PVOH (PPV).

Specimen	Glycerol (phr)	PVOH (phr)	CaS (phr)	Phosphoric acid (g)
PPV	40	100	2	4.18

2. Experimental

2.1. Materials

Fully hydrolysed PVOH grade BF-17H (viscosity 25–30 cps, hydrolysis 99.4–99.8 mole %, ash < 0.7%) used in this study was manufactured by Chang Chung Petrochemical Co., Ltd., China. Native *cassava* starch (CSS) was obtained from Thailand, Cap Kapal ABC. Glycerol ($C_3H_8O_3$) at 99.5% purity was purchased from Fisher Scientific, United States. Calcium stearate (CaS) was supplied by Sun Ace Kakoh Sdn. Bhd., Malaysia and phosphoric acid at 85% purity was obtained from Merck, Germany. All these materials were used as received.

2.2. Specimens preparation

PVOH, glycerol, CaS, and phosphoric acid were pre-mixed using Chyau Long Machinery Co., Ltd., Taiwan, CL-10 high speed mixer for 15 min. The glycerol and CaS were used as plasticizer and internal lubricant, respectively. The phosphoric acid acted as heat stabilizer additive to prevent occurrence of pre-processing thermal degradation. The mixtures were then compounded using a twin screw co-rotating extruder Sino PSM 30 B5B25 (built by Sino-Alloy Machinery Inc., Taiwan) to produce plasticized PVOH (PPV). The composition of PPV is shown in Table 1. A side feeder was used to transfer the mixtures into the barrel which has four heating zones. All heating zones were set at 160 °C while the screw speed was set at 250 rpm. After that, PPV, CSS and glycerol were mixed again in the high speed mixer. The compositions of these PPV–CSS mixtures are shown in Table 2. The mixtures were compounded again in the twin screw co-rotating extruder. Four heating zones were set at 140 °C. Then, the extruded compounds were palletized and immediately sealed in polyethylene bags.

2.3. Rheological measurement

A capillary rheometer – Gottfert® Rheograph 75 was used to measure the shear rate–viscosity of these specimens at 190 °C. The capillary dies of 1 mm in diameter with length/diameter ratio (L/D) of 10 and 20 were used. Initially, the specimen was filled into a barrel through a funnel and packed down slowly with a piston until a small amount of extrudate was discharged from the capillary exit. Once packed, the specimens were left in the barrel for 15–20 min to equilibrate at 190 °C. The shear rates were varied from 10 to 2000 s^{-1}. The pressure loss effects were taken into account using Bagley corrections and the results were generated automatically from the bundled computer software. Bagley corrections are very important in order to obtain the shear rate–viscosity at actual polymer processing conditions (British Standard Institutions, 2005). All the reported data as shown in Fig. 1 are true shear rate–viscosity of the specimens.

Table 2
Compositions of PPV blending with *cassava* starch (CSS).

Specimen	PPV (wt.%)	CSS (wt.%)	Glycerol (phr)
PPV28	20	80	20
PPV37	30	70	20
PPV46	40	60	20
PPV55	50	50	20

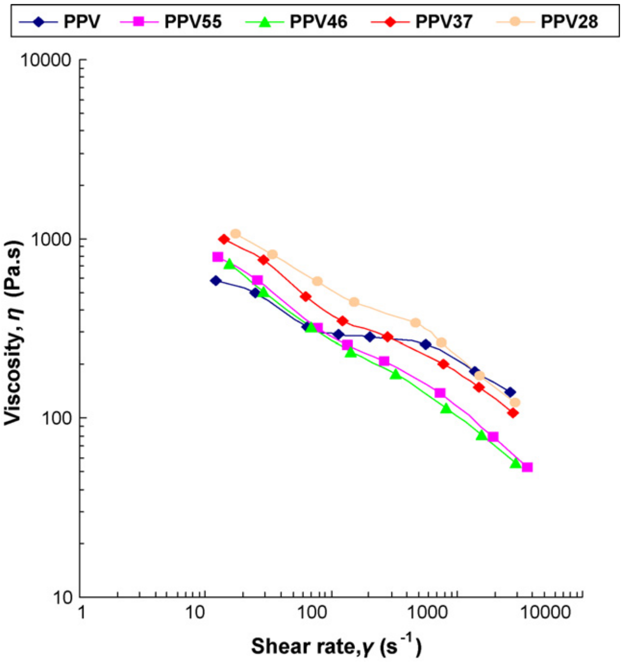

Fig. 1. Shear rate–viscosity of PPV and PPV–CSS compounds at 190 °C.

2.4. Thermal transition measurement

The specific volumes of the polymers as a function of temperature at 200 bar (20.265 MPa) were measured by the PVT apparatus model SWO PVT 100. Initially, the known amount of specimen was filled into a cylindrical test cell with a piston inserted. Hydraulic pressure was applied to the specimens via the piston with an inert polytetrafluoroethylene (PTFE) seal to avoid potential leakage of molten specimen during testing. After this pre-compression, the sample was heated for 5 min in the test cell until it equilibrates at 200 °C. The chosen pressure at 200 bar (20.265 MPa) was applied and the initial volume was determined from the cell diameter and piston position. The tests were conducted at a low cooling rate 5 °C/min to ensure uniform temperature distribution within the specimen. The position of the piston was recorded continuously corresponding to the decreasing temperatures. Finally, the specific volumes were calculated and plotted as a function of temperature as shown in Fig. 2.

3. Results and discussion

Fig. 1 shows the shear rate–viscosity of PPV and PPV–CSS compounds. All PPV–CSS specimens exhibited shear thinning

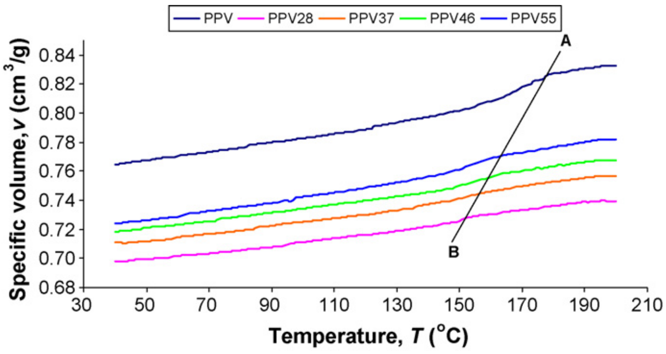

Fig. 2. Thermal transitions of PPV and PPV–CSS compounds at 200 bar (20.265 MPa).

behaviour at high shear rate. However, the rheology behaviour of PPV showed differently with a lower change of viscosity at the region 100–1000 s^{-1}. A transition has occurred at this region with a possibility due to gradual loss of physical bonds (e.g. hydrogen bond and van der Waals forces) when PPV is subjected to shear stress (Lin & Ku, 2008). Glycerol blended in PVOH started to flow freely among the PVOH chains at high shear rate with weaker physical bonds. The glycerol has helped to promote PVOH chain sliding by lowering viscosity. On the other hand, PPV–CSS compounds exhibited a stable drop of viscosities at high shear rate. This indicates that CSS has gelatinized and interacted effectively with PVOH and glycerol during the melt blending process. High crystallize structure of amylopectin has been disrupted during the compounding stage and thus CSS is more susceptible to melt deformation (Liu et al., 2009). According to Klingler, Meuser, and Niediek (1986), starch undergoes fragmentation when subjected to melt mixing at high shear effect. Fragmentation is very important to promote gelatinization and conversion of native starch into thermoplastic starch properties under the reaction of compatible plasticizers. In spite of that, the viscosities of PPV–CSS compounds have also been reduced by having higher amount of PPV with an optimum percentage at 40–50%. PVOH and glycerol at an optimum percentage can form strong bonding interactions with starch and promote movement among the starch molecules (Liu et al., 2009). Therefore, the processability properties of PPV–CSS compounds at this composition are rheologically comparable to polyolefins (Gahleitner, 2001).

The isobaric thermal transitions of the specimens are shown in Fig. 2. It can be observed that all the specimens exhibited thermal transition behaviour of crystalline polymers with noticeable high transition of specific volumes at melting stage 160–180 °C. This indicates a presence of crystal structure within the specimens (Zoller & Walsh, 1995). However, the transition started to reduce at higher percentage of CSS in the compounds. This is due to the different molecular sizes and structures between starch and PVOH has disrupted the crystallinity morphology of the compounds. Besides that, the specific volumes of PPV–CSS exhibit dependence on the composition of starch. Starch is denser than PVOH due to high branched of amylopectin structures resisting the mobility of polymer chains and promote a substantial formation of hydrogen bonds (Liu et al., 2009). CSS is one the starches that has been found to possess semi-crystalline long-branched structures (Liu et al., 2009). On the other hand, the transition of onset melting points of PPV and PVOH–CSS can be clearly identified at the line A–B in Fig. 2. This result showed an agreement with the previous differential scanning calorimetry study that onset melting points were detected at a range of 160–180 °C (Salleh, Rahman, & Sin, 2009). When the amount of starch increased, onset melting points would shift gradually to lower temperatures. Incorporation of starch has eliminated the crystalline content of PPV to an extent of approaching the behaviour of amorphous polymer. In short, PVOH has significantly changed the processing behaviour of starch through the influence of the blending morphology and interactions. PPV–CSS compounds are preferable to be melt processed at temperature >170 °C in order to achieve absolute molten state. It is postulated that injection moulding of PPV–CSS has a lower volume shrinkage than PPV due to its lower thermal transition and crystallinity.

4. Conclusions

Rheological and thermal transition analyses of PPV–CSS blends were conducted in this study. The following findings were obtained:

(1) Blending of PPV has changed the processing behaviour of *cassava* starch.
(2) Blending of PPV has reduced the viscosity of CSS. PVOH has formed strong interactions with starch and promote movement of the starch molecules when the blending is subjected to shear force.
(3) Blending of CSS has reduced the crystallinity of the PPV due to lower transition of specific volumes at melting stage.
(4) It is postulated that injection moulding of PPV–CSS compound has a lower volume shrinkage than PPV due to its lower thermal transition and crystallinity.

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