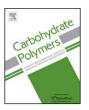
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Characterization of α -tocopherol as interacting agent in polyvinyl alcohol–starch blends



Lee Tin Sin^{a,*}, Soo-Tueen Bee^a, Tiam-Ting Tee^a, A.A.H. Kadhum^b, Chi Ma^c, A.R. Rahmat^d, P. Veerasamy^a

- ^a Department of Chemical Engineering, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Jalan Genting Kelang, 53300 Setapak, Kuala Lumpur, Malaysia
- ^b Department of Chemical Engineering, Faculty of Engineering and Built Environment, National University of Malaysia, 43600 UKM Bangi, Selangor, Malaysia
- ^c Research Institute of Polymer Materials, Shenyang University of Chemical Technology, Shenyang Economical and Technological Development Zone, Street No.11, Shenyang 110142, China
- d Department of Polymer Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

ARTICLE INFO

Article history: Received 6 November 2012 Received in revised form 14 July 2013 Accepted 23 July 2013 Available online 7 August 2013

Keywords: α-Tocopherol Starch Polyvinyl alcohol

ABSTRACT

In this study, the interactions of α -tocopherol (α -TOH) in PVOH–starch blends were investigated. α -TOH is an interacting agent possesses a unique molecule of polar chroman "head" and non-polar phytyl "tail" which can improve surface interaction of PVOH and starch. It showed favorable results when blending PVOH–starch with α -TOH, where the highest tensile strengths were achieved at 60 wt.% PVOH–starch blend for 1 phr α -TOH and 50 wt.% for 3 phr α -TOH, respectively. This due to the formation of miscible PVOH–starch as resulted by the compatibilizing effect of α -TOH. Moreover, the enthalpy of melting ($\Delta H_{\rm m}$) of 60 wt.% PVOH–starch and 50 wt.% PVOH–starch added with 1 and 3 phr α -TOH respectively were higher than $\Delta H_{\rm m}$ of the neat PVOH–starch blends. The thermogravimetry analysis also showed that α -TOH can be used as thermal stabilizer to reduce weight losses at elevated temperature. The surface morphologies of the compatible blends formed large portion of continuous phase where the starch granules interacted well with α -TOH by acting as compatilizer to reduce surface energy of starch for embedment into PVOH matrix

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1. Introduction

 α -Tocopherol (α -TOH) is a natural biological antioxidant which is widely used as the anti-aging agent to protect cells from damaging as caused by free radicals actions (Frank, 2005; Yoshida, Niki, & Noguchi, 2003). The α -TOH compound can inhibit the hydroper-oxide formation which attack the backbone of the macromolecule backbones leading to chain reaction that cause severe degradation of the entire composition (Lerf, Zurbrügg, & Delfosse, 2010). Generally degradation of polymers can be divided into three phases: (I) initiation, (II) propagation and (III) termination. The addition of α -TOH tends to avoid the reaction to pursue from initiation to propagation phases by scavenging the free radicals via the inhibition scheme (IV) (Burton & Traber, 1990).

(I) Initiation: Production of R• (carbon-centered radical)

(II) Propagation: $R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ (fast)

 $ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \text{ (H atom abstraction)}$ (III) Termination: $ROO^{\bullet} + ROO^{\bullet} \rightarrow \text{inactive products}$

(IV) Inhibition: α -TOH + ROO• $\rightarrow \alpha$ -TO• + ROOH

 α -TO• (α -tocopherol

radical) + ROO $^{\bullet}$ \rightarrow inactive products.

Previous researches (Lerf et al., 2010; Oral, Rowell, Micheli, Lozynsky, & Muratoglu, 2010) have employed α -TOH as the stabilizer in radiation crosslinked ultra-high-molecular-weight polyethylene (UHMWPE) compound. Lerf et al. (2010) reported a when α -TOH was applied at the concentration as low as 0.05%, it was able to effectively protect highly cross-linked UHMWPE against oxidation when expose to direct oxygen. In addition, α -TOH was also able to prolong initial stability against a supplementary attack by hydrogen peroxide and reactive radicals (Lerf et al., 2010). On the other hand, Oral et al. (2010) found that the addition of α -TOH induced high crosslink density on the surface of UHMWPE. The stabilized UHMWPE possesses superior wear resistance and improved fatigue strength. This is favorable especially

^{*} Corresponding author. Tel.: +60 3 4107 9802; fax: +60 3 4107 9803. E-mail addresses: leets@utar.edu.my, direct.tinsin@gmail.com (L.T. Sin).

Fig. 1. Stereochemistry structure of α -tocopherol with polar "head" and non-polar "tail".

for the application of UHMWPE in body implants for reducing the incidences of fracture when subjected to high stresses.

Since decade, many studies have been conducted on the PVOH-starch blends, claiming that the respective blends have the potential to be used as biodegradable plastic materials (Rahmat, Rahman, Sin, & Yussuf, 2009; Russo et al., 2009; Tang & Alavi, 2011). Although the blending of PVOH and starch is favorable to yield higher strength products at reasonable cost, practically mass production of PVOH-starch has found its difficulty due to experience severe thermal degradation when processed at the molten temperature (Rahman, Sin, Rahmat & Samad, 2010). The highly reactive hydroxyl (-OH) functional groups tend to generate hydroxyperoxide radical when heating, leading to self hydrolysis reaction as well as attacking the backbone causes chain cleavages. This can be observed when PVOH-starch melt-processed at temperature above 190 °C was yellowish sighted indicating severe degradation has occurred (Sin, Rahman, Rahmat, & Mokhtar, 2011). Commonly, plenty of high polarity oxo-type plasticizers such as glycerol, propylene glycol, polyethylene glycol, sorbitol and etc. are added to reduce the melt temperature while improving the flowability of PVOH-starch in molten state. Nonetheless, substantial addition of high polarity plasticizer can cause inferiority to the properties as well as plasticizer migration problem.

Basically, α -TOH molecular structure as shown in Fig. 1 is consisted of two different parts, the chroman "Head" and phytyl "Tail" as stated by Burton and Traber (1990). The head is polar with the presence of hydroxyl (-OH) and alkoxy (R-O-R) functional groups. The phenyl ring in the head plays important role in stabilizing free radical excess electrons. Meanwhile, the tail section is built up of hydrocarbon which is non-polar and hydrophobic. Such characteristic is favorable to provide necessary attachment to the polymer chains for the non-polar tail section, whereas the polar head can interact with hydrophilic filler like starch which results good interfacial adhesion of different phases. Hence, when α -TOH is added to the PVOH-starch, it is expected that α -TOH can provide addition protective layer through the interaction of backbone structure upon the occurrence of dehydration process via the tail section. Subsequently, PVOH-starch blend can sustain elevate thermal attack from rapid damage while also providing the plasticizing effect to improve the flexibility and flowability of the PVOH-starch blends.

2. Methodology

2.1. Materials

Fully hydrolysed polyvinyl alcohol Denka POVAL grade K-17C with viscosity of 24–30 mPa s, hydroysis 98.7–99.7 mol% and ash less than 0.7% manufactured by Denki Kagaku Kougyo Kabushiki Kaisya (DENKA), Japan was used in this study. Native *cassava* starch was obtained from Thailand- Cap Kapal ABC. α -tocopherol was obtained from Sigma–Aldrich, Malaysia at 99.5% purity. All these materials were used as received.

Table 1 Composition of PVOH–starch blends in preparation of cast films using 0, 1 and 3 phr of α -TOH.

Sample	PVOH:starch (wt.%)	α -TOH (phr)
PV	100	0
PVT-91	90:10	0
PVT-82	80:20	0
PVT-73	70:30	0
PVT-64	60:50	0
PVT-55	50:50	0
PV-1	100	1
PVT-91-1	90:10	1
PVT-82-1	80:20	1
PVT-73-1	70:30	1
PVT-64-1	60:50	1
PVT-55-1	50:50	1
PV-3	100	3
PVT-91-3	90:10	3
PVT-82-3	80:20	3
PVT-73-3	70:30	3
PVT-64-3	60:50	3
PVT-55-3	50:50	3

2.2. Sample preparation

The solution cast samples of PVOH–starch– α -TOH was prepared according to Table 1. Samples were prepared by dissolving PVOH and starch (total materials weight of 10 g) in 300 ml of distilled water and heated in a water bath at $97\pm2\,^{\circ}\text{C}$ for 30 min until all particles dissolved. A motor driven stirrer was set at 800 rpm to help the mixture to fully dissolve and gelatinize. After that, 100 ml of distilled water was added to refill the vaporized water during the first heating and this mixture was heated at $97\pm2\,^{\circ}\text{C}$ for 30 min again. Finally, α -TOH was added for stirring of 5 min before removing from the water bath. The mixtures were cast with similar weights of 30 g on Petri dishes and were further dried in an oven at 65 $^{\circ}\text{C}$ to achieve constant weight by obtaining film thickness of 25 μ m. The samples were then immediately sealed in a polyethylene bags and stored under room temperature 25 $^{\circ}\text{C}$ at 65% relative humidity for conditioning purpose.

2.3. Samples characterizations

2.3.1. Tensile test

Tensile test was performed according to ASTM D882 standard. The samples were cut in the form of standard rectangular-shaped. The specimen was placed in the grips of the Instron 5848 Microtester with the crosshead speed of 50 mm/min. An average of five samples was tested for each formulation and the results were averaged to obtain mean value and standard deviation.

2.3.2. Thermal analysis

Thermal analysis was conducted using Mettler Toledo DSC823 Differential Scanning Calorimeter. Samples were weighted into standard aluminum pans. A sealed empty pan was used as reference while nitrogen gas was purged at $20\,\mathrm{ml/min}$ during experiments. Initially, each sample was heated to $50\,^\circ\mathrm{C}$ and scanning was carried out with temperature ranging from 50 to $250\,^\circ\mathrm{C}$ at $10\,^\circ\mathrm{C/min}$. An average of five samples was tested for each formulation and the results were averaged to obtain mean value and standard deviation. On the other hand, the thermogravimetric analysis was conducted using Mettler Toledo TGA SDTA851e with the scanning rate $10\,^\circ\mathrm{C/min}$ under nitrogen gas purging condition.

2.3.3. Scanning electron microscopy (SEM) analysis

The morphologies of the fracture surface for all samples from tensile test were observed using JEOL model JSM-6301F Scanning Electron Microscope (SEM). The fractured surfaces of the samples

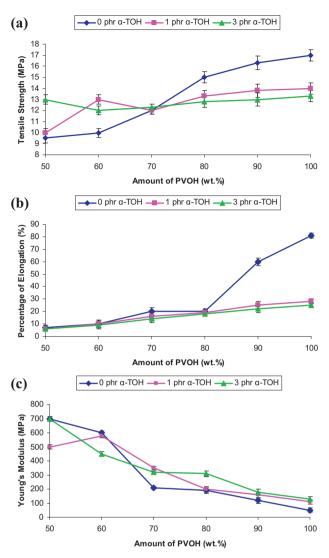


Fig. 2. Mechanical properties of PVOH–starch added with α -TOH. (a) Tensile strength. (b) Percentage of elongation. (c) Young's modulus.

were cut into a smaller portion prior conducting the scan. The cut samples were placed and mounted onto the copper stub with the fractured surface was facing up. These samples were coated with a thin layer of gold and ready for scanning. The samples were scanned under the magnification of $3000\times$ with the electron beam voltage of $15\,\text{kV}$.

3. Results and discussion

3.1. Tensile properties

Fig. 2(a) shows the tensile strength of the PVOH–starch for different composition of α -TOH. First of all, it can be noticed that the amount of starch has significantly reduced tensile strength of the blends. Although the interaction of PVOH and starch is favorable via hydrogen bonds, the lack of irregularity structure leads to low compaction of the polymer chains arrangement (Sin, Rahman, Rahmat, & Khan, 2010; Sin, Rahman, Rahmat, & Samad, 2010). The absence of crystallinity is the main factor that causes the loss of tensile strength of starch added PVOH blend. On the other hand, it can found that the addition of α -TOH has deteriorated the tensile strength of the neat PVOH. This can be explained that α -TOH is an oily compound which behaves as a lubricant in the PVOH structure

to promote chain sliding when extension. The typical addition of 1 phr of α -TOH has caused a dramatically decline of tensile for 100% PVOH from 17.1 MPa to 14.2 MPa. However, further increment of the α -TOH to 3 phr has shown small quantum of reduction. This indicated when α -TOH was applied at small amount, the α -TOH can penetrate into the PVOH structure to induce lubricating effect. When the amount of α -TOH has reached 3 phr, a saturation level can be observed with pronounce formation of larger phase droplet in the blending morphology. Such observation is further discussed in detail in the SEM section of this paper.

It can be observed that the incorporation of starch in PVOH- α -TOH blends possesses the similar declining trends of tensile strength up to the level of 60-70 wt.% of starch. Meanwhile, the presence of the maximum point for the blends with α -TOH is noticeable, where the highest tensile strengths were achieved at 60 wt.% PVOH–starch blend for 1 phr α -TOH and 50 wt.% for 3 phr α -TOH, respectively. This can be explained through the phenomenon known as favorable miscible blends. When good miscible stage of the two different polymers have achieved, the loss of free volume will occur corresponding to a negative volume change of mixing due to favorable interactions between polymers blends (Fried, 2003). In other words, the polymer chains of the PVOH and starch can be arranged in ordered manner with higher crystallinity which leads to difficulty in chain sliding. Such interaction was not found when comparing to the PVOH-starch blends without the addition of α -TOH, which exhibited addition of starch causing inferiority. Moreover, it can be noticed that the amount of α -TOH added has direct related to the amount of starch incorporated into PVOH, where certain amount of α -TOH can induce positive effect to the PVOH-starch. For instance, such condition can be noticed where the maximum tensile strength has shifted to 50 wt.% PVOH when the amount of α -TOH has increased to 3 phr. This is because predominant amount of starch has caused the irregularity structure where the cyclic form of D-glucose unit has dense polar structure to interact mutually well with PVOH. The addition of α -TOH with the unique polarity of "head" structure can harmonize the cyclic structure as well as the linear "tail" proceed to interact with PVOH chains. Hence, α-TOH added PVOH-starch blend can interact in a favorable manner which enables consistent load distribution when subjected to extension.

Further investigation on the percentage of elongation of α -TOH added PVOH-starch blends as shown in Fig. 2(b) observed that the elongation of the PVOH has dropped drastically with the addition of starch. This is mainly contributed by the irregularity structure restrict the chain movement. However, it was noticed that the addition of α -TOH caused the reduction of the percentage of elongation to take place in a harmonize manner. This indicates that the favorable lubrication interaction presents among the three components, i.e. PVOH, starch and α -TOH. Such opinion can be justified by examining the PVOH at range 50-60 wt.% showed the addition of α -TOH at 1 and 3 phr have equal percentage of elongation compared to PVOH-starch without addition of α -TOH. This is unlike to the addition of α-TOH into PVOH-starch blends at range 80-100 wt.% exhibited significant declined for the percentage of elongation. At high amount of PVOH, the α -TOH would become incompatible with PVOH-starch blends system, because the linear hydrophilic structure of PVOH cannot interact with the polar "head" of the α -TOH. But, as the composition of PVOH has reduced, α -TOH acts as compatilizer medium to enhance the interfacial adhesion of PVOH–starch blends. It can be assumed that α -TOH has the cyclic "head" structure can interact effectively with the cyclic helix of D-glucose which built up the starch macromolecules. Hence, such interactive bond works well among polymer blends components up to the level when substantial molecular separation occurs leading to breakage and failure of the polymer structure. Further investigation on the Young's modulus of the samples (Fig. 3(c)) has also

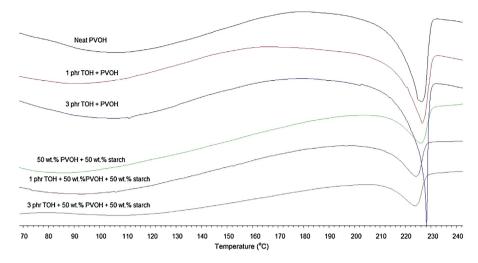


Fig. 3. DSC thermograms of α -TOH added PVOH–starch blends.

found the maximum point occurs at 60 and 80 wt.% PVOH for 1 phr α -TOH and 3 phr α -TOH, respectively, whereas the modulus of the sample decreases in relation to the starch composition when α -TOH was absence. This is because the addition of irregular structure of starch with PVOH restricted the polymeric chains movement, subsequently lead to higher rigidity, whereby the maximum modulus might be due to the synergistic interaction found in this ternary blending system. Besides, it can also be observed when the PVOH composition has reached >70 wt.%, the PVOH–starch with addition of α -TOH has modulus higher than the neat PVOH–starch compound. This can be assumed that α -TOH has interacted in the PVOH–starch system by formation a secondary bonding which limits deformation.

3.2. Thermal analysis

The differential scanning calorimetry thermograms of the selected samples are shown in Fig. 3. It can be observed that the incorporation of starch and α -TOH has influenced the thermal behavior of PVOH. The broad peak of thermogram exhibits presence range of molecular interaction within the blending system. It can be noticed that the neat PVOH peak is broad and moderately sharp; whereas the addition of α -TOH in PVOH has caused the melting peak to become narrower and sharper. This indicates that α -TOH has affected the molecular arrangement of PVOH. The shaper and narrower peaks of the samples exhibit the addition of α -TOH has actually diminished the arrangement of the low molecular weight compound, where α -TOH can diffuse and reduce the structural rigidity for the shorter chains of PVOH. However, the longer chain PVOH tends to possess superior interaction as a result of entanglement as well as hydrogen bonding interactions which limit the substantial penetration of α -TOH. Hence, the melting peak has shifted to higher temperature showing that the enthalpy of melting is mainly contributed by the high molecular weight PVOH. Besides that, this can also be explained via miscibility perspective that α -TOH possesses the non-polar tail which is partially miscible with PVOH. As the result, the addition of α -TOH has weakened the interaction with a narrower peak indicates limited interaction. On the other hand, the addition of starch in PVOH has caused a significant reduction of the melting temperature peaks. Inasmuch as incorporation of starch with large irregularity molecules has affected the arrangement in the blending system thus leading to low crystallinity with shorter peak (Sin, Rahman, Rahmat, & Khan, 2010). Further of comparison of thermograms for 50 wt.% PVOH-starch blends also found that the broadness of the peaks are

identical while the peak temperature shifts lower after adding α-TOH. This evidences that α -TOH did not weaken the interaction of the PVOH-starch but tends to act as a lubricant which reduces the rigidity of the structure. In other words, a lower temperature is required to induce internal molecular kinetic energy to overcome the rigid solid state for transforming into molten condition. Hence, the melting peak of the PVOH-starch system with higher amount of α -TOH is lower compared to binary PVOH-starch blend. This can be further analyzed by referring to Table 2 where the average peak melting temperatures for samples with starch composition >30 wt.% are decreasing with higher amount of α -TOH. The analysis of relationship between average peak melting temperature and interaction is reasonable because the higher melting temperature always indicates extra kinetic energy is required to overcome the strong interaction among the polymer molecules to reach the melting state.

Moreover, enthalpy of melting ($\Delta H_{\rm m}$) of the sample as summarized in Fig. 3 can observe an identical trend with the tensile test as discussed early. The enthalpy of melting for the PVOH has reduced in relation to the amount of starch. Most of the time, the enthalpy of melting can be related to the crystallinity of the polymers. In this context, the addition of starch has reduced the crystallinity of the PVOH as caused by the irregular and amorphous structure. In addition, enthalpy of melting analysis also provides complementary information about the physical bonding of polymers blends (Sin, Rahman, Rahmat, & Khan, 2010a) such as hydrogen bonds, van der Waals or crystallization. Hence, based on the $\Delta H_{\rm m}$ of 100 wt.% PVOH, it is possible to conclude using following understanding:

(a) When experimental $\Delta H_{\rm m}$ is larger than theoretical $\Delta H_{\rm mi}$, it means that there are somewhat extra physical bonding formation between PVOH and starch. The particular amount of α -TOH

Table 2 Average peak melting temperature of $\alpha\mbox{-}TOH$ added PVOH starch blends.

PVOH:Starch (wt.%)	Average peak melting temperature (°C)		
	0 phr α-TOH	1 phr α-TOH	3 phr α-TOH
100:0	225.3 (0.14)	225.7 (0.12)	227.5 (0.12)
90:10	225.3 (0.13)	225.2 (0.14)	226.9 (0.12)
80:20	224.8 (0.13)	224.3 (0.12)	225.3 (0.13)
70:30	224.5 (0.11)	224.2 (0.11)	223.1 (0.08)
60:40	224.3 (0.13)	223.7 (0.09)	223.3 (0.11)
50:50	223.8 (0.13)	223.2 (0.12)	222.1 (0.11)
0:100	No detection	No detection	No detection

Parentheses values representing standard deviation.

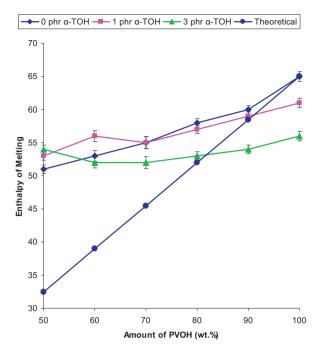


Fig. 4. Comparison of experimental enthalpy of melting ($\Delta H_{\rm m}$) of α-TOH added PVOH starch blends with theoretical values ($\Delta H_{\rm mi}$).

has not weakened the interactions between PVOH and starch. The blending interaction is strong.

(b) When experimental $\Delta H_{\rm m}$ is lower than theoretical $\Delta H_{\rm mi}$, it means that addition of α -TOH has weakened physical bonding between PVOH and starch. The blending interaction is weak.

The results of $\Delta H_{\rm m}$ and $\Delta H_{\rm mi}$ are plotted in Fig. 4. $\Delta H_{\rm mi}$ was calculated based on the $\Delta H_{\rm m}$ of 100 wt.% PVOH and multiplied with the percentage of PVOH for each sample. For example, 20 wt.% PVOH-starch contains 20 wt.% of PVOH and 80 wt.% starch, thus the ΔH_{mi} , 20 wt.% PVOH-starch = 0.2 ΔH_{m} , 100 wt.% PVOH. Since melting state of the starch was not detected and contributed individually to $\Delta H_{\rm m}$, thus starch was assumed not to influence intramolecularly (among starch molecules) but intermolecularly (between PVOH and starch molecules) toward $\Delta H_{\rm m}$. Basically, the theoretical $\Delta H_{\rm mi}$ increases proportional to percentage of PVOH in the blends. However, the experimental $\Delta H_{\rm m}$ have deviated out of expectation. The PVOH-starch without addition of $\alpha\text{-TOH}$ always possesses the experimental $\Delta H_{\rm m}$ higher than $\Delta H_{\rm mi}$ indicates that PVOH and starch pursue favorable strong intermolecular interaction. Although the different structural has influenced the packing arrangement of the blending system, but the formation of hydrogen bonding has induced superior interactions of both polar components of PVOH and starch. On the other hand, the incorporation of α -TOH in PVOH has shown inferiority which was due to incompatibility of the α -TOH and PVOH. The incompatibility is mainly due to the different solubility of α -TOH in PVOH leading to phase separation as shown in scanning electron microscopy section later. Nevertheless, The $\Delta H_{\rm m}$ of 60 wt.% PVOH-starch and 50 wt.% PVOH-starch added with 1 phr and 3 phr α-TOH respectively is higher than ΔH_m of the PVOH-starch blends alone. This is because α -TOH has interacted well with starch through favorable compatibilization effects that improves the molecular linkage.

Further analysis of thermal stability effect of α -TOH on PVOH–starch blends via thermogravimetry analysis exhibited promising outcomes. According to Fig. 5, when neat PVOH were heated at elevated temperature, it was susceptible to the highest

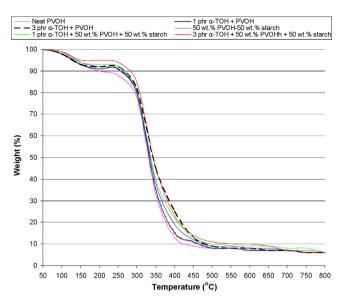


Fig. 5. Thermogravimetry analysis of α -TOH added PVOH–starch blends.

weight loss among the samples. However, the PVOH become more resistible to thermal attack with lower weight losses when α -TOH was added at 1 and 3 phr. This showed that α -TOH has inhibited the formation of radicals from propagation to attack the polymer backbone. On the other hand, it was found that the addition of starch has improved resistivity of PVOH from thermal attacks as well. This is agreed with the previous work as conducted by Sin et al. (2011) that the presence of cyclic hemiacetal structure in starch is sustainable to thermal attacks. Besides, the addition of α -TOH has further improved the thermal resistance of the PVOH-starch blends, where the 3 phr α -TOH added 50 wt.% PVOH–50 wt.% starch compound has the lowest weight loss among the samples. When comparison were done with previous work (Sin et al., 2011), the thermogravimetry weight at 200 °C of 50 wt.% PVOH-50 wt.% starch compound was about 90%, whereas the samples of this work with the addition of 1 and 3 phr α -TOH have the thermogravimetry weight of 93.2 and 95.1%, respectively. Again, this indicates that α -TOH possesses functionality as thermal stabilizer in PVOH-starch

3.3. Scanning electron microscopy (SEM)

Fig. 6 shows the selected morphology of the α -TOH added PVOH-starch blends. Initially, the 100 wt.% PVOH presents smooth and single phase morphology. When starch is added into PVOH, it shows the starch agglomeration has taken place as resulted by the irregular structure of starch. The starch granules as shown by the white spots are distributed all over the PVOH matrix. Since the starch granules are obviously visible, this indicates incompatibility of starch and PVOH. Indeed, this is the main factor that contributes to the inferior effect on the mechanical properties. On the other hand, the addition of α -TOH also showed obvious droplet like spot on the PVOH matrix. The different polarity of α -TOH and PVOH has caused the phase separation. Such phase separation is favorable to induce lubrication effect for polymer flexibility. However, when α -TOH are added into PVOH-starch blends, it can be seen compatibilizing effect occur in between both components. This is obviously found for the 60 wt.% PVOH-starch blend with 1 phr α -TOH and 50 wt.% PVOH-starch with 3 phr α -TOH, where the morphologies of these blends behave in a smoother and consistent manners. The surface morphologies of the compatible blends have large portion of continuous phase where the starch granules

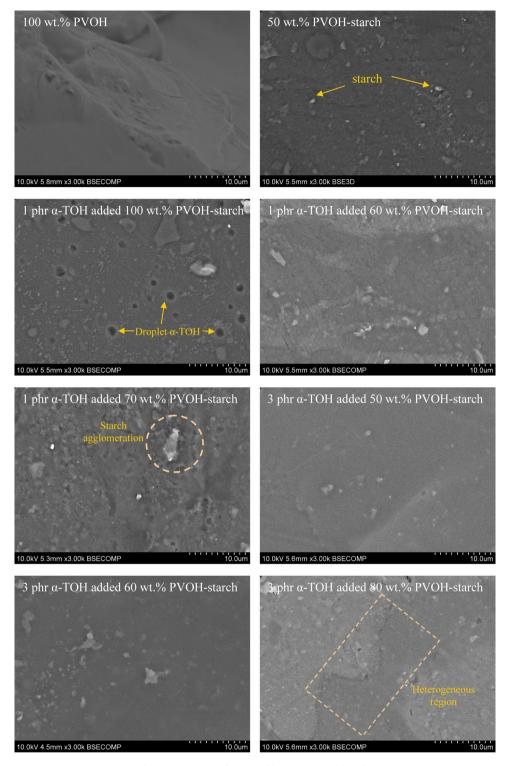


Fig. 6. SEM images of $\alpha\text{-TOH}$ added PVOH–starch blends.

have interacted well due to α -TOH acts as compatilizer in order to reduce surface energy of starch to embed into PVOH matrix. Subsequently, the strong binding energy compatilized PVOH and starch would enhance mechanical properties as indicated by higher tensile strength (Sin, Rahman, Rahmat, & Samad, 2010b). Nevertheless, this condition is limited to selected composition as stated above. Upon deviation from the optimum state, the significant phase separation can be observed with rougher surface. This can be

explained by referring to the image of 1 phr $\alpha\text{-}TOH$ added 70 wt.% PVOH–starch when the starch granules gradually agglomerate due to insufficient $\alpha\text{-}TOH$ to homogenize with PVOH matrix. In opposite when incorporating excess amount of $\alpha\text{-}TOH$, the starch tends to interact with $\alpha\text{-}TOH$ to form a heterogeneous region with the PVOH matrix as shown in the image of 3 phr $\alpha\text{-}TOH$ added 80 wt.% PVOH–starch blends. This is mainly due to the incompatibility of $\alpha\text{-}TOH$ with PVOH which enable $\alpha\text{-}TOH$ alternatively to dissolve

starch and subsequently form a separation region, resulting the blends possess weaker in mechanical properties.

4. Conclusions

The addition of α -TOH with PVOH is incompatible which causes inferior effect to the mechanical properties, where the tensile strength has reduced from 17.1 MPa to 14.2 MPa after addition of 1 phr α -TOH. Nevertheless, it has shown favorable results when blending PVOH-starch with α -TOH, where the highest tensile strengths were achieved at 60 wt.% PVOH-starch blend for 1 phr α -TOH and 50 wt.% for 3 phr α -TOH, respectively. This can be explained through the phenomenon known as favorable miscible blends. The addition of α -TOH with the unique polarity of "head" structure can harmonize the cyclic structure as well as the linear "tail" proceeds to interact with PVOH chains. Hence, α -TOH added PVOH-starch blend can interact in a favorable manner which enables consistent load distribution when subjected to external drawing. Besides that, the $\Delta H_{\rm m}$ of 60 wt.% PVOH–starch and 50 wt.% PVOH-starch added with 1 phr and 3 phr α -TOH respectively was higher than $\Delta H_{\rm m}$ of the mere PVOH-starch blends. This is because α -TOH has interacted well with starch through favorable compatilizing effects that improves the molecular linkage. Thermogravimetry analysis PVOH-starch blend also showed that α -TOH can act as the thermal stabilizer to reduce the weight loss at elevated temperature. When α -TOH are added into PVOH-starch blends, it can be seen a compatibilizing effect occur in between both components. This can be obviously found for the 60 wt.% PVOH-starch blend with 1 phr α -TOH and 50 wt.% PVOH-starch with 3 phr α -TOH, where the SEM morphologies of these blends behave in a smoother and consistent manners. The surface morphologies of the compatible blends have large portion of continuous phase where the starch granules have interacted well with α -TOH acts as compatilizer to reduce surface energy of starch to embed into PVOH matrix. In conclusion, α -TOH possesses triple functionalities as plasticizer, compatilizer and thermal stabilizer in PVOH-starch blends.

Acknowledgements

Special thanks to Nigel Foong from Universiti Tunku Abdul Rahman, Kampar Campus on assisting the DSC and thermogravimetry analyses.

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