International Journal of Engineering & Technology, *7 (4.42) (2018) 81-83*

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Thermal Properties and Moisture Content Analysis of Starch Fiber Filled Polyvinyl Alcohol-Polyvinyl Acetate (Pva-Pvac) Biofilm

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Abstract

This study aimed to determine the effect of starch fiber onto thermal properties of Polyvinyl Alcohol (PVA)-Polyvinyl Acetate (PVAc) blends. Starch fiber was used in this study as the reinforced filler. The starch fiber (SF) was prepared by extracting the potato's peels. Prior to the preparation of biofilms, the PVA and PVAc were plasticized using glycerol and distilled water. The biofilm of SF-PVA-PVAc were produced using casting technique. A thermal analysis was conducted on the biofilms to investigate the thermal stability of the sample using Thermogravimetric Analysis (TGA). Besides the moisture content of the derive biofilm was also studied. It was found that biofilm with higher composition of SF (50wt%) noted the highest degradation temperature (Tdg) at 297°C. Conversely, biofilm with highest composition of SF recorded the lowest moisture content. This may be attributed to the content of fiber which predominated the matrix of biofilm.

Keywords: *Fiber, Polyvinyl Acetate, Polyvinyl Alcohol*

1. Introduction

Over the past century, considerable research has been conducted to develop and apply bio-based polymers made from a variety of agricultural commodities and/or of food waste products [1-3]. Biocomposites (biodegradable composites) consist of biodegradable polymers as the matrix material and biodegradable fillers, usually bio-fibers. Since both components are biodegradable, the composite as an integral part is also expected to be biodegradable [4]. Another important bio-composite category is based on agro polymers matrixes, mainly focused on starchy materials. Plasticized starch, called thermoplastic starch (TPS) is obtained after disruption and plasticization of native starch, with water and plasticizer by applying thermo-mechanical energy in a continuous extrusion process [5].

Unfortunately, TPS shows some drawbacks such as a strong hydrophilic character, rather poor mechanical properties compared to conventional polymers and an important post-processing variation of the properties of the produced biofilm [6]. On the other hand, the starch fiber is the fiber crops that contains starch and fiber in the same compound. Fiber crops have existed in human society since the beginning of time. History shows that humans collected raw materials from the wild to use as ropes or textiles [7]. Moreover, it also acts as a good reinforcing filler in the matrix blends of biocomposites. Among the biopolymer matrices being utilized to produce bioplastics, starch fiber (SF) is considered the most widely used material. Starch-based plastics have been projected to comprise the largest production capacity amounting to 1.3 metric tonne in 2020 while the remaining production is based on polylactic acid (PLA), polyhydroxyalkanoates (PHA), bio-based polyethylene, and others [8].

Starch content in starch fiber (SF) is a carbohydrate, which is naturally digested by organisms. When the starch fiber-based plastic is composed in soil, fungi will growth and digest the starch fraction. This will weaken the polymer matrix and increases the surface volume ratio, hydrophilic and permeability to further undergo synergistic natural degradation such as hydrolysis and catalysis [9].

To date, many biodegradable polymers have been introduced since the 1980s [10]. The presence of fiber in starch fiber (SF) and PVA-PVAc blends improves the stiffness and strength of the produced composite [11]. Composite PVA-PVAc and starch/starch fiber was reported to produce a material having excellent mechanical properties and barrier behavior [12].

There is evidence that Polyvinyl alcohol (PVA) is regarded as the synthetic water-soluble polymer. Several hundred kton/yr of PVA was produced all over the world making it the largest synthetic biodegradable polymer ever produced each year [13]. PVA is also derived through the hydrolysis of polyvinyl acetate. PVA and PVAc were chosen as matrix because both PVA and PVAc are polar polymer with limited hydrophilicity. Its hydrophilicity can be placed in between the hydrophilic starch and fiber [14]. It is anticipated that strong interaction may form between hydroxyl rich groups which will be reflected to the strong hydrogen bond [14]. This will strengthen the interface of the biofilm matrix.

PVA and PVAc have an excellent chemical, mechanical and physical properties mainly as a solution in water [15]. On the other hand, PVA and PVAc also having a major drawback since PVA has a compact crystallinity structure making it unstable in its native form [15]. Therefore, the composite of PVA and PVAc are unable to be processed at higher temperature. The incorporation of SF into PVA-PVAc blends is a crucial step. Prior to blending process, it is necessary for PVA and PVAc to be plasticized with the plasticizer, so that PVA and PVAc can be safely processed without traceable brownish colour of the processed compound. Plasticizers are one of the additives that was tremendously used to improve the processability of the polymers.

This article aims at investigating the effect of fiber content in PVA-PVAc biofilm. The results were used to analyze the thermal properties of the formulated biofilm which later processed via thermoplastic processing equipment.

2. Experimental design

2.1. Materials

PVA fully hydrolyzed grade and PVAc were used as the synthetic biodegradable polymer. Starch Fiber (SF) was extracted from potato's peel. The moisture content of SF is in the range of 11.5% by drying the SF for 8 hours at 70^{o}C. Glycerol (glycerin, C3H8O3) from Fisher Chemicals (molecular weight = 92gmol-1) was used as a plasticizer.

2.2. Blend preparations

Prior to blending preparation, PVA, PVAc, Glycerol and distilled water were mixed together to produce plasticized PVA-PVAc using melt mixing method. The plasticized PVA-PVAc, then was added to SF, glycerol, and distilled water in melt mixing equipment for 30 minutes. The blend was consistently stirred at 1000 rpm. Then, it was preceded until a viscous homogeneous paste was formed. The paste was immediately casted onto the designated mold. The casted blend was dried at 95^{o}C for 3 hours. Table 1 shows the composition of the prepared biofilms. The structural integrity of the biofilm prepared deteriorated beyond the 50wt% SF biofilm (B5) resulting the fragmented surface of the biofilm. Therefore, the SF composition was capped only up to 50 wt%.

Table 1: Composition of Prepared Blends

Sample (SF-PVA-PVAC)	SF (wt%)	PVA (wt%)	PVAc (wt%)	Glycerol (phr)	Distilled Water (phr)
Biofilm 10 (B1)	10	45	45	20	60
Biofilm 20 (B2)	20	40	40	20	60
Biofilm 30 (B3)	30	35	35	20	60
Biofilm 40 (B4)	40	30	30	20	60
Biofilm 50 (B5)	50	25	25	20	60

2.3. Moisture Content Analysis

Moisture content analysis was determined by using Moisture Content Analyzer MAX (RADWAG, Poland). This equipment analyzes the moisture content based on evaporation method. These methods rely on measuring the mass of water in a known mass of sample. The moisture content is determined by measuring the mass of a sample before and after the water is removed by evaporation: Mass was used as the subject to show how much the moisture content in the sample. Initial mass for all samples was equally same as much asset at 0.5 g. The moisture content determined by using the equation as below:

$$\text{moisture content\%} = \frac{(m_{\circ} - m)}{m_{\circ}} \times 100$$

Where, $m_{\circ}$= initial mass (g), m = final mass (g)

2.4. Thermogravimetric analysis

Thermal analysis of the PVA-PVAc-SF blends was carried out using TGA-DSC (Netzsch Jupiter STA 449 F3 Simultaneous Thermal Analyzer). Thermogravimetric analysis (TGA) was used to determine thermal stability of the material and its fraction of volatile components by monitoring the weight change that occurs as the specimen was heated. The weight was recorded as a function of increasing temperature. The measurement was performed in a lean oxygen atmosphere (1 to 5% O2 in N2 or He) to slow down the oxidation. In most cases, TGA analysis was performed in an oxidative atmosphere (air or oxygen and inert gas mixtures) with a linear temperature ramp. The maximum temperature was selected so that the specimen weight was stable at the end of the experiment, implying that all chemical reactions was completed (i.e., all of the carbon is burnt off leaving behind metal oxides) complete run. This approach provides two information of: ash content (residual mass, M) and oxidation temperature (To). The TGA was carried out from 300C to 6000C at a heating rate of 2000C/min under a nitrogen atmosphere. The weighted of the sample was 10 to 15 mg.

3. Results and discussion

Thermal analyses of Polyvinyl alcohol-Polyvinyl acetate-starch fiber (PVA-PVAc-SF) blends at different SF composition was summarized in Table 2. The tabulated data from Table 2 recorded the highest onset degradation temperature (Tdg) in formulation B5. It was also found that the Tdg shifted to a higher temperature with the addition of SF. This trend was due to the matrix of SF component which consist of cyclic hemiacetal. The stability and packed structure of the cyclic hemiacetal in SF was contributed in five-or-six-member rings in their structure [16]. A dense close cluster from cyclic form of D-glucose unit arrangement provide the shielding effect and thus higher energy is required to break the bonding [17]. Conversely, the composition of carbonaceous and char residue for B2 and B3 were higher than B5. B4 formulation showed the lowest carbonaceous and char residue content. These results due to the facts that the SF incorporated into the PVA-PVAc matrix packed homogenously making degradation of the biofilm difficult [18]. Also, the degradation profile of B5 biofilm exhibited nearly 27% weight loss at 297^{o}C. In this formulation the SF predominate the matrix of the biofilm which led to the degradation of amylose present in the starch [19].

The thermogram curves for sample B1 until B5 were shown in the Figure 1. As shown in Figure 1, the same degradation trends were displayed for all biofilm at different composition of SF. The thermogram indicated that three steps decomposition occurred. The three steps are step 1- below 200^{o}C, step 2- 250 to 300^{o}C, and step 3- above 400^{o}C. An early decomposition was observed to occur at step 1 and it represents the water and volatile material in blends was degraded as shown in Figure 1.

The extent of volatiles released (including moisture) was determined by the physical interactions of blending components. In the case with the addition of glycerol into PVA and PVAc, it could lower the boiling point of glycerol. Pure glycerol has boiling point of 290^{o}C, yet in this case, PVA has disrupted the genuine bonding among glycerol molecules [17]. Thus, lower energy was required to vaporize glycerol. Significant decomposition occurred at step 2 and 3 approximately in between 250-400^{o}C, representing the decomposition of fiber component.

Table 2: Percent (%) weight lost at onset degradation temperature

Biofilm	Percent (%) weight lost at Onset Degradation Temperature	Onset Degradation Temperature (^{0}C)
B1	16.71	191.8
B2	38.35	293.9

B3	30.96	290.6
B4	16.62	201.0
B5	27.89	297.7

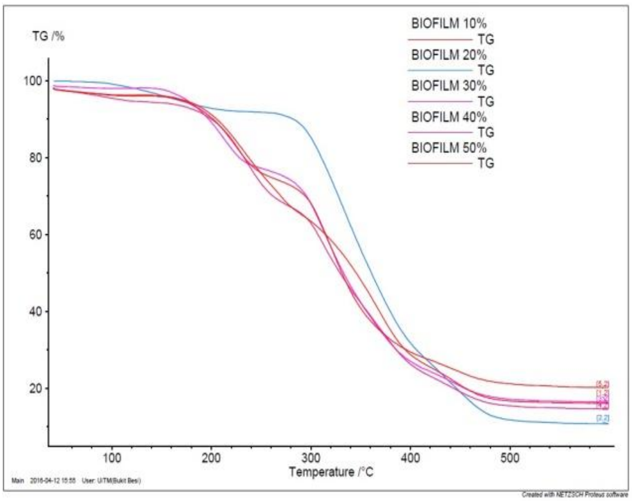

Fig. 1: TGA thermogram for SF-PVA-PVAc Biofilm

Table 3 shows the moisture content of various composition of SF filled PVA-PVAc. The formulation of B1 recorded the highest moisture content compared to the others biofilm. This is probably due to the components of biofilm such as glycerol, PVA-PVAc which soluble in water and naturally hygroscopic. Starch in the SF also contributed an additional hydrophilic group which directly influences the compound to gain more water to absorb. In spite of that, the incorporation of more SF into the biofilm was led to the predomination of fibre compound in the matrix. This situation can be justified by the lowest moisture content recorded for biofilm B5. Natural fibre is regarded as a hydrophobic material hence caused the sample to be less sensitive towards moisture [20]. This indicated, that high loading of fiber is synergistically-compatible and able to process via conventional thermoplastic processing equipment.

Table 3: Moisture Content of different composition of SF

Biofilm	**Moisture Content %**
B1	16.06
B2	14.41
B3	12.67
B4	12.59
B5	12.44

4. Conclusion

This study was conducted with the objectives focusing the thermal stability of bio-composites of starch fiber (SF) filled PVA-PVAc through TGA technique. This provides the fundamental theory of processing property and revealed the following:

It was found that the thermal stability of the SF-PVA-PVAc bio-composite was suitable to be processed via conventional thermoplastic equipment at high temperatures. The SF in the matrix provides the cyclic shape hemiacetal to overcome the thermal attacks.

The addition of SF into the bio-composites are causing the extra hydrophobic presence inside the blending system. Thus, decrease the moisture content of biofilm filled PVA-PVAc.

Acknowledgement

The authors were thankful and grateful to Research Management Centre (RMC) of Universiti Teknologi Malaysia supporting and funding this research (grant number 4J305).

References

[1] Elsabee MZ & Abdou ES (2013). Chitosan based edible films and coatings: A review, *Mater. Sci. Eng. C*, 33(4), pp.1819–1841.

[2] Souza VC & Quadri MGN (2014). Preparation and properties of cellulose nanocrystals derived from corn cobs: Application as a reinforcing material for ‘green nanocomposite’ films, *J. Biobased Mater. Bioenergy*, 8(5), pp. 495–505.

[3] Iucolano F, Caputo D, Leboffe F, & Liguori B (2015). Mechanical behavior of plaster reinforced with abaca fibers, *Constr. Build. Mater.*, 99, pp. 184–191.

[4] Nadras O, Azleen NA, Hanafi I (2011). Thermal properties of polyvinyl alcohol (PVOH)/corn starch blend film, *M. P. Journal*, 6(6), pp. 147–154.

[5] Julkapli NM & Akil HM (2010). Influence of a plasticizer on the mechanical properties of kenaf-filled chitosan bio-composites, Polym. Plast. Technol. Eng., 49(9), pp. 944–951.

[6] Woranuch S & Yoksan R (2013). Eugenol-loaded chitosan nanoparticles: II. Application in bio-based plastics for active packaging, *Carbohydr. Polym.*, 96(2) , pp. 586–592.

[7] Akil HM, Omar MF, Mazuki AAM, Safiee S, Ishak ZAM, & Bakar AA (2011). Kenaf fiber reinforced composites: A review,” Mater. Des., 32(8–9), pp. 4107–4121.

[8] Agustin MB, Ahmmad B, Alonzo SMM, & Patriana FM (2014). Bioplastic based on starch and cellulose nanocrystals from rice straw, *J. Reinf. Plast. Compos.*, 33(24), pp. 2205–2213.

[9] Van Der Zee M (2004). Biodegradability of polymers-mechanisms and evaluation method. catio bastioli., In C. Bastioli (Ed.), Handbook of Biodegradable Polymers, United Kingdom: Rapra Technology Limited, pp. 2–4.

[10] Isabelle V & Lan T (2009). Biodegradable polymers, *Materials*, 2, pp. 307-344.

[11] Yu L, Dean K, & Li L (2006). Polymer blends and composites from renewable resources, *Progress in Polymer Science*, 31(6), pp. 576–602.

[12] Siddaramaiah RB & Somashekar R (2004). Structure-property relation in polyvinyl alcohol/starch composites, *J. of Applied Polymer Science*. 91, 630-635.

[13] Lin CA & Ku TH (2008) Shear and elongational flow properties of thermoplastic polyvinyl alcohol melts with different plasticizer contents and degrees of polymerization, *J. Mater. Process. Technol.*, 200(1–3), pp. 331–338.

[14] Garcia de Rodriguez NL, Thielemans W, & Dufresne A (2006). Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites, 13(3), pp. 261–270.

[15] Shahrul M, Salleh N, Mohd N, Omar Z, & Saadon N (2015). Comparison of starch fiber filled-polyvinyl alcohol and native starch filled-polyvinyl alcohol under tensile analysis, *Adv. Mater. Res.*, 1113, pp. 19–22.

[16] Wade LG (1999). Organic chemistry, (4th ed.) New Jersey: Prentice Hall.

[17] Rahman WAWA, Sin LT, Rahmat AR, & Samad AA (2010). Rheology and thermal transition state of polyvinyl alcohol-cassava starch blends, Carbohydrate Polym., 81(4), pp. 805–810.

[18] Kargarzadeh H, Johar N, & Ahmad I. (2017). Starch biocoposite film reinforce by multiscale rice husk fiber, *Composites Science and Technology*, 151. pp. 147-155.

[19] Waghmare VS, Wadke PR, Dyawanapelly S, Deshpande A, Jain R, & Dandekar P (2018). Starch based nanofibrous scaffolds for wound healing applications, *Bioactive Materials*. 3(3), pp 255-266.

[20] Ramaraj B & Poomalai P (2006). Ecofriendly poly (vinyl alcohol) and coconut shell powder composite films: Physico mechanical, thermal properties, and swelling studies, *Journal of Applied Polymers Science*, 102, pp. 3862-3867.