ENHANCING THERMAL PROPERTIES OF WATER-SOLUBLE POLY (VINYL ALCOHOL) COMPOSITES FOR 3D PRINTING APPLICATIONS

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Abstract

Water-soluble support materials are needed for the fabrication of 3D printing components, particularly using molten material deposition (FDM) technology. Polyvinyl alcohol (PVA) was considered a potentially ideal candidate for use in rapid prototyping technology, but its properties and procedural characteristics required improvement for widespread use. This paper attempted to use thermoplastic corn starch (TPS) as a modifying additive to modify the thermal and mechanical properties of polyvinyl alcohol. PVA-based filaments with different TPS contents were prepared by extrusion. The results showed that with increasing TPS content, the PVA-based filaments showed a decrease in crystallinity and melting point, while the initial degradation temperature and melting index increased. The addition of TPS reduced the melting temperature to 173.04 °C, and a PVA composite with crystallinity of 4.5% was obtained. Due to the formation of a hydrogen bond between TPS and the hydroxyl group of PVA, the tensile strength and modulus of elasticity of PVA decreased slightly, while the tensile strain increased significantly, to 470.24%, indicating a good plasticizing effect of TPS.

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1. Introduction

Fused deposition modeling (FDM) is an additive manufacturing technology that builds parts up layer-by-layer by heating and extruding thermoplastic filament. It is an effective process to create parts from concept models to production parts in a short time and low quantities.[1,2] Due to the durable materials like ABS and polycarbonate used, prototypes with outstanding thermal and chemical resistance, and excellent strength-to-weight ratios could be created.[3,4] To build durable components with complex geometries, two kinds of materials are required to create a finished product: a support materials that acts as a structure for the modeling material that will comprise the final piece or prototype.

FDM support materials acts as a scaffold to support the object as it is being printed. Currently, once an object comes off the FDM printer, its support materials are usually striped off by hand. People are seeking a kind of water-soluble support materials which can be removed by soaking the object in a water or detergent solution. Soluble support material provides advantages over traditional support materials such as build parts faster, expand design freedom. In fact, several studies on acrylic acid (AA) copolymer, polystyrene (PS), and poly(vinyl alcohol) (PVA) have been conducted to develop water soluble support materials. An AA copolymer which can be partially dissolved by ultrasonic cleaning or lye has been developed. However, it takes a long synthesis cycle. A PS water-soluble support material which could be dissolved in the lemon also has been developed, but it takes a long time to dissolve and it is not cost effectively. Presently, increasing attention is devoted to the preparation of environmentally compatible PVA-based materials for a wide range of 3D printing application.

PVA is the largest and most popular water-soluble and biocompatible synthetic polymer with high tensile strength, flexibility, as well as high oxygen and aroma barrier. [6,7] The degree of solubility, biodegradability as well as other physical properties can be controlled by varying the molecular weight and the degree of hydrolysis of its mother polymer-poly(vinyl acetate). [8–10] PVA is used in a broad range of applications in tissue engineering, drug release, and membranes. However, its low processability limited the further wide application in 3D printing and demand physical and chemical modification. [11–13]

Recently, incorporation of oligomer such as glycerol, amides, and alcohol amine into PVA matrix has been explored as an important strategy for obtaining PVA-based composite with high processing performance. [14–22] The oligomer could form hydrogen bonds with the hydroxyl groups of the PVA molecule, thus reducing the formation of hydrogen bonds between PVA molecule chains. Moreover, the existence of oligomer as a role of lubricant increased free volume of PVA. The thermal proper- ties of PVA membranes was improved and Young's modulus was decreased due to the phase separation occurred. [23,24] Wang et al.[25] investigated the effects of water and water/caprolactam mixture on PVA thermal processing and found hydrogen bonding was formed with PVA molecule by replacing the self intra and intermolecular hydrogen bonding of PVA. However, the wet melting process is complicated and instability. The effect of native starch and glycerol mixture on the thermal properties of starch/PVA mixtures was investigated. Thermal properties and phase separation were found to improve because the addition of glycerol to the starch changes its structure, allowing the starch to acquire the properties of a thermoplastic material. Glycerol interacts with starch by forming hydrogen bonds between starch and glycerol molecules, which leads to a decrease in the degree of crystallinity of starch and an increase in its mobility. Thus, starch becomes more pliable and can be used to create various shapes and products using thermoplastic molding, including 3D printing.

Thus, in this work, the effect of the TPS mixture on the structure and properties of PVA was investigated to gain further insight into the modification mechanism and provide possible ways to improve PVA as an auxiliary material in 3D printing. In this study, PVA/TPS filaments were prepared by extrusion from a mixture of PVA and TPS. Consequently, the microstructure, thermal and mechanical properties of PVA-based composites were investigated. This study made it possible to create a PVA-based composite and to propose a water-soluble, efficient support material with improved technological properties for a wide range of applications in 3D printing.

Experimental
Materials
Potato starch with crystallinity degree $\chi = 26.5\pm3.2\%$ produced by Allegro- Species LLC, (Russia). Polyvinyl alcohol (PVA, Mw=124000-186000 g/mol $\approx$ 1, hydrolysis 88-92%) was obtained from SINOCHEN NANJING CORPORATION (China). Reagent glycerin CJSC "Vekton" (Russia) was used as plasticizer.

Sample Preparation
Preparation of the filament

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To prepare the mixture for the filament based on PVA/TPS we used granules of PVA and thermoplastic starch mixed in the right ratio: wt % 10-40% TPS. After loading the mixture into the extruder at 140-160 degrees Celsius. For 5-10 minutes, mixed the mixture while heating until it became malleable. To improve mixing, glycerin was added to the mixture as a plasticizer. All the ingredients were mixed until a homogeneous mass was obtained. The extruded filament was cooled and cut into 50 cm lengths.

X-ray Diffraction Measurements (XRD)
XRD patterns were recorded in the reflection mode using a Dmax-2500PC diffractometer (Rigaku, Japan) operated at the Cu-Kα radiation (15.4 nm) at 2θ values ranging from 5 to 40° at a scanning rate of 1°/min. The testing conditions were 50 kV and 100 mA. The crystallinity of each specimen was obtained with the area integral method.

Differential Scanning Calorimeter (DSC)
DSC analysis was performed under nitrogen flow with a TGA DSC STA PT 1600 derivatograph (Linseis, Germany). The specimens were first heated from 25 to 160 °C and hold for 5 min, and then cooled to 25 °C to remove the effects of thermal history. The ramp rates were maintained at 10 °C/min in this process. Subsequently, the specimens were reheated to 300 °C at a heating rate of 2 °C/min. The melting temperature was determined as the peak temperature of the melting endotherm.

Thermogravimetric Analysis (TGA)
Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a TGA DSC STA PT 1600 derivatograph (Linseis, Germany) at a heating rate of 10°C/min. The initial, mean and final transition temperatures Tg were calculated using the tangents drawn on the displacement curve. The midpoint was regarded as the Tg of the filaments.

Melt Flow Rate (MFR)
As specified in ASTM 1238, MFR of each specimen was measured with a melt flow index tester MFR1211 (Jinjian-test, China) at 210 °C ± 0.5 °C under a 2.16 kg load. The diameter of the die was 2.095 ± 0.005 mm. At least five specimens without bubble were selected. The MFR is defined as the extrudate weight in grams per 10 min and can be calculated as follow formula,

$$MFR(\theta, m_{nom}) = \frac{t_{ref} * m}{t}$$

Where:
θ - test temperature;
m_{nom} - nominal load;
t_{ref} - reference time (10 min);
m - average weight of cutting specimen;
t - cutting interval (10 s).

Tensile Tests
The physical and mechanical tests were carried out on a ZWISK tensile testing machine. To evaluate the tensile strength and modulus of elasticity of the obtained polymer mixtures we prepared samples according to STATE STANDARD 11262-80 and STATE STANDARD 9550-81. The ultimate tensile strength (TS) and percentage of relative elongation at break (% ε) of 10×90 mm specimens were calculated. Ten repetitions were measured and the values of the specimens broken in the centre of the film were taken. The mean value and standard deviation were indicated.

2. Results and Discussion

XRD Analysis
The microstructure of PVA modified with different content of TPS/ glycerin is typically elucidated using X-ray diffraction measurements. The obtained XRD patterns of pure PVA and PVA with different content of TPS mixture are shown in Figure 1.
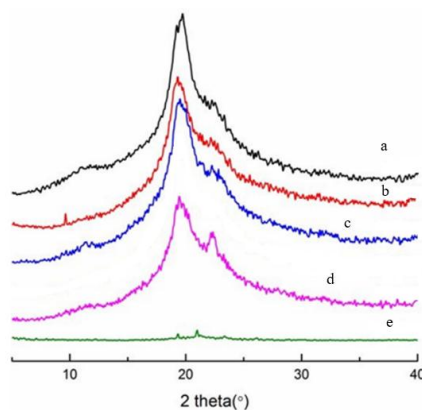

Figure 1. X-ray diffraction patterns of pure PVA and PVA with different content of TPS/ Glycerine mixture.

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a) PVA; b) PVA/TPS 10%; c) PVA/TPS 20%; d) PVA/TPS 30%; e) PVA/TPS 40%.

The degree of crystallinity of all of the samples were calculated and listed in Table 1. On the XRD curve of pure PVA, the diffraction peaks at $2\theta =$

20.0 ° of (101) for PVA were clearly shown. The relatively sharp and broad peak centered indicates the semicrystalline nature of PVA containing crystalline and amorphous region.

Table 1. Thermal Characteristics and Crystallinity of Specimens Added with Different Amount Additives

Specimens	T_m (°C)	T_d (°C)	crystallinity (%) (calculated by XRD)
PVA	203.62±3.55	211.27±1.71	40.85
PVA/TPS 10%	184.80± 4.38	198.35± 1.84	20.67
PVA/TPS 20%	179.79± 1.25	203.54± 1.68	13.41
PVA/TPS 30%	173.04± 1.36	209.95± 3.10	4.50
PVA/TPS 40%	170.54±1.23	211.51± 3.79	0.65

There was not any new crystalline peak observed on the XRD curves of the samples, indicating TPS mixture could disperse into PVA without affecting the crystalline structure of PVA. The diffraction peaks of PVA decreased gradually in intensity with the increase of TPS content and almost disappeared with the content of TPS was up to 40%. O atoms in the "C=O" group in thermoplastic starch have strong electronegativity, which makes their electronegativity relatively stronger than the oxygen atoms in the "-OH" groups in polyvinyl alcohol. This causes easier formation of hydrogen bonds between the oxygen atoms of the "C=O" group in thermoplastic starch and the hydroxyl groups in polyvinyl alcohol. In such a case, in composites of polyvinyl alcohol and thermoplastic starch, the intermolecular hydrogen bonds replace the intermolecular hydrogen bonds in pure

polyvinyl alcohol materials, and then the ability of polyvinyl alcohol to crystallize is suppressed.

DSC Analysis and Thermal Properties of PVA Composites

DSC measurements were conducted to investigate the change of the melting temperature of PVA composites. The thermograms of the second heating scans at the heating rate of 2 °C/min of pure PVA and plasticized PVA films are shown in Figure 2. Table 1 tabulates the numerical values of the melting temperatures obtained from the second heating scan, and their changing tendency is reflected in Figure 3. It can be seen that with the increase of TPS mixture content, the melting temperature of PVA films decreased.
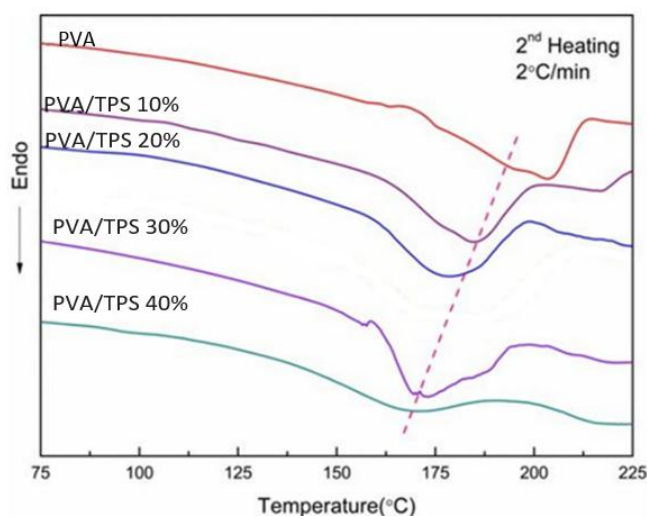

Figure 2. DSC thermograms of pure PVA and PVA with different content of TPS mixture.

When the weight ratio of TPS mixture was up to 40%, the T_m of PVA was decreased from 204 °C to 170.5 °C. Due to the strong hydrogen bonding with hydroxyl groups in PVA molecule chains instead of self intra and inter-molecular hydrogen bonding of PVA, the intermolecular interaction in PVA was reduced. Furthermore, the addition of TPS and glycerin which act as lubricant increased the inter-molecular distance of the PVA macromolecules and free volume thus increased the chain segment activity of PVA. The above effects led to a decrease in T_m, also decreased the perfection degree of the PVA crystal.
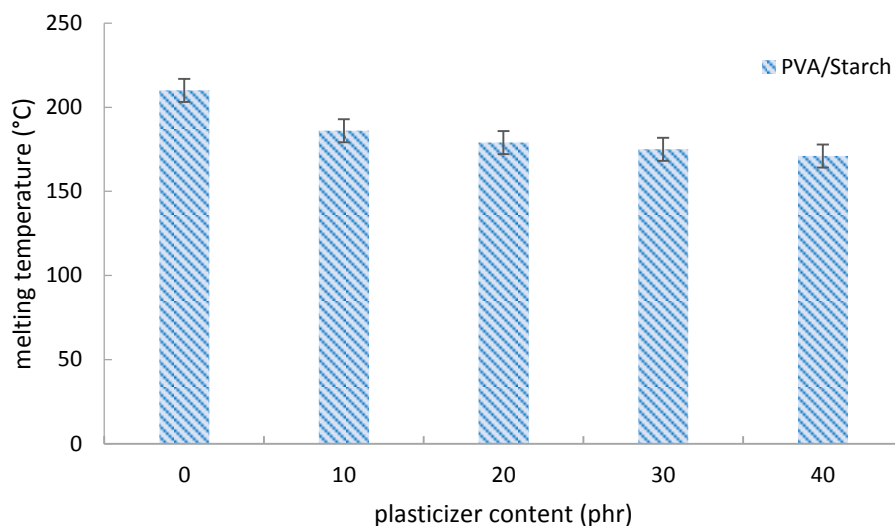

Figure 3. T_m of PVA with different content of TPS mixtures.

When 30 wt % plasticizer was added, the T_m of PVA/TPS 30% was 173.04 °C, the plasticizing effect of TPS was better, it was because TPS showed better performance on the destruction of the intra and intermolecular hydrogen bonds of PVA, and be more effective to reduce the degree of crystallinity of PVA.

TGA Analysis and Thermal Stability

The thermal stability of PVA with the effect of hydrogen bonding was investigated by TGA analysis. The obtained TGA curves of pure PVA and plasticized PVA are shown in Figure 4.
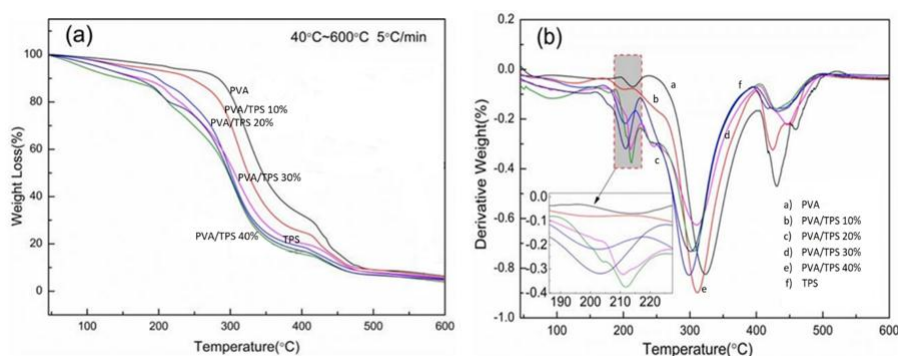

Figure 4. The (a) TG and (b) DTG curves of PVA added with different amount additives.

It can be seen that both pure PVA and plasticized PVA films exhibit three-stage degradation. The first-stage degradation occurred at 200 °C, the decomposition products of first stage degradation reported were mainly water, which was a product of the elimination of hydroxyl groups on the molecular chain and acetate side groups. [28,29]

The second stage degradation occurred with the increasing temperature, the main chain of PVA fragmented to produce an aldehyde, ketone, furan, benzene, and benzene derivatives. The third stage degradation happened when the temperature was up to 400 °C, the carbonation of polymer matrix of the polymer chains decomposed. Decomposition

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temperature (T_d) was determined as the peak temperature of the first stage degradation in DTG curves. As can be seen in Figure 6, it can be seen that T_d increased with the increase of TPS content. However, the T_d of PVA was nearly to PVA/TPS 40%, higher than other plasticized PVA. As a partially hydrolyzed PVA, the thermal degradation of pure PVA was affected by the residual acetate groups and hydroxyl groups. The stability of hydroxyl groups was conducive to the thermal stability of PVA. Double bonds generated by the removal of acetate groups can promote the remove of adjacent acetate group in the main chain of PVA, thus residual acetate group contributed to the acceleration of thermal degradation reaction. When 10 wt % TPS was added, the crystallinity of PVA decreased from 40.85% to 20.67%, a looser aggregation structure of PVA formed and the chain segment activity of PVA increased. Then the activity of acetate group improved and thus the promoting effect of acetate on thermal degradation was enhanced. TPS could also form hydrogen bonding with hydroxyl groups in the molecular chains of PVA, which was beneficial to the stability of the hydroxyl groups. However, the promoting effect of acetate on thermal degradation played a leading role. Then, T_d of PVA/TPS 10%

is lower than T_d of PVA. With the increase of TPS content, there was little further increase in the activity of acetate group, while the stability of hydroxyl groups was found to increase. Therefore, T_d was found to increase with the UC content. When 30 wt % plasticizer was added, the T_d of PVA/TPS 30% appeared at 211.02 °C. It indicated that PVA/TPS 30% exhibited better thermal stability in the first degradation step. The volatilization and degradation of the plasticizer also occur at this stage. It also suggested that hydroxyl groups in PVA/TPS 30% were more stable as the weight loss ratio of PVA/TPS 30% was 14.13% at 210 °C, the using temperature of water-soluble support material, was higher than that of PVA/TPS 30%, 19.56%. PVA/TPS 30% was more suitable to meet the requirement of the thermal stability of water-soluble support materials.

Melt Flow Rate and Viscosity

Figure 5 and Table 2 show the melt index of PVA with different plasticizer content. Since the Tm and the Td of pure PVA was too closed, and the viscosity of the samples was so high at the testing temperature, the melt index of pure PVA could not be measured and no data was collected.
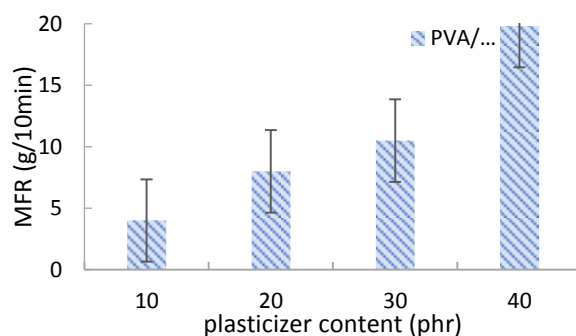

Figure 5. The melt index of PVA with different plasticizer content.

However, with addition of TPS mixture, it was found that the melt index of PVA increased, indicating the processing window of PVA composites with TPS mixture was much improved compared to pure PVA. As mentioned above, TPS

had significant effect on the destruction of intra and intermolecular hydrogen bonding of PVA, and thus the interaction between PVA chain segments was destroyed.

Table 2. The Melt Index of PVA Composites

Specimens	PVA	PVA/TPS 10%	PVA/TPS 20%	PVA/TPS 30%	PVA/TPS 40%	TPS
MFR (g/10 min)	—	4.49 ± 0.20	8.15 ± 0.10	10.04 ± 0.50	19.53 ± 0.15	8.17 ± 0.11

Besides, the addition of glycerin which act as lubricant could increase the intermolecular distance of PVA macromolecules and free volume. The melt index of PVA/TPS 30% was increase, indicating that the segmental mobility and melt flow ability of PVA/TPS 30% was better.

Mechanical Properties

The mechanical properties of pure PVA and PVA-based compo- sites were examined by tensile tests. Figure 6 shows the tensile strength, elongation at break, and Young's modulus of PVA specimens with different concentration of plasticizer. The corresponding value of each property is listed in Table 3. As can be seen in Figure 6, pure PVA

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processes high tensile strength, low Young's modulus, and brittle as a result of its high density
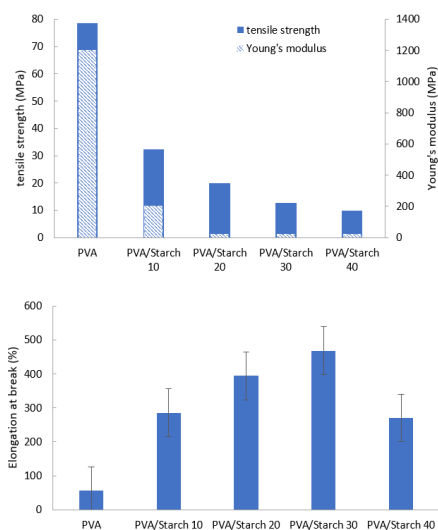
polar group.

Figure 6. Mechanical properties of PVA and modified PVA: (a) tensile strength and Young's modulus, (b) elongation at break.

With an increase in the amount of TPS mixture, the tensile strength of PVA films decreased, while the elongation at break and Young's modulus increased. It was mainly because that strong hydrogen bonding could be produced between TPS mixture and hydroxyl groups in PVA molecule chains, thus the intermolecular interaction of PVA was reduced. Moreover, the addition of TPS increased the intermolecular distance of the PVA macromolecules.

Table 3. Mechanical Properties of Pure PVA and PVA Composites

Specimens	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PVA	77.8 ± 0.8	31.2 ± 5.0	1210.8 ± 59.6
PVA/TPS 10%	32.9 ± 0.8	277.3 ± 34.6	210.6 ± 4.0
PVA/TPS 20%	18.4 ± 1.1	373.7 ± 3.7	36.4 ± 0.2
PVA/TPS 30%	9.9 ± 0.2	470.2 ± 46.1	26.7 ± 2.6
PVA/TPS 40%	6.9 ± 0.5	274.5 ± 38.4	15.5 ± 1.4

It was also found that the elongation at break of PVA/TPS 40% was lower than that of PVA/TPS 30% which was caused by the excessive amount of the plasticizer was added and stress concentration was caused by precipitates, which had a negative effect on its tensile properties.

3. Conclusions

PVA-based films with different content of additives were pre- pared by solution casting method. It was found that the addition of TPS improved the thermal and mechanical properties of PVA. With the increase of TPS, PVA films showed decreased crystallinity and melting temperature, while the initial degradation temperature and melt index were increased. The corporation of TPS decreased the melting temperature to 173.04 °C and PVA composites with 4.5% crystallinity were fabricated.

Due to the formation of hydrogen bonding between TPS and the hydroxyl group of PVA, the tensile strength and modulus of PVA were slightly decreased, while strain-at-break was significantly enhanced, as high as 470.24%, indicating TPS behaved as good plasticizing effect. The microstructure examination via scanning electron microscopy showed that when the content of TPS was less than 30% in the composites, homogeneous phase could be observed, indicating good compatibility between these two components.

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