

EFFECT OF RELATIVE HUMIDITY ON MECHANICAL PROPERTIES OF STARCH-POLY VINYL ALCOHOL BLENDS

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ABSTRAK

Telah dilakukan blending starch berkadar amilosa tinggi dengan polyvinyl alcohol (PVA) hidrolisa parsial menggunakan metode ekstrusi. Pemlastis yang digunakan adalah air. Hot press digunakan untuk membentuk hasil ekstrusi menjadi lembaran film. Film yang dihasilkan fleksibel dan transparan. Dari pengujian sifat mekaniknya, kelembapan relatif (RH) yang rendah memberikan sifat rapuh pada film. Sebaliknya, spesimen yang diletakkan dalam desikator pada RH 70% menunjukkan sifat ulet. Nilai maksimum dari kuat tarik (tensile strength) dan Modulus Young masing-masing adalah 43 MPa and 1100 MPa. Semua nilai maksimum ini didapat saat film dikondisikan pada RH 43%. Sementara penambahan konsentrasi PVA meningkatkan elongation-to-break sampel.

Kata Kunci: pati, Polyvinyl Alcohol (PVA), ekstrusi biopolimer, sifat mekanik polimer

INTRODUCTION

Plastic wastes have become one of major problems in the environment because they cannot be degraded by microorganisms in soil/compost. Growing in ecological concern has led scientists to find polymers which are biodegradable and renewable. These polymers are so called biopolymer. It is known that bio-based products obtained from renewable sources could maintain carbon dioxide neutrality.¹ In the family of biopolymers, starch has been considered as one of the most promising materials because it is readily available, low cost, real biodegradable, and renewable.^{2,3} However, starch-based materials have not been fully marketed yet, even though it shows many benefits. The reasons are numerous: the materials are hydrophilic (poor moisture barrier), they undergo aging, and they have low mechanical properties, impact strength, and inappropriate chemical structures.⁴

One effort to overcome the mechanical deficiencies of starch is by blending starch with other polymers. Ideally, starch and the second polymer should be covalently bonded through

existing functional groups or by introduction of new functional groups.⁵ Some investigations were carried out on blending starch with poly(vinyl alcohol).^{4,6,7,8,9} Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer which has a hydrophilic character and exhibits susceptibility to biodegradation. PVA polymers are strong and tough materials. Mao and co-workers⁸ reported that addition of PVA in starch-glycerol blends prevented the development of surface crack and significantly improved both the tensile strength and elongation of the extruded materials.

Starch, as a hygroscopic material, absorbs varying amounts of moisture under different relative humidities.¹⁰ Absorbed moisture introduces swelling stresses and also acts as a plasticizer, which lowers the glass transition temperature (T_g). Consequently, the mechanical properties are affected.¹⁰

Decreasing % hydrolysis of PVA will increase flexibility¹¹ which will affect the elongation at break. On the other hand, decreasing hydrolysis will decrease tensile strength.¹¹ Mao et al.⁸ cited that the effect of PVA molecular weight

on physical properties of the films was obtained by extrusion method. However, the samples were not conditioned under control relative humidity. The aim of this work was to investigate the effect of relative humidity and to examine PVA content on the mechanical properties of the starch-PVA blends.

THEORY

The tensile test is done in order to get the mechanical properties of materials. In a tensile test, a specimen with tabs at the end is typically fixed at one end, whereas the other is moved outward at a constant velocity. The typical specimen for tensile test is shown in Figure 1.

The force F necessary to carry out the stretching deformation is monitored as a function of time along with the instantaneous sample length, L . From the measured load versus extension behavior, the stress, and strain can be calculated as follows:

$$\sigma = \frac{F}{A} \quad (1)$$

$$\varepsilon = \frac{L_t - L_0}{L_0} \quad (2)$$

where σ is stress, F is force, A is a cross-sectional area, ε is the strain, L_t is the length at certain time (Figure 1), and L_0 is the initial length. Various possible load–extension curves for polymers are shown schematically in Figure 2.

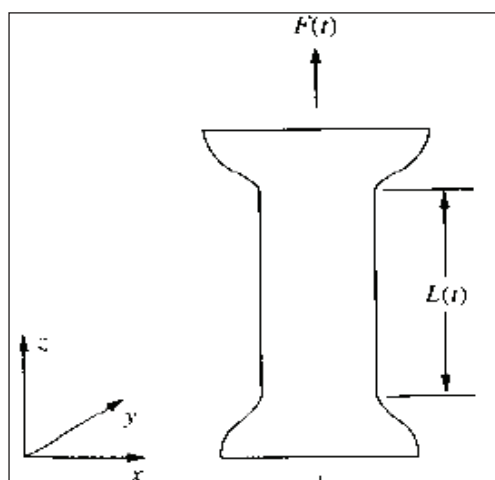


Figure 1. Typical specimen for tensile test¹²

The slope of the stress–strain curve evaluated at the origin is termed the elastic modulus or Young's modulus, E , and is taken to be a measure of the stiffness of the material.¹² The stress at fracture is called the strength of the material. The strain at fracture is known as the elongation-to-break; the larger the value of this quantity, the more ductile the material tested.¹²

MATERIALS AND METHODS

This research was conducted at several stages: sample preparation including materials, extrusion process and compression moulding, conditioning, and tensile testing.

Materials and Sample Preparation

The sample preparation and extrusion were done in the Extrusion Laboratory, Centre for High Performance Polymers, University of Queensland, Australia on October 2008. PVA (Elvanol® 52-22) was purchased from DuPont, Australia. Elvanol® 52-22 has percent hydrolysis of 87-89% which is called partially hydrolyzed. Hydroxypropylated high amylose starch (Gelose 939) with 80% of amylose content and 14.9% of moisture content was supplied by Penford Australia. Stearic acid (Sigma Aldrich Reagent grade 95%) was added to the starch by portion of 0.56 gram of stearic acid for every 90 gram of starch and then mixed manually for 3-5 minutes. This

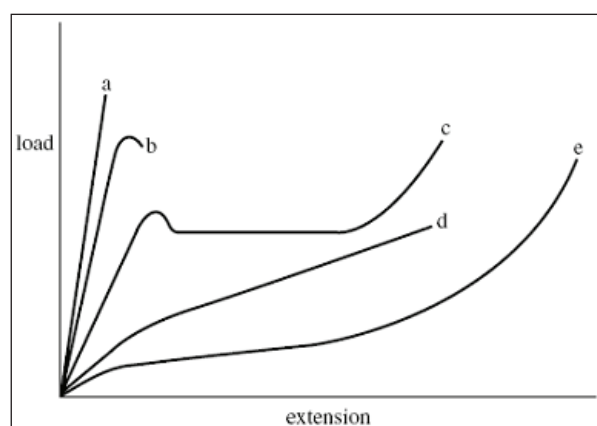


Figure 2. Possible forms of the load–extension curves for a polymer: (a) low extensibility followed by brittle fracture; (b) localized yielding followed by fracture; (c) necking and cold drawing; (d) homogeneous deformation with indistinct yield; (e) rubber-like behaviour¹³

mixture was stored in transparent bulk container. Water content of this mixture was measured prior to extrusion using Sartorius Moisture Analyzer MA30 at 110°C.

The next procedure was to prepare 15 wt% PVA solution. First, partially hydrolyzed PVA was added into the cool tap water little by little in order to prevent the formation of swelling lumps, which were very difficult to completely dissolve. The mixture was then stirred using magnetic stirrer for approximately 10 minutes to allow the PVA particles well disperse and swell. Partially hydrolyzed PVA is more likely to produce foam, so rapidly stirring is to be avoided. When the PVA particles seemed to disperse well, the temperature was increased up to 60–70°C (below gelatinization temperature) to save dissolution time. This solution was stored in refrigerator to avoid bacteria's growth.

Extrusion

Blending of starch and PVA was carried out using EUROLAB Prism 16 mm twin screw extruder. The extruder was divided into ten zones which were counted from hopper to die. The dry feed mixture (starch and stearic acid) was fed into the extruder at zone 1 using a single screw in the hopper. The PVA/water feed was fed into the extruder at zone 3 using Masterflex L/S Pump with Masterflex precision tubing 06419-16. The initial temperature profiles were a series of 25, 50, 75, 85, 100, 100, 100, 85, 90, and 90°C from feed to die. Calibration of the hopper and the pump were done straightaway after turning on the extruder and setting the initial temperature profile. When the temperature reached the initial set value, the liquid feed (pump) and screw were started at 50 rpm, simultaneously along with a timer. Screw speed was 200 rpm after 8 minutes, while the pump speed was constant at 50 rpm. At 11 minutes, the hopper was on at 5% and increased slowly until 25% at 25 minutes. At this stage, the temperature setting from hopper to die was changed to 25, 80, 90, 110, 120, 120, 110, 95, 90, and 90 °C. The first product was taken when the barrel temperature reached their setting. Pump speed, hopper speed, and screw speed were 50 rpm, 25%, and 200 rpm, respectively. This product was coded 25HP. In order to check the ef-

fect of PVA content on the mechanical properties of the blend, the hopper speed was then changed to 19%. The second product, which was coded 19HP, was taken after the output was stabilized.

The extruder product (extrudate) was chopped into pellets. The pellets were processed into films of 0.9 mm thickness using a compression moulder, Rondol Hot Press. The compression moulder was heated to 125°C and to a force of 30 kN for 5 minutes. The compression moulder was then cooled to room temperature over approximately 10 minutes, and the pressure was released. After compression moulding, the films were punched out using an ASTM Standard D 638M (1996)¹⁴ Type M–III dumbbell, specified for tensile test specimens. They were then placed in desiccators maintained at 43%, 54%, and 70% relative humidity for 2 weeks to allow for equilibration. Each relative humidity environment was achieved using appropriate salt solution in the base of desiccators; potassium carbonate (K_2CO_3), magnesium acetate ($Mg(NO_3)_2$), and potassium iodide (KI) for 43%, 54%, and 70% respectively.¹⁵

Mechanical Testing

Tensile tests were carried out on an INSTRON 4505 based on ASTM D 638M (1996). This machine was equipped with 1 kN load cell and pneumatic grips to avoid slippage. The crosshead speed was 5 mm min⁻¹ and the gauge length was 10 mm. The Young's modulus was calculated using the initial slope of the stress–strain curves. Sample's thicknesses and widths were measured using micrometer digital just prior to testing. Five specimens were tested for each conditioning (43%, 54%, and 70% RH) and types of extrusion (19HP and 25HP).

RESULT AND DISCUSSION

Sample Preparation and Extrusion

The water content of starch and stearic acid mixture was checked before doing extrusion. It was 18.44%. This value was probably only the free water. The tightly bound water cannot be detected using this technique. Moreover, some other volatile substances can be released by the

heating process.¹⁰ Therefore, the true water content must be higher than the nominal measured.

The preparation of partially hydrolyzed PVA solution was easier than making fully hydrolyzed PVA solution. It is because the presence of residual acetate groups in partially hydrolyzed PVA weakens the hydrogen bonds between intra- and intermolecular hydroxyl groups and allows solubility at lower temperatures.¹¹ In addition, partially hydrolyzed PVA solution was more stable in room temperature rather than solution of fully hydrolyzed PVA. The benefit of this characteristic is it could be stored in longer time.

The process utilized in the preparation of PVA/starch mixtures could affect the compatibility between the two components.² Accordingly, extruded starch/PVA films were expected to result in more homogenous dispersions rather than casting method because of the intense mixing and mechanical stress in the extruder, which helps to finalize the destructure of starch granules.² In this experiment, the films appeared smooth, flexible, and transparent. Sample 19HP contained 7.7% PVA, while sample 25HP contained 5.7% PVA due to decreasing hopper speed which led to decrease starch content in the extruder product.

Conditioning the samples in different relative humidity caused little difference in the thickness of samples, as shown in Table 1.

After two weeks conditioning, the thickness of specimens for tensile testing decreased to about 0.05-0.14 mm due to shrinkage. Moreover, Chaleat *et al.*¹⁰ found that relative humidity has relationship with moisture content. Increasing the relative humidity will increase the moisture

content in the samples and then increase the thickness as can be seen in Tabel 1. Increasing the thickness due to conditioning in higher relative humidity can be explained by an increase in free volume due to plasticization with water molecules at higher relative humidities.¹⁶

Mechanical Properties

Tensile testing was done to investigate the effect of relative humidity and Polyvinyl Alcohol (PVA) content on starch-PVA blends. In general, it was found that the relative humidity (RH) has a strong influence on mechanical properties of starch-PVA blends.

Figure 3 and 4 show the tensile strength and Young's modulus of the samples, respectively.

Tensile strength was inversely proportional to relative humidity (Figure 3) with almost similar slope between 19HP and 25HP. These results are consistent with earlier findings of Chen *et al.*⁹ However, the nominal of tensile strength obtained from this measurement was lower than those data reported by Chen *et al.*⁹ because in this experiment, partially hydrolyzed PVA was used while Chen and co-workers used fully hydrolyzed PVA. This result was consistent with the statement written by Marten¹³ that tensile strength will decrease with decreasing hydrolysis level.

The Young's modulus plot (Figure 4) follows similar decreasing trends with increasing relative humidity. A wide range of mechanical behaviour can be achieved just by varying slightly the water uptake of this material,¹⁰ which was done by varying the relative humidity. The samples'

Table 1. Thickness of samples

Sample Code	Ratio Strach:PVA	Relative Humidity %	Thickness mm
19HPD	12 : 1	43	0.772 ± 0.012
19HPE	12 : 1	54	0.778 ± 0.015
19HPF	12 : 1	70	0.786 ± 0.013
25HPA	16 : 1	43	0.817 ± 0.009
25HPB	16 : 1	54	0.838 ± 0.019
25HPC	16 : 1	70	0.845 ± 0.018

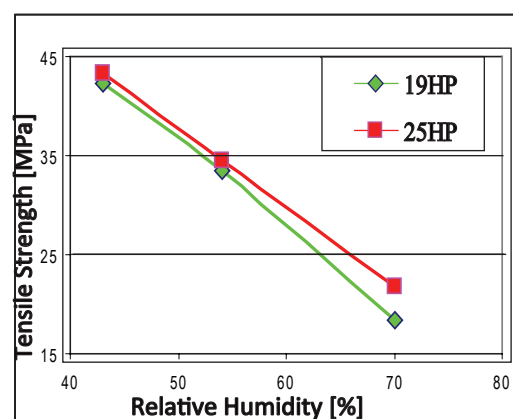


Figure 3. Tensile strength as a function of relative humidity in starch-PVA blend

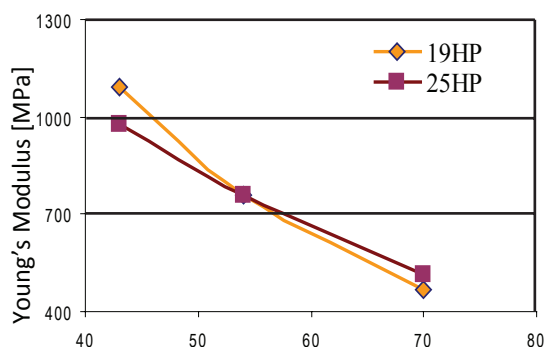


Figure 4. Young's modulus as a function of relative humidity in starch- PVA blend

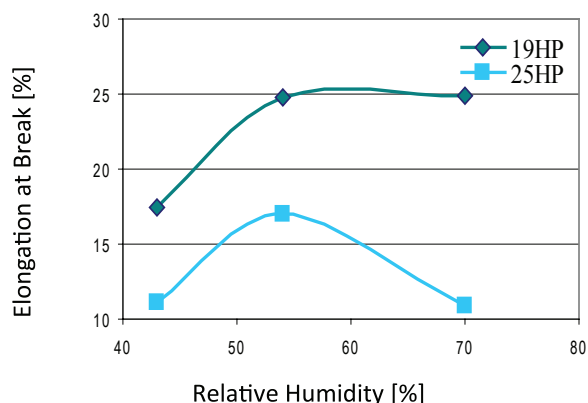


Figure 5. Elongation-to-break as a function of RH in starch-PVA blends

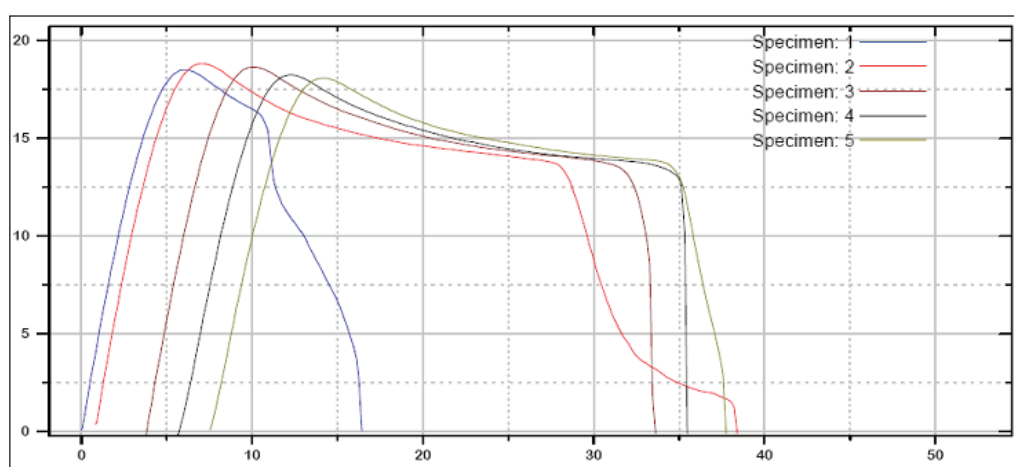


Figure 6. Stress-Strain curve of 19HPF (70% RH)

stiffness dropped by 50% when the samples stored at RH between 43% and 70%. Figure 5 shows the elongation-to-break as a function of relative humidity.

Meanwhile, the elongation of starch-PVA films improved considerably with increased relative humidity as can be seen in Figure 5. Decreasing elongation at break in sample 25HP at 70% relative humidity (RH) could not give the sign that this phenomenon did not match with the theory or the result from other studies. This can be explained that the data was not enough to show the trend. It is possible to find that the elongation is more than 17% for RH more than 70%. This result showed similar trend to the result reported by Chen and co-workers.⁹ On the other hand, additional PVA for only 2% from 5.7% (25HP) to 7.7% (19HP) led to increase the elongation at break significantly. As described in the theory,

decreasing level of hydrolysis will increase the flexibility of the films.

Indeed, samples failed in a brittle manner when the samples conditioned at low relative humidity (RH) indicated reduced chain mobility. Brittle fracture in glassy thermoplastics occurs by crazing mechanism. As the relative humidity increased, moisture content of the samples was increased and ductile behaviour was observed from the materials. Stress-strain curve of sample 19HPF which was conditioned at 70% RH can be shown in Figure 6.

It can be seen from the figure that most specimens have necking and cold drawing in the graph. The strain at break could be evaluated at around 33–38%. From Figure 4, specimen 1 shows the very different result with the others. This could be indicated that there was a physical defect in that specimen. This assumption can be



Figure 7. Sample 19HPF before and after testing

proved by looking at the specimen photo after testing (Figure 7).

From Figure 7, it can be seen that stress whitening occurred around the failure zone on most specimens conditioned at 70% RH except for specimen 1 (second from the right). The white region reveals some plastic deformation.

CONCLUSION

Samples were conditioned in the low RH exhibited brittle behaviour. On the other hand, the specimens were placed in the desiccators at 70% RH exhibited ductile behaviour which had neck and cold drawing in the stress-strain curve. Increasing in humidity leads to decrease in tensile strength and Young's modulus which are in a good agreement with the result reported by Chaleat and co-workers. Increasing PVA content will increase the elongation-to-break, while there was no significant improvement on tensile strength and Young's modulus as PVA concentration increased.

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