

Biodegradation Studies of Polyvinyl Alcohol/Corn Starch Blend Films in Solid and Solution Media

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Abstract: *In this study, polyvinyl alcohol (PVOH)/corn starch (CS) blend films were prepared using the solution casting method. The biodegradability of the films was investigated based on enzymatic absorbency in water and an acidic solution as well as by burial in soil and compost. The tensile properties were examined using a tensile test. The structure of the film was characterised by scanning electron microscopy. Compared to a film without corn starch, the films containing corn starch were found to be more highly biodegradable by enzymes as well as in soil and compost. However, the results from the tensile and elongation at break tests showed that as the corn starch content increased, the strength decreased. The morphology study revealed the distribution of corn starch in the PVOH.*

Keywords: PVOH/CS blend film, biodegradation, enzymatic, acidic solution, compost burial

Abstrak: *Dalam kajian ini, polivinil alcohol (PVOH)/kanji jagung (CS) campuran filem telah disediakan dengan menggunakan kaedah larutan pengacuan. Biodegradasi filem dianalisa berdasarkan kuantiti enzim dalam air dan larutan berasid serta oleh perkuburan di dalam tanah dan kompos. Ciri-ciri tegangan telah diperiksa menggunakan ujian tegangan. Struktur filem adalah bercirikan oleh imbasan mikroskop electron. Berbanding dengan filem tanpa kanji jagung, filem-filem yang mengandungi kanji jagung telah didapati lebih tinggi terbiodegradasikan oleh enzim serta perkuburan di dalam tanah dan kompos. Walaubagaimanapun, hasil daripada tegangan dan pemanjangan pada ujian pemecahan menunjukkan bahawa apabila kandungan kanji jagung meningkat, kekuatan menurun. Kajian morfologi menunjukkan taburan kanji jagung di dalam PVOH.*

Kata kunci: campuran filem PVOH/CS, biodegradasi, enzimatik, solusi asid, penanaman kompos

1. INTRODUCTION

The use of synthetic polymer materials has caused significant environmental problems. Solid waste from these materials is a major contributor to environmental pollution because it can take up to a thousand years to degrade. Therefore, a great deal of attention has been given to the development of various biodegradable materials to overcome this serious problem. The development of environmental friendly polymer materials can be classified into two categories based on the raw material used: degradable synthetic polymers and renewable natural polymers.¹ Renewable natural polymer resources include starch, cellulose and chitosan. These materials have been tested alone and in combination with plastic to enhance the plastic properties and biodegradation potential of the product.

Among these three renewable natural polymer resources, starch is the most attractive candidate because of its low cost, widespread availability and potential for mass production from renewable resources.²⁻⁴ Starch can be thermally processed when a plasticiser, such as water, is added to it. When various materials are blended with starch, their performance changes during and after processing as a result of the hydrophilicity of starch.⁵ Starch has been considered a suitable material source due to its inherent biodegradability, availability and relative low cost.³ However, the poor mechanical properties and relatively hydrophilic nature of starch compared to most petroleum-based polymers prevent its use in widespread applications.⁶ Moreover, packaging films composed entirely of starch lack the strength and rigidity to withstand the stress that many packaging materials are subjected to, and their application is therefore limited. Starch is the mixture of amylose and amylopectin; amylose is a linear polymer of α -D-glucopyranosyl units containing both 1,4- α -D-glucosidic linear linkages and 1,6- α -D-glucosidic linkages at the branch points. α -amylase is the main enzyme involved in the hydrolysis of the 1,4- α -D-glucosidic linkage in starch. Therefore, starch will rapidly degrade with the addition of enzymes because enzymes typically catalyse the hydrolysis of natural biodegradable polymers, and α -amylase catalyses the hydrolysis of starch.⁷

Recently, several attempts have been made to blend starch with biodegradable synthetic polymers. Among these polymers is polyvinyl alcohol (PVOH) because it is well known as a synthetic biodegradable polymer⁸ and possesses excellent mechanical properties.⁹ Its biodegradability in various microbial environments has been reported, and PVOH is one of the best options to be blended with starch.¹⁰ Much interest lies in blending starch with PVOH¹⁰ because starch/PVOH blends have demonstrated excellent compatibility.^{4,12}

PVOH is a versatile polymer, and it may be the only synthesised polymer with a backbone that consists primarily of –OH bonds that is absolutely biodegradable. PVOH is also an interesting water-soluble synthetic polymer with a broad range of applications. Due to the solubility and biodegradability of PVOH, PVOH films are increasingly used in packaging applications.¹³ However, the biodegradability of PVOH depends on its degree of hydrolysis and its molecular weight. PVOH has the advantages of good film formation, strong conglutination and high thermal stability. In recent years, PVOH has been increasingly applied in the material industry and has been combined with starch.¹⁴

Inspired by those studies, the aim of this work was to investigate the biodegradation potential of PVOH/CS blend films in solid and solution media. The blend films were also characterised using scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1 Materials

PVOH was purchased from Merck Inc. (DP 1799 ± 50; average molecular weight: 145,000; hydrolysis rate: 90%; pH: 4.5–7; density: 1.3 g/cm³). Corn starch containing 1.7% moisture, 0.23% protein and 0.075% fat was purchased from Thye Huat Chan (M) Sdn. Bhd. Water-soluble hexamethylenetetramine (HMTA) with a density of 1.331 g/m³ was supplied by Fluka Chemical Corp. through Sigma-Aldrich (M) Sdn. Bhd. Glycerol was produced by BDH and supplied by VWR International. Tween-80 with a density of 1.07 g/m³ was purchased from Merck (M) Sdn. Bhd. Paraffin wax was purchased from Sigma-Aldrich (M) Sdn. Bhd., and de-ionised water was used as a solvent.

2.2 Sample Preparation

The samples were prepared according to Xiong et al.¹⁴ PVOH and corn starch were poured into a round flask. Then, de-ionised water was added, and the mixture was stirred with a high speed mixer in a constant temperature water bath for 30 minutes. An approximate amount of hexamethylenetetramine was added to the blend (1% on a dry basis of the combined weight of starch and PVOH) and stirred for another 40 minutes. The plasticiser glycerol, the deformer Tween-80 and paraffin wax were then added, and the solution was mixed for 10 minutes until a smooth film surface was obtained. After that, the mixture was cast onto a glass plate that was placed on a flat surface. The blend was dried in an enclosed environment for almost 12 hours and then cured in the oven for 30 minutes.

Finally, the film was peeled off of the glass plate. These steps were repeated for all samples.

3. CHARACTERISATION

3.1 Enzymatic Testing

An enzymatic mixture containing certain amounts of distilled water, α -amylase and β -amylase were placed in a conical flask. The dried samples were cut into 3×3 cm square specimens, and the samples were then weighed accurately using a digital balance and immersed in a conical flask.⁴

The flasks were placed in a shaking incubator at a rate of 120 rpm for 60 hours at 30°C. The samples were removed and rinsed with distilled water to remove the enzymatic mixture and dried in a desiccator under vacuum for 24 hours before being weighed. The degree of enzymatic degradation [DED (%)] was calculated using Equation 1:²

$$\text{DED}(\%) = \frac{W_i - W_H}{W_i} \times 100 \quad (1)$$

where W_H is the dry weight of the specimen after the enzymatic treatment, and W_i is the initial dry weight of the specimen.

3.2 Soil Burial Test

The films were buried in composted soil that was purchased from a flower nursery; the test was performed according to the method published by Thakore et al.¹⁵ with a slight modification. Two different pots were filled to their approximate capacity of 10 L with soil and compost. The samples were cut into 30×50 mm pieces and buried in the soil at a depth of 10 cm. The soil was placed in the laboratory, and the moisture of the soil was maintained by sprinkling water at regular time intervals. The excess water was drained through a hole at the bottom of the pot.

The degradation of the samples was determined at regular time intervals (7 days) by carefully removing the sample from the soil and washing it gently with distilled water to remove soil from the film. The sample was dried under vacuum until a constant weight was obtained. Weight loss of the sample over time was used to indicate the degradation rate of the soil burial test.

The soil burial test was studied by evaluating the weight loss of the film over time. The weight loss was determined every seven days from the starting day, and was calculated using Equation 2:

$$\text{Weight Loss (\%)} = \frac{W_i - W_d}{W_i} \times 100 \quad (2)$$

where W_d is the dry weight of the film after being washed with distilled water, and W_i is the initial dry weight of the specimen.

3.3 Kinetic Studies of Water Absorption and Water Solubility Testing

Dried films were immersed in distilled water and in an acidic solution containing 0.2 M sulphuric acid (H_2SO_4) at room temperature (25°C). A reading was taken every 3 days until the film reached equilibrium weight. The moisture on the surface film was removed, and the weight of the film was measured. The moisture content (M_t) absorbed by each sample was calculated from its weight before absorption, W_o , and after absorption, W_t , using Equation 3.

$$W_t (\%) = \frac{W_t - W_o}{W_o} \times 100 \quad (3)$$

From the water absorption, we can determine the diffusion coefficient or diffusivity, D , that was calculated from the slope of moisture content, M_t , versus the square root of time, \sqrt{t} , as shown in Equation 4:

$$D = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (4)$$

where M_m is the maximum moisture content, and h is the thickness of the sample. Assuming the absorption process was linear at an early stage of immersion, the time was taken at the beginning of absorption process so that the weight change was expected to vary linearly with the square root of time.¹⁶

For the water solubility testing, the dried films were immersed in distilled water and an acidic solution made from 0.2 M H_2SO_4 at room temperature (25°C). After equilibrium was reached (24 hours), the moisture on the surface of the film was removed and the weight of the film was measured. The swelled films were dried again for 24 hours at 60°C . Their water solubility (W_s) was then calculated using Equation 5:

$$W_s (\%) = \frac{W_o - W_d}{W_o} \times 100 \quad (5)$$

where W_d is the dry weight of the swelled film, and W_o is the weight before the absorption.¹⁷

3.4 Tensile Properties Test

The tensile test was performed using an Instron 3366 testing machine according to ASTM D882. Each sample had a width of 6.4 mm. The average thickness of the samples was about 0.060 mm. The tensile test was conducted using a cross head speed of 1.3 mm/min.

3.5 Scanning Electron Microscopy (SEM)

The PVOH/CS blend films were cryogenically frozen in liquid nitrogen. After that, the samples were manually fractured after removal from the liquid nitrogen. The fractured surfaces were vacuum-coated with gold. The morphology of the samples was investigated using a scanning electron microscope (SUPRA 35VP, ZEISS).

4. RESULTS AND DISCUSSION

4.1 Enzymatic Testing

The weight loss of the film is shown in Figure 1. The DED was calculated after the sample had been immersed in the enzymatic solution for 60 hours. The graph shows an increase in degradation with increasing corn starch content. The degradation rate of pure PVOH was slower than that of PVOH/CS composite films. A higher degradation rate was observed for the 30/70 weight percent PVOH/CS sample, which underwent 92.45% weight loss after 60 hours of immersion. This observation was due to the PVOH/CS films absorbing more of the amylase solution than pure PVOH because of the excess of -OH group that facilitated the penetration of α - and β -amylase into the PVOH/CS blend films and subsequently enhanced the amylase attack on the corn starch.¹⁸ The films tended to absorb more of the enzymatic solution as the CS content increased. Therefore, the CS content affected the weight loss of the sample.

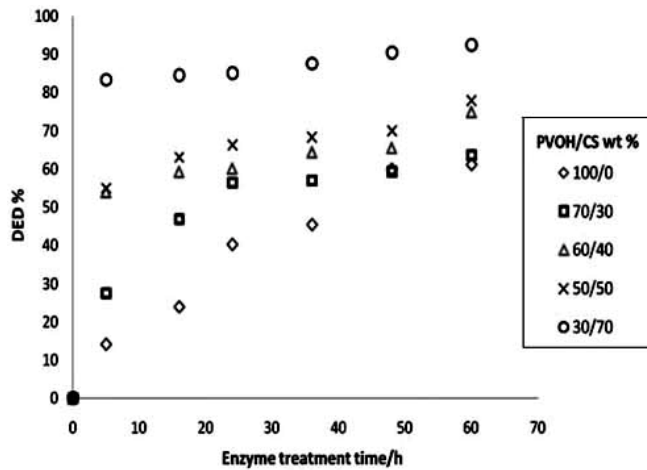


Figure 1: Enzymatic degradation of PVOH (100/0) and PVOH/CS films using α -amylase and β -amylase.

Furthermore, α -amylase and β -amylase function in different ways to hydrolyse the acetal bonds of starch. β -amylase generally hydrolyses only the main chain acetal bonds and does not affect the branch point. However, α -amylase attacks both the main chain as well as the branch.⁴ α -amylase enzymes are endoamylases, which catalyse the hydrolysis of the internal α -1,4-glucosidic linkage in the starch in a random manner. These enzymes break down the starch into smaller sugar units, which are eventually converted to the individual basic glucose unit.

β -amylase enzymes are exohydrolases, which release β -maltose from the non-reducing ends of α -1,4-linked poly- and oligoglucans until the first 1,6-branching point along the substrate molecule is encountered.¹⁹ α -amylases hydrolyse starch more rapidly than β -amylase because α -amylase attacks both the main and branched chains. The hydrolysis of the starch weakens the interaction between starch and PVOH and thereby results in higher weight loss by the PVOH/CS film. The corn starch also leaches out from the sample, which results in higher weight loss by the PVOH/CS samples due to amylase enzymes attacking the corn starch at the sample surface. This result shows that starch is more susceptible to being attacked by enzymes.

4.2 Soil Burial Test

Figures 2 and 3 show the weight loss of the pure PVOH and PVOH/CS films in soil and compost, respectively. In the figures, the biodegradability

increased up to 85% as the burial time increased in both the soil and compost for 8 weeks. All of the films in soil and compost degraded rapidly in the first 7 days. This rapid degradation was due to the composting process, which occurred in two main stages: an active composting stage and a curing period. In the first stage, the temperature rose and remained elevated as long as there was available oxygen, which resulted in strong microbial activity.

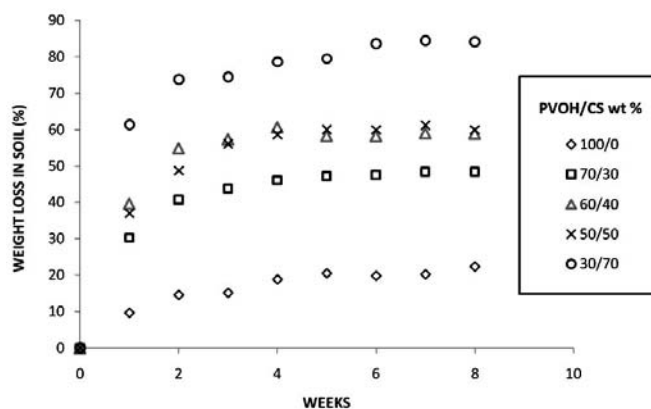


Figure 2: Weight loss of PVOH/CS films after 8 weeks in soil.

In the second stage, the temperature decreased but the film continued to compost at a slower rate.²⁰ In both the soil and compost, the 30/70 PVOH/CS sample showed the highest weight loss while pure PVOH showed the lowest weight loss over time. This finding was attributed to the corn starch content in the film because corn starch is more biodegradable than pure PVOH. The PVOH, which is biodegradable due to its high hydrolysability, exhibited a higher resistance against soil burial degradation.¹⁰ The addition of compost resulted in an approximate 2–3% increase in the degradation rate. Compost is composed of organic materials derived from plant and animal matter that have been decomposed largely through aerobic decomposition. It can be rich in nutrients. The compost itself is beneficial for the land in many ways because it can act as a soil conditioner, a fertiliser, an addition of vital humus or humic acids, and a natural pesticide for soil. The nutrients in the compost can degrade the film more rapidly than unamended soil.

As shown in Figure 3, for the duration of 14 to 30 days, the weight loss was slightly lower but the composting process did not stop at a particular point. Rather, it continued slowly until the last remaining nutrients were consumed by the remaining micro-organisms and almost all of the carbon had been converted into carbon dioxide.²⁰

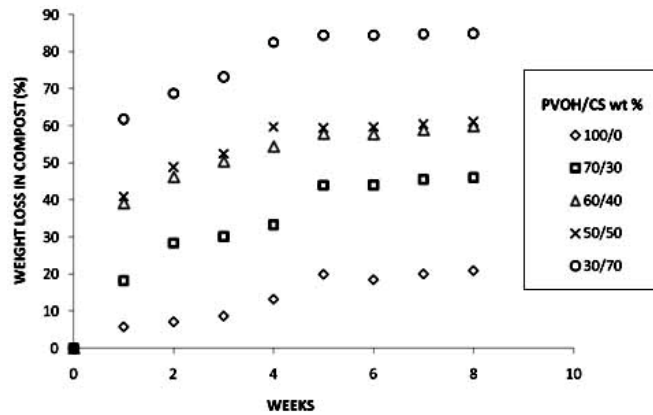


Figure 3: Weight loss of PVOH/CS films after 8 weeks in compost.

4.3 Kinetic Studies of Water Absorption and Water Solubility Testing

One of the major drawbacks to the utilisation of starch-based material is its water absorption tendency, and any improvement in water resistance is therefore highly important.¹¹ Figures 4 and 5 show the percentage of moisture absorption, M_t , of pure PVOH and PVOH/corn starch blend films as a function of $t^{1/2}$ in distilled water and in acidic solution.

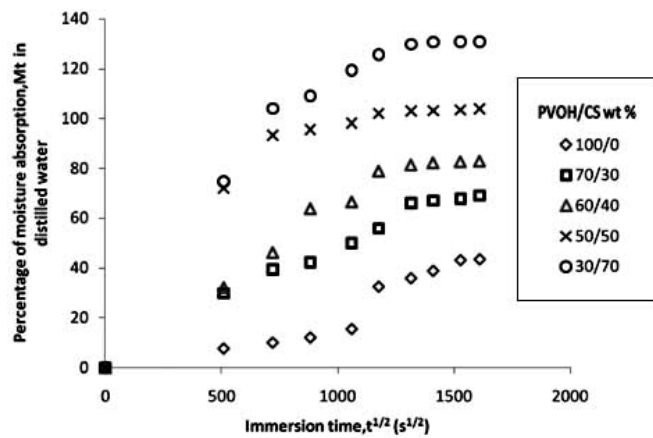


Figure 4: Effect of corn starch on water uptake of PVOH composites in distilled water.

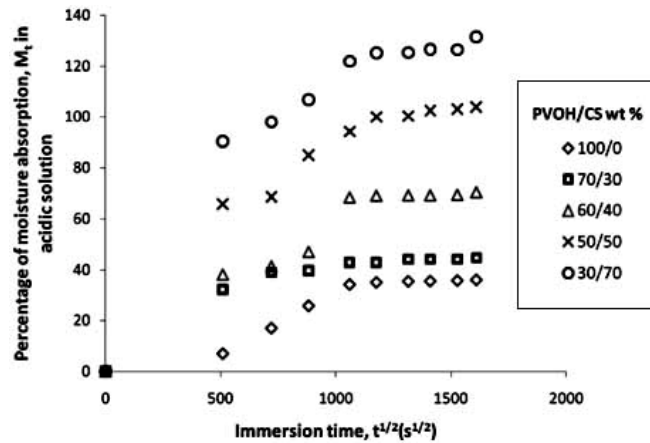


Figure 5: Effect of corn starch on water uptake of PVOH composites in an acidic solution.

The PVOH films that contained starch demonstrated higher water uptake than the pure PVOH films. Water uptake increased with increasing immersion time and starch content. This finding is due to the hydrophilic character of natural starch, which is responsible for the water absorption in the composites. Therefore, a higher starch content led to a higher amount of water being absorbed.²⁰ The gelatinised starch favoured degradation of the blends when immersed in water; this was likely due to the rupture of the grains during starch gelatinisation.²¹ The water uptake behaviour of both pure PVOH and the PVOH/CS blend films obeyed Fick's law because an initial linear relationship between M_t and $t^{1/2}$ was observed and was followed by saturation. For the first few days of immersion, the graph shows a rapid moisture uptake. The M_m and D values are summarised in Table 1.

Table 1: The effect of corn starch on the diffusion constant (D) and the maximum moisture content (M_m) of PVA composites in distilled water and in the acidic solution.

PVOH/CS	100/0	70/30	60/40	50/50	30/70
<i>Distilled water</i>					
D ($\times 10^{-9}$ m ² /s)	0.2310	1.4846	1.9291	6.1599	14.1995
M_m (%)	43.503	67.012	83.002	103.256	130.76
<i>Acidic solution</i>					
D ($\times 10^{-9}$ m ² /s)	0.29731	3.4684	3.8802	5.1300	22.301
M_m (%)	35.5	42.702	69.236	102.98	126.265

As shown in Table 1, the PVOH/corn starch films immersed in distilled water gave higher M_m values that kept increasing as the corn starch content increased. This finding is due to the presence of large molecules in the acidic solution that slow the diffusion process into the matrix of the composite material and thereby result in lower absorption kinetic parameters.²² The values of M_m and D were higher in the PVOH/CS blend films than in the pure PVOH film; this finding is attributed to the hydrophilic nature of the PVOH and corn starch due to the presence of hydroxyl groups that are available in both PVOH and corn starch to interact with water molecules.¹⁸ It was expected that the PVOH/CS blend films would absorb moisture more rapidly than the pure PVOH film because starch is prone to moisture and water absorption due to its hygroscopic nature. Water molecules may act as a natural plasticiser by making the starch more flexible compared to its characteristic as a hard and rigid filler in a complete dry state.²³ Water absorption may drop slightly with increasing immersion time because some starch particles are leached away from the sample.²⁴ It was expected that the starch would absorb moisture faster than pure PVOH.

Figure 6 shows the water solubility trends of the films. The graph shows an increase in water solubility percentage with increasing corn starch content. PVOH/CS (30/70) shows the highest water solubility in distilled water and in the acidic solution because of the amylopectin branch structure of the starch. The water absorption and water solubility of the film are directly proportionate. This finding is a normal behaviour as an increase in water absorption will make the film easier to dissolve in water. When water is absorbed onto the hydrophilic group, mainly through hydrogen bonding or weak electrostatic interactions,²⁵ the film can be easily dissipated with water molecules. Therefore, it is relevant to relate the effect of the hydroxyl group in the water absorption mechanism. However, the water solubility properties of PVOH depend on the degree of hydrolysis and polymerisation with its maximum at 88% of hydrolysis, where higher solubility shows lower degree of polymerisation.²⁶ The solubility means the materials are capable of dissolving in the solvent used. In this case, it can be seen that the percentage of water solubility in distilled water is higher than that in the acidic solution. This is because the films are capable of dissolving in distilled water rather than in the acidic solution, which has a higher concentration than distilled water.

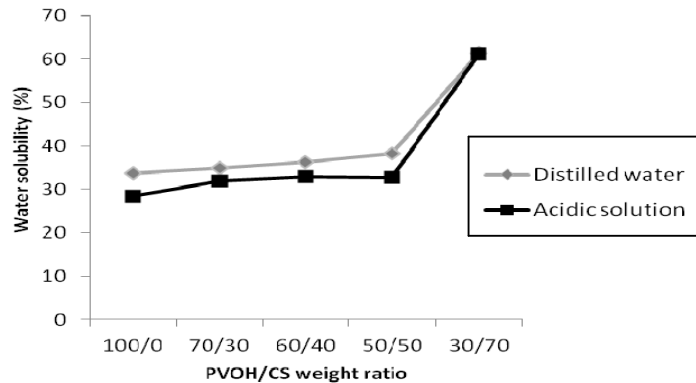


Figure 6: Water solubility of PVOH/CS films in distilled water and in an acidic solution.

4.4 Tensile Properties Test

A tensile test was performed to investigate the tensile properties of the PVOH/CS films. Because polymer materials, such as films, may be subjected to various kinds of stress during use, the determination of the mechanical properties involves not only scientific but also technological and practical aspects.² Figure 7 shows the effect of the blend ratio on the tensile strength of PVOH/corn starch blend films. It shows that as the amount of corn starch increased, the tensile strength of the films decreased accordingly. This result is because of the amorphous nature of starch,³ which leads to a lower tensile strength of the film. The pure PVOH film showed the highest tensile strength at 35.35 MPa. When corn starch was introduced, the 70/30 PVOH/CS sample gave the highest result (9.58 MPa) compared to other PVOH/CS films. The decrease in tensile strength with the incorporation of the starch is due to the filler-matrix interaction. With higher starch loading, filler-filler interactions become more pronounced than filler-matrix interactions.²⁷

The elongation at break also showed the same pattern and proportions as the tensile strength graph. The percentage of elongation at break continuously decreased as the amount of corn starch in the matrix was increased. However, the modulus of the samples increased with increasing corn starch content. The same pattern was observed for tensile strength; pure PVOH showed the highest percentage of elongation at break at 327.2% while the 70/30 PVOH/CS film showed the maximum percentage of elongation at break at 119.1%. The smallest PVOH weight percent showed the lowest percentage of elongation at break for the PVOH/CS films.

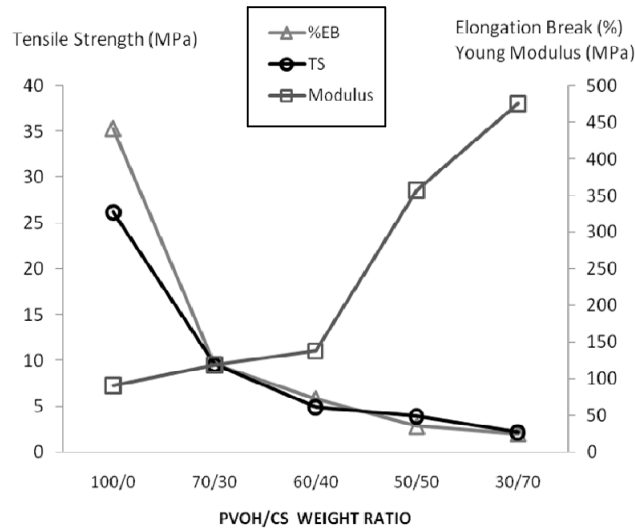


Figure 7: Mechanical properties of blends with different PVOH/CS contents.

4.5 Scanning Electron Microscope (SEM) Analysis

The morphologies of PVOH and PVOH/CS blend films are shown in Figure 8. Figure 8(a) depicts the corn starch granules, which are elliptical in shape. Pure PVOH contained voids, which indicate that the bubble was trapped in the sample during the casting. As the corn starch content increased, the corn starch phase changed from the dispersed phase, which indicates that amorphous starch is partially miscible with PVOH. Corn starch was finely dispersed in the PVOH matrix. Adding up to 70% more corn starch caused the cryo-fractured surface to become rougher and more brittle. PVOH was finely dispersed in the corn starch granules, but the starch granules coalesced significantly at the same time. The viscosity of the starch granules is much higher than PVOH, and the mechanical properties of the PVOH/CS blend reduced when the concentration of the corn starch was increased from 30% to 70%.¹⁰

From the SEM micrograph, it can be concluded that the corn starch granules dispersed well in the 70/30 PVOH matrix. This dispersion helps to improve the mechanical properties of the film and shows an agreement with the tensile property results.

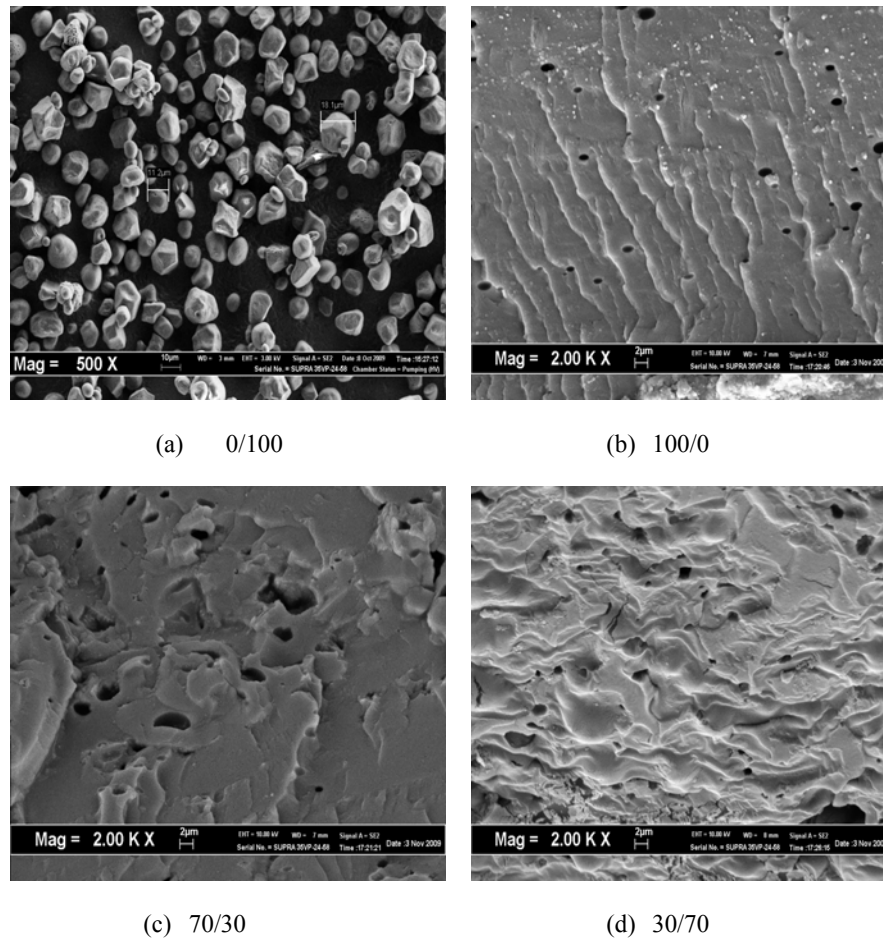


Figure 8: SEM micrographs of (a) corn starch granules, (b) PVOH/CS, (c) 70/30 PVOH/CS and (d) 30/70 PVOH/CS.

5. CONCLUSION

The obtained results can be summarised as follows: the addition of corn starch to the PVOH matrix increases the degradation rate of the sample. The degradation process increases as the corn starch content increases. The water absorption of PVOH/CS films followed Fick's law of diffusion. The D and M_m values increased as the corn starch content increased. The diffusion coefficient in the acidic solution is higher than for distilled water, whereas the M_m value in the acidic solution was less than in distilled water. PVOH/CS composites were more

soluble in the distilled water medium relative to the acidic solution. The tensile properties of the film decreased with increasing corn starch content in PVOH compared to pure PVOH film. The best tensile strength of a PVOH/CS blend was at 9.579 MPa; its elongation at break was at 119.1% and its PVOH/CS content was 70/30. In the morphology study, it was observed that adding up to 70% more corn starch caused the cryo-fractured surface to become rougher and more brittle. From the SEM figure, it can be concluded that corn starch granules disperse well in the 70/30 PVOH/CS matrix. This dispersion is useful to improve the mechanical properties of the film and shows an agreement with the tensile property results. This study shows that starch increases the degradable properties but retards the strength of PVOH/CS composites.

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7. REFERENCES

1. Yang, J-H., Park, J., Kim, D. & Lee, D-H. (2004). Effects of calcium carbonate as the expanding inhibitor on the structural and mechanical properties of expanded starch/polyvinyl alcohol blends. *J. Appl. Polym. Sci.*, 93(4), 1762–1768.
2. Guohua, Z., Ya, L., Cuilan, F., Min, Z., Caiqiong, Z. & Zongdao, C. (2006). Water resistance, mechanical properties and biodegradability of methylated-cornstarch/poly(vinyl alcohol) blend film, polymer degradation and stability. *Polym. Degrad. Stab.*, 91(4), 703–711.
3. Tang, S., Zou, P., Xiong, H. & Tang, H. (2007). Effect of nano-SiO₂ on the performance of starch/polyvinyl alcohol blend films. *Carb. Polym.*, 72(3), 521–526.
4. Yun, Y-H., Wee, Y-W., Byun, H-S. & Yoon, S-D. (2008). Biodegradability of chemically modified starch (RS4)/PVA blend films: Part 2. *J. Polym. Environ.*, 16(1), 12–18.
5. Byung, C. J., Soo, Y. H., Jeong, G. J. & Young, C. B. (2001). Mechanical properties and morphology of the modified HDPE/Starch reactive blend. *J. Appl. Polym. Sci.*, 82(13), 3313–3320.
6. Funke, U., Bergthaller, W. & Lindhauer, M. G. (1998). Processing and characterization of biodegradable product based on starch. *Polym. Degrad. Stab.*, 59(1–3), 293–296.

7. Tuovinen, L., Peltonen, S., Liikola, M., Hotakainen, M., Lahtela-Kakkonen, M., Poso, A. & Jarvinen, K. (2004). Drug-release from starch-acetate microparticles and films with and without incorporated α -amylase. *Biomater.*, 25(18), 4355–4362.
8. Nakashima, T., Xu, C., Bin, Y. & Matsuo, M. (2001). Morphology and mechanical properties of poly(vinyl alcohol) and starch blends prepared by gelation/crystallization from solutions. *Colloid Polym. Sci.*, 279(7), 646–654.
9. Huang, X. & Netravali, A. (2009). Biodegradable green composites made using bamboo micro/nano fibrils and chemically modified soy protein resin. *Compos. Sci. Technol.*, 69(7–8), 1009–1015.
10. Zou, G-X., Jin, P-Q. & Xin, L-Z. (2008). Extruded starch/PVA composites: Water resistance, thermal properties and morphology. *J. Elastomers Plas.*, 40(4), 303–316.
11. Wang, J., Lu, Y., Yuan, H. & Dou, P. (2008). Crystallization, orientation morphology, and mechanical properties of biaxially oriented starch/polyvinyl alcohol films. *J. Appl. Polym. Sci.*, 110(1), 523–530.
12. Kondo, T., Sawatari, C., Manley, R. S. J. & Gray, D. G. (1994). Characterization of hydrogen bonding in cellulose-synthetic polymer blends systems with regioselectively substituted methycellulose. *Macromol.*, 27(1), 210–215.
13. Pavol, A., Darina, K., Miroslav, K., Dusan, B. & Barbora, S. (2002). Poly(vinyl alcohol) stabilisation in thermoplastic processing. *Polym. Degrad. Stab.*, 78(3), 413–421.
14. Xiong, H-G., Tang, S-W., Tang, H-L. & Zou, P. (2008). The structure and properties of a starch-based biodegradable film. *Carb. Polym.*, 71(2), 263–268.
15. Thakore, I. M., Desai, S., Sarawade, B. D. & Devi, S. (2001). Studies on biodegradability, morphology and thermomechanical properties of LDPE/modified starch blends. *Eur. Polym. J.*, 37(1), 151–160.
16. Md Akil, H., Cheng, L. W., Mohd Ishak, Z. A., Abu Bakar, A. & Abd Rahman, M. A. (2009). Water absorption study on pultruded jute fibre reinforced unsaturated polyester composites. *Compos. Sci. Technol.*, 69(11–12), 1942–1948.
17. Park, H. R., Chough, S. H., Yun, Y. H. & Yoon, S. D. (2005). Properties of starch/PVA blend films containing citric acid as additive. *J. Polym. Environ.*, 13(4), 375–382.
18. Yew, G. H., Mohd Yusof, A. M., Mohd Ishak, Z. A. & Ishiaku, U. S. (2005). Water absorption and enzymatic degradation of poly(lactic acid)/rice starch composites. *Polym. Degrad. Stab.*, 90(3), 488–500.
19. Moriyama, T. & Ikeda, H. (1996). Hydrolase acting on glycosidic bonds: Chromatographic and electrophoretic separations. *J. Chromatogr. B: Biomed. Sci. Appl.*, 684(1–2), 210–216.

20. Kale, G., Kijchavengkul, T., Auras, R., Rubino, M., Selk, S. E. & Singh, S. P. (2007). Compostability of bioplastic packaging materials: An overview. *Macromol. Biosci.*, 7(3), 255–277.
21. Rosa, D. S., Guedes, C. G. F., Pedroso, A. G. & Calil, M. R. (2004). The influence of starch gelatinization on the rheological, thermal, and morphological properties of poly(ϵ -caprolactone) with corn starch blend. *Mater. Sci. Eng. C*, 24(5), 663–670.
22. Daly, H. B., Brahim, H. B., Hfaied, N., Harchay, M. & Boukhili, R. (2007). Investigation of water absorption in pultruded composites containing fillers and low profile additives. *Polym. Compos.*, 28(3), 355–364.
23. Preechawong, D., Peesan, M., Supaphol, P. & Rujiravanit, R. (2004). Characterization of starch/poly (ϵ -caprolactone) hybrids foams. *Polym. Test.*, 23(6), 651–657.
24. Ke, T. Y., Sun, X. Z. & Seib, P. (2003). Blending of poly(lactic acid) and starches containing varying amylose content. *J. Appl. Polym. Sci.*, 89(13), 3639–3646.
25. Brazel, C. S. (2003). In Ottenbrite, R. M. & Kim, S. W. (Eds.). *Polymeric drugs and drug delivery system*. Lancaster, PA: CRC Press.
26. Alexy, P. et al. (2003). Poly(vinyl alcohol)-collagen hydrolysate thermoplastic blends: II. Water penetration and biodegradability of melt extruded films. *Polym. Test.*, 22(7), 811–818.
27. Sharma, N., Ismail, H. & Mohd Ishak, Z. A. (2000). Mechanical, water absorption and enzymatic degradation properties of sago starch filled linear low density polyethylene. *Intern. J. Polymeric Mater.*, 47(2–3), 351–366.