

Effect of Molecular Weight of Polyvinyl Alcohol on Properties of Starch Film Cross-linked with Glutaraldehyde

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Abstract—Development of biodegradable packaging film is a need of the day to avoid environmental pollution. In this study, effect of molecular weight (14,000 Da and 1,25,000 Da) of polyvinyl alcohol has been studied on the mechanical property and water vapour barrier property of film developed from starch-polyvinyl alcohol blend, stored for 30-90 days. PVOH-L showed better mechanical properties, namely higher tensile strength and elongation for the period of 30-60 days. Molecular weight shows no effect on water vapor barrier property.

Keywords: Biodegradable films; Corn starch; Cross-linking; Polyvinyl Alcohol; Mechanical properties; Barrier properties.

1. INTRODUCTION

Packaging protects the food from various damages caused by microorganisms, physical parameters, or other biochemical reactions [1-3]. Additionally, packaging renders ease in handling, attractiveness, and information about the packed product [1]. The ideal food packaging material should serve these purposes and should be cost effective. The use of multilayer flexible synthetic plastic films made from petroleum-based raw materials is increasing for food packaging because of low cost and functional advantages over other materials [1]. Such films, however, are non-biodegradable, non-recyclable and therefore create serious environmental pollution [4].

Triggered by the risk arising from synthetic packaging films, several attempts are being taken to develop biodegradable alternatives. Starch has been a target raw material for this purpose as it is inexpensive, abundantly available and renewable. It is composed of linear amylose (poly- α -1,4-D-glucopyranoside) and branched amylopectin (poly- α -1,4-D-glucopyranoside and poly- α -1,6-D-glucopyranoside) [5]. However, pure starch films show low elongability and poor water vapour barrier properties [6-9]. To improve the properties, researchers have blended starch with other biodegradable polymers such as methyl cellulose and hydroxyl propylmethyl cellulose [9] polyhydroxyalkanoates [10] poly

lactic acid (PLA) [11-12] and poly vinyl alcohol (PVOH) [13-17]. PVOH contains secondary hydroxyl group [18] that easily forms hydrogen bonds with starch [18-20]. Films from starch and PVOH blends not only show improved mechanical properties over starch alone [13-17] but also are biodegradable [19].

Poly vinyl alcohol (PVOH) is produced by hydrolysis of poly vinyl acetate and molecular weight (MW) of resultant alcohol highly depends on degree of hydrolysis (DH) [21]. The physical characteristics and specific functional uses of PVOH e.g., solubility in water, crystallisation, etc., depend on its molecular weight. Influences of degree of hydrolysis and molecular weight of PVOH on properties of fish myofibrillar protein/PVOH blend films have been studied by Limpan et al. [21]. Maria et al. [22] investigated the effect of the degree of hydrolysis of the PVOH on the color, opacity, and thermal and mechanical properties of films based on PVOH and gelatin blends.

The report on properties of starch/PVOH film affected by the molecular weight of PVOH is scanty in literature. Very recently, Negim et al. [23] studied the effect molecular weight of PVOH on physical and mechanical properties of PVOH/starch blend films was studied. Sen and Das [13] reported structural alteration during storage of starch/PVOH blend film cross-linked with glutaraldehyde. The present study aims to investigate the effect of molecular weight of polyvinyl alcohol on properties of starch film cross-linked with glutaraldehyde, when stored for different time periods. .

2. MATERIALS AND METHODS

2.1 Ingredients for film making

The ingredients in film making included corn starch (ANGEL LK18 procured from Angel Starch and chemicals, Tamil Nadu, India), polyvinyl alcohol (PVOH: LobaChemie, MW 1,25,000

and 14,000), glycerol (Merck, 98% GR), glutaraldehyde (Merck, 25%) and distilled water.

2.2 Methods

2.2.1 Casting and storing of film

Blend was prepared in 250 ml conical flask. Measured amount of PVOH was put in 30 ml of distilled water and kept for overnight. The mixture was heated in boiling water bath in order to obtain clear solution of PVOH. Measured amount of corn starch, glycerol and glutaraldehyde were added to this solution followed by volume make up by rest of distilled water. The blend was heated in boiling water bath. After gelatinisation had completed, the mass was poured in the semi cylindrical vessel of 250 ml thin layer chromatography applicator. The cast film was dried in an incubator at 40°C for 24 h. The dried film was peeled off from the plate, and put in paper flap. Flaps in stack was kept in polythene bag, and stored for 3 months in ambient condition. Replicates were prepared for each composition. The composition of the blends is shown in the Table 1. Chowdhury and Das [9] have described a detail of film preparation and storing.

Table 1: Composition of starch-PVOH blend

Component	Quantity (w/w)
Corn Starch	6.47
PVOH(L/H)*	0.59
Glycerol	2.90
Glutaraldehyde	0.59
Water	89.45

* L: low MW and DH 98.5-99.2 mol %; H: high MW and DH 86-89 mol %

2.2.2 Conditioning

The films were conditioned prior to any test at 50% RH and 25±1°C for 48 hours (ASTM D618). It helped to maintain the water activity at 0.5 during measurement.

2.2.3 Determination of film properties

The following methods were used to measure thickness, tensile strength and elongation, and water vapour barrier properties of the films.

2.2.3.1 Film thickness

Thickness was measured by Dial thickness gauge (Mitutoya 7301) with an accuracy of 0.01 mm, at least at 5 random positions of the film samples.

2.2.3.2 Mechanical properties

Ultimate tensile strength (UTS) and elongation were measured as per the standard methodology (ASTM D882-97) using Instron Universal Testing machine (INSTRON 5965 U 2597, Universal Testing Machine, USA). UTS represents the maximum stress (peak force/cross-sectional area enduring the

force) that a material can withstand while being stretched at a constant rate or pulled before failing or breaking, and is expressed in MPa. Elongation is considered at break point, and presented as 'elongation at break (EAB)'. It is represented as extension in length of tensile specimen due to pulling, and expressed as % of original length.

Strips (100 mm effective length x 10 mm breadth) of films were cut both vertically (along the web) and horizontally (perpendicular to the web) as shown in Fig. 1. Cut samples were conditioned and the thickness measured as mentioned above. Samples were then pulled at a rate of 10 mm/min, and the readings were noted.

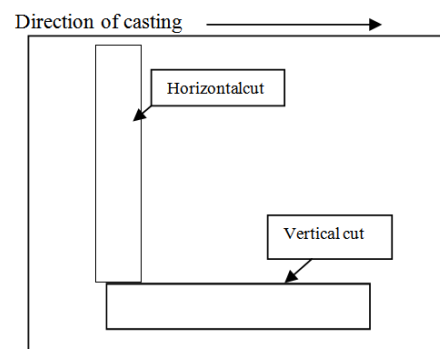


Fig. 1: Cutting of film

2.2.3.3 Water vapor permeability

Water vapor permeability of films was determined by using gravimetric cup method by as per ASTM E96 methodology. A perplex cup was filled half of its capacity with distilled water (100% relative humidity, RH). The test film cut in the form of circular disc followed by conditioning and measurement of thickness was put on the top of permeable cup. A silicon rubber washer was placed on the film followed by fixing the collar lid on it. The cup was then placed inside a desiccator maintained at 50% RH. The desiccator was kept at 25 °C inside an incubator. Thus, a fixed RH gradient was maintained across the film surface. Initial weight of the cup (W_1 , g) and the final weight (W_2 , g) after 24 h were recorded, and WVP value was calculated using eq. (1)

$$\text{WVP (g. mm/kPa. m}^2\text{. h)} = \frac{(W_1 - W_2) h}{(P_{A1} - P_{A2}) A_1 T_1} \quad (1)$$

Where

W_1 = Initial weight of the cup (g)

W_2 = Final weight of the cup (g)

h = Film thickness (mm),

P_{A1} = Partial pressures (KPa) of water vapor at 100% RH

P_{A2} = Partial pressures (KPa) of water vapor at 50% RH

A_1 = Area of the exposed film (m^2) and

T_1 = Time (hour, h) during which the change in weight had taken place

2.3 Statistical analysis

The effect of storage days (treatment) on the respective mean value of response (treatment mean) was analyzed statistically following analysis of variance (F-test) at 1 or 5% levels of significance using single factor experiment with completely randomized design with equal replications [24]. Significant F-test assures that the observed difference among the treatment means is real and not due to chance. Further, in case of positive F-test the least significant differences (LSD) amongst the mean values of response i.e. treatment means were estimated at 1 or 5% probability ($p < 0.01$ or 0.05) levels to ascertain any significant difference among the pair of treatments. When treatment was only two, then pair comparison was done based on t-test for equal replications [25]. All these calculations including the evaluation of mean value and standard deviation (SD) were done using Microsoft Excel 2007 (Microsoft Corp., USA).

3. RESULTS AND DISCUSSIONS

Irrespective of molecular weight of PVOH, the produced films were transparent, self-supporting and flexible.

3.1 Thickness

Thickness of the films was found to be in the range of 0.08mm – 0.108mm. Such thickness is quite comparable to the thickness of films developed from starches from yam, sago, and corn as reported by several scientists [26-27] and [9].

3.2 Tensile strength and elongation

ANOVA revealed that storage period exerts significant effect on tensile strength and elongation for both low and high molecular PVOH incorporated films.

3.2.1 Tensile strength

Tensile strength of starch/PVOH films recorded after every 30 days interval is presented in Table 2. For easy visualization, the data are also shown in Fig. 2. In case of PVOH-L film, tensile strength increases for the interval of 30-60 days (LSD, $p < 0.05$) (59%), following no significant change thereafter upto 90 days. For PVOH-H film, though the trend apparently indicates an increasing tendency, the difference on the basis of ($LSD_{0.05}$) is insignificant for each successive interval.

Table 2: Tensile strength of starch/PVOH film for different storage period.

Days	Tensile strength@, MPa (PVOH-L)	Tensile strength@, MPa PVOH-H	t0.05
30	6.30+1.41*	6.46+1.13§*	1.895
60	10.02+2.27§	7.34+1.38§	2.935
90	10.91+3.92§*	9.48+3.97§*	3.71
LSD0.05	3.395	3.113	
LSD0.01	5.04	4.621	

*Mean values are insignificantly different ($t_{0.05}$) in row; @ F-test positive ($p < 0.05$) for a column; §Mean values are insignificantly different in column.

Concerning molecular weight, it can be seen from the Table that on 30th and 90th day, high and low MW show no significant difference on tensile strength by paired t-test, whereas a significant difference is observed only on 60 day, PVOH-L showing much higher value i.e., 10.02 MPa compared to 7.34 MPa for PVOH-H (36.5% difference). Decrease of strength for pure PVOH films with increase in its molecular weight has been observed by El-Kader et al.[28]. According to them, increase of molecular weight might have lead to an increasing degree of disorder in the film matrix reducing the strength of film. On the other hand Limpan et al. [21] reported that the fish myofibrillar protein/PVOH blend films with higher MW of PVOH were more tensile resistant, as indicated by the greater tensile strength. Negim et al. [23] did not observe prominent effect of MW also in case of corn-starch/PVOH blend film.

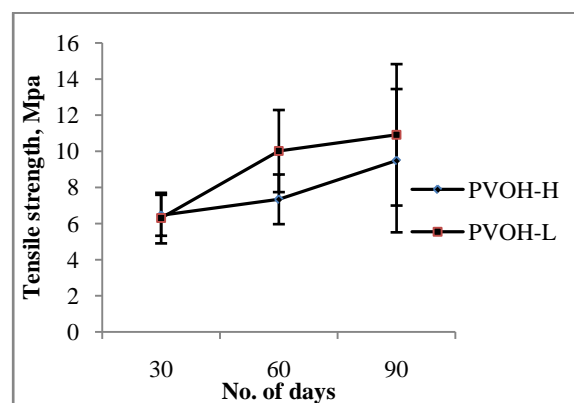


Fig. 2: Variation of tensile strength of starch/PVOH films with storage days

3.2.2 Elongation

Table 3 presents the values of elongation at break, %, of starch/PVOH films recorded after every 30 days interval for both types of film. The trend of the same is shown in Fig. 3.

Table 3: Elongation of starch/PVOH film for different storage period.

Days	Elongation@, % PVOH-L	Elongation@, % PVOH-H	t0.05
30	66.97+5.97	37.01+6.54§	4.29
60	43.06+8.79	35.88+7.08§	3.58
90	10.58+8.97*	10.96+4.21*	4.29
LSD0.05	23.82	19.41	
LSD0.01	35.36	28.81	

*Mean values are insignificantly different ($t_{0.05}$) in row; @ F-test positive ($p < 0.05$) for a column; §Mean values are insignificantly different in column.

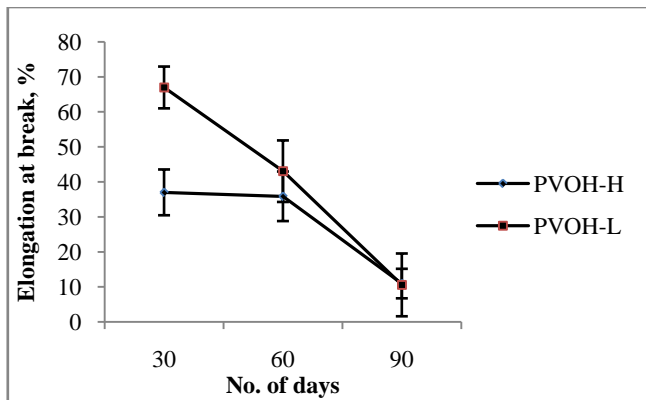


Fig. 3: Variation of elongation at break of starch/PVOH films with storage days

For PVOH-L incorporated films, % elongation decreased significantly (LSD, $p < 0.05$) over each interval of storage time. Thus, over 90 days storage, elongation decreases from 66.97% to 10.58%, i.e., amounting 84.2% reduction. In case of PVOH-H film, significant ($p < 0.05$) decrease is observed over 60-90 days only, and the reduction is $\approx 70.4\%$. This could be due to progress of interactions between starch and PVOH molecules with storage time, as evidenced by Sen and Das [13] by FTIR.

Based on $t_{0.05}$ values, elongation at break of PVOH-L film is found to be greater than that of PVOH-H film on 30th and 60th days. On 90th day, the values are almost same. In this context it may be interesting to state that Maria et al. [22] reported that DH and MW of PVOH did not affect UTS and EAB of pig skin gelatin/PVOH blend film except for the 31-50 KDa MW arising from 88% DH of PVOH, which rendered lowest tensile properties of the film. Silva et al. [29] also reported no noticeable difference of EAB of the pig skin gelatin/PVOH blend film with different DH of PVOH.

3.2.3 Water vapor permeability

The values of water vapor permeability ($\text{g}\cdot\text{mm}/\text{KPa}\cdot\text{m}^2\cdot\text{h}$) of starch/PVOH films corresponding to different MW of PVOH and storage periods are shown in Table 4 and Fig. 4.

Table 4: Water vapour permeability of starch/PVOH film for different storage period.

Days	Water vapour permeability, $\text{g}\cdot\text{mm}/\text{KPa}\cdot\text{m}^2\cdot\text{h}$ (PVOH-L)**	Water vapour permeability, $\text{g}\cdot\text{mm}/\text{KPa}\cdot\text{m}^2\cdot\text{h}$ (PVOH-H)**	$t_{0.05}$
30	0.15+0.04#	0.15+0.05#	2.71
60	0.18+0.019#	0.14+0.003#	2.92
90	0.19+0.012#	0.15+0.019#	2.08

** Duration of storage show insignificant (F test, $p > 0.05$) effect on WVP for both PVOH-L and PVOH-H

#For any particular day, paired t test indicates mean value of PVOH-L and PVOH-H as insignificantly ($p > 0.05$) different

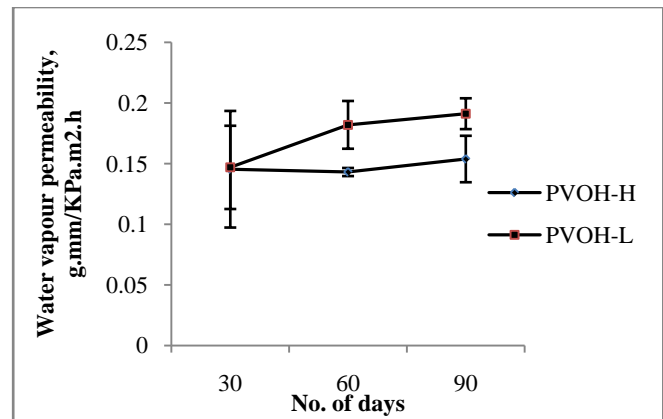


Fig. 4: Variation of water vapour permeability, ($\text{g}\cdot\text{mm}/\text{KPa}\cdot\text{m}^2\cdot\text{h}$), of starch/PVOH films with molecular weight of PVOH and number of days of storage.

No significant effect of storage days (F test, $p > 0.05$) and molecular weight is observed on water vapour permeability of both types of films.

No difference in WVP of fish myofibrillar protein/PVOH blend films containing PVOH with different MW and DH were found ($p > 0.05$) by Limpan et al. [21].

4. CONCLUSION

There was no significant effect of molecular weight of PVOH or storage days on water vapour permeability. Mechanical property like tensile strength and elongation of corn starch/PVOH blend film cross linked with glutaraldehyde is influenced by storage time and molecular weight of PVOH. Between low and high molecular weight PVOH, PVOH-L showed better mechanical properties, namely higher tensile strength and elongation for the period of 30-60 days. Elongation sharply falls after this, during 60-90 days the effect of molecular weight gradually faded. Neither storage period nor molecular weight of PVOH controls the water vapour permeability.

REFERENCES

- [1] Marsh, K. and Bugusu, B., "Food packaging: roles, materials, and environmental issues", *Journal of Food Science*, 2007, 72, R39-R55.
- [2] Robertson, G. L., "Food Packaging: Principles and Practice", 2nd ed., CRC Press: Boca Raton, FL, 2006, pp. 1-42.
- [3] Nielsen, L. E. and Landel, R. F., "Mechanical Properties of Polymers and Composites", 2nd ed., Marcel Dekker, Inc.: New York, 1994; pp 1-32.
- [4] Tang, X. Z., Kumar, P.; Alavi, S. and Sandeep, K. P., "Recent advances in biopolymer-based food packaging materials", *Critical Reviews in Food Science and Nutrition*, 2011, DOI: 10.1080/10408398.2010.500508

- [5] Dean, K. M., Do, M. D., Petinakis, E. and Yu, L., "Key interactions in biodegradable thermoplastic starch/ poly (vinyl alcohol)/ montmorillonite micro- and nanocomposites", *Composites Science and Technology*, 2008, 68, 1453–1462.
- [6] Tang, X., Alavi, S. and Herald, T. J., "Barrier and mechanical properties of starch-clay nanocomposite films", *Cereal Chemistry*, 2008, 85, 433–439.
- [7] Tang, X., Alavi, S. and Herald, T. J., "Effects of plasticizers on the structure and properties of starch-clay nanocomposite films". *Carbohydrate Polymers*, 2008, 74, 552–558.
- [8] Dean, K., Yu, L. and Wu, D. Y., "Preparation and characterization of melt-extruded thermoplastic starch/clay nanocomposites", *Composites Science and Technology*, 2007, 67, 413–421.
- [9] Chowdhury T. and Das M., "Optimization of amount of amylose, methylcellulose and hydroxypropylmethylcellulose for maximum tensile strength and minimum water vapour permeability of corn starch based self-supporting films", *Indian Journal of Chemical Technology*, 2014, 21, 96-104.
- [10] Parulekar, Y. and Mohanty, A. K., "Extruded biodegradable cast films from polyhydroxyalkanoate and thermoplastic starch blends: fabrication and characterization", *Macromolecular Material and Engineering*, 2007, 292, 1218–1228.
- [11] Jun, C. L., "Reactive blending of biodegradable polymers PLA and starch", *Journal of Polymers and the Environment*, 2000, 8, 33–37
- [12] Jang, W. Y., Shin, B. Y., Lee, T. J. and Narayan, R., "Thermal properties and morphology of biodegradable PLA/starch compatibilized blends", *Journal of Industrial and Engineering Chemistry*, 2007, 13, 457–464.
- [13] Sen C. and Das M., "Effect of Compositions and Ageing on Mechanical and Barrier Properties of Starch Based Biodegradable Films", in *Proceedings of National Conference on Emerging Technology Trends in Agricultural Engineering (ETTAE)*: 2014. 218-223.
- [14] Mao, L. J., Imam, S., Gordon, S., Cinelli, P. and Chiellini, E., "Extruded cornstarch-glycerol-polyvinyl alcohol blends: mechanical properties, morphology, and biodegradability", *Journal of Polymers and the Environment*, 2000,8, 205–211
- [15] Yang, S.Y. and Huang, C.Y., "Plasma treatment for enhancing mechanical and thermal properties of biodegradable PVA/starch blends", *Journal of Applied Polymer Science*, 2008, 109, 2452–24.
- [16] Zou, G.X., Ping-Qu, J. and Liang-Zou, X., "Extruded starch/PVA composites: water resistance, thermal properties, and morphology", *Journal of Elastomers and Plastics*, 2008, 40, 303–316.
- [17] Follain, N., Joly, C., Dole, P. and Bliard, C., "Properties of starchbased blends. Part 2. Influence of poly vinyl alcohol addition and photocrosslinking on starch based materials mechanical properties", *Carbohydrate Polymers*, 2005, 60, 185–192.
- [18] Marten, F. L. and Zvanut, C. W., "Hydrolysis of Polyvinyl Alcohol to Polyvinyl Acetate. In Polyvinyl Alcohol: Developments", 2nd ed.; Finch, C. A., Ed.; John Wiley & Sons Ltd: Chichester, England, 1992; pp. 57-76.
- [19] Russo, M. A. L., O'Sullivan, C., Rounsefell, B., Halley, P. J., Truss, R. and Clarke, W. P., "The anaerobic degradability of thermoplastic starch. polyvinyl alcohol blends: potential biodegradable food packaging materials", *Bioresource Technology*, 2009, 100, 1705–1710.
- [20] Tang, X. and Alavi, S., "Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability", *Carbohydrate Polymers*, 2011, 85, 7–16.
- [21] Limpan, N., Prodpran, T., Benjakul, S., and Prasarpran, S., "Influences of degree of hydrolysis and molecular weight of poly (vinyl alcohol)(PVA) on properties of fish myofibrillar protein/PVA blend films", *Food hydrocolloids*, 2012, 29(1), 226-233.
- [22] Maria, T. M., De Carvalho, R. A., Sobral, P. J., Habitante, A. M. B. and Solorza-Feria, J., "The effect of the degree of hydrolysis of the PVA and the plasticizer concentration on the color, opacity, and thermal and mechanical properties of films based on PVA and gelatin blends", *Journal of Food Engineering*, 2008, 87(2), 191-199
- [23] Negim, E., Rakhmetullayeva, R., Yeligbayeva, G., Urkimbaeva, P., Primzharova, S., Kaldybekov, D. and Craig, W., "Improving biodegradability of polyvinyl alcohol/starch blend films for packaging applications", *International Journal of Basic and Applied Sciences*, 2014, 3(3), 263-273.
- [24] Gomez, K. A. and Gomez, A.A., "Statistical procedures for agricultural research", *John Wiley and Sons, Inc.*, Singapore, 1984.
- [25] Snedecor, G.W. and Cochran, W.G., "Pair Comparisons. In: Statistical methods", Chapter 4, 5th ed. Oxford and IBH Publishing Co., New Delhi, 1967, pp. 45-83.
- [26] Mali, S., Grossmann, M., Victoria, E., Garcia, M.A., Martino, M.N. and Zaritzky, N.E., "Barrier, mechanical and optical properties of plasticized yam starch films", *Carbohydrate Polymers*, 2004, 56: 129–135.
- [27] Maizura, M., Fazilah, A., Norziah, M.H. and Karim, A.A., "Antibacterial activity and mechanical properties of partially hydrolyzed sago starch–alginate edible film containing lemongrass oil", *Journal of Food Science*, 2007, 72 (6): C324–C330.
- [28] El-Kader, K. A., Hamied, S. A., Mansour, A. B., El-Lawindy, A. M. Y. and El-Tantaway, F., "Effect of the molecular weights on the optical and mechanical properties of poly (vinyl alcohol) films", *Polymer testing*, 2002, 21(7), 847-850.
- [29] Silva, G. G. D., Sobral, P. J. A., Carvalho, R. A., Bergo, P. V. A., Mendieta-Taboada, O. and Habitante, A. M. Q. B., "Biodegradable films based on blends of gelatine and poly(vinyl alcohol): effect of PVA type or concentration on some physical properties of films", *Journal of Polymers and the Environment*, 2008,16, 276-28.