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Water Vapour Transport Properties of Cassava Starch/Poly(Vinyl Alcohol) Films via Experimental and Fickian Methods

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ABSTRACT

Background and Objective: Water vapour permeability is a critical property of packaging materials as it has marked effect on both the shelf-life and quality of packaged food products. Therefore, a study of water vapour transport properties through these films, as well as an understanding of the sorption kinetics provide a better understanding of how to optimize the water barrier properties of the films. **Materials and Methods:** In this research, the water vapour transport properties including the permeability and sorption behaviour of cassava starch/poly(vinyl alcohol) (PVA) films were studied over a range of starch-PVA compositions (PVA, 0-60%). Two methods were used to determine the water vapour permeability namely the experimental cup method and the theoretical Fickian method obtained by multiplying the sorption and diffusion parameters. **Results:** It revealed that the incorporation of 60% PVA into starch film was found to markedly reduce the water vapour permeability by 25.3% (experimental method) and 46.2% (Fickian method). The values of water vapour permeability obtained from both methods were found as the same order of magnitude. **Conclusion:** The study concluded that starch/PVA films have potential for biodegradable packaging applications.

KEYWORDS

Transport properties, starch, poly(vinyl alcohol), packaging, water vapour permeability

INTRODUCTION

Food deterioration caused by the penetration of moisture, oxygen and organic vapours is a major problem in the food industry. Storing food in the proper environment slows down the deterioration process and better preserves the food[1]. The use of synthetic polymeric packaging material with good material properties has severe environmental limitations. In view of this, the development of biodegradable plastics from renewable resources particularly for packaging and disposable applications is receiving considerable attention. Among these biopolymers, starch has been considered one of the most promising materials because of its large availability, low cost, renewability and inherent biodegradability[2]. However, the technological application of starch films in food and drug packaging is limited due to their brittleness and poor mechanical and barrier properties. Plasticizers increase the flexibility of starch-based films due to

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their ability to reduce internal forces between polymeric chains while increasing the intermolecular space[3]. Polyols such as glycerol are considered the best choice in starch-based films because of their high compatibility with the starch polymers[4]. The mechanical and barrier properties of plasticized starch films can be improved by blending with polyvinyl alcohol (PVA). The polyvinyl alcohol is a semi-crystalline synthetic polymer. It is biodegradable and has good compatibility with starch[5].

The study of water vapour transport properties through films provides a better understanding of the nature of interactions between these films and water molecules. This property is of great importance in the area of packaging, as it helps to know the type of product where the film can be applied i.e. whether as an efficient barrier to prevent hydration or dehydration[6]. An understanding of the mechanism of water transport through polymeric film can be explained through a four-step simple model: (i) Absorption of water vapour onto the polymer matrix surface, (ii) Dissolution of water vapour into the polymer matrix, (iii) Diffusion of water vapour through the matrix and (iv) Desorption of water vapour from the other surface of the film[7]. Therefore WVP, of these films is based on the solution-diffusion mechanism as it depends on the hydration or solubility of water in the film as well as the water mobility within the film matrix[7]. Although, several researches have been carried out on the physiochemical properties of plasticized starch-PVA films[8,9], however, the mechanism of water vapour transport through starch-PVA as packaging films remains a subject of continuing research interest.

Thus this study aimed to determine the water vapour transport properties of starch-PVA films via two methods-sorption and permeation methods and to provide a comprehensive comparison of both methods to find effective methods for analyzing the WVPs of hydrophilic films with potential application as packaging material. Also, to investigate the effect of PVA on the sorption properties of cassava starch films.

MATERIALS AND METHODS

Study area and sites: This research took place in Benin City, Edo State, Nigeria, which is positioned at a Latitude of 6.34°N and a Longitude of 5.63°E. The city's elevation is 88 m above sea level, with a population of over 2,125,058. Benin City is the largest urban area in Edo State. This study spanned from September, 2021 to July, 2023.

Sample collection and analysis: The 10 kg of cassava starch, poly(vinyl alcohol) (PVA) and glycerol of analytical grade were purchased from a chemical supply store in Benin City. All other chemicals and reagents used were of analytical grade.

Preparation of cassava starch-PVA films: The cassava starch/PVA films were prepared using the method described by Patil *et al.*[10]. In a typical experiment, aqueous dispersion of starch was used with aqueous solution of PVA under magnetic stirring for 60 min and then heated at 90°C for 30 min followed by the addition of glycerol as plasticizers. The mixture was kept at 80°C for 30 min and subsequently cast on a glass plate and then allowed to air-dry in an enclosed environment for 12 hrs and then dried at 60°C for 4 hrs. The thickness of the films was measured by means of a digital caliper while their density was determined by calculations prior to further analysis.

Characterization of films: The films were characterized in terms of microscopic surface morphology, structure and thermal stability using Scanning electron microscope (Phenom ProX by phenom World Eindhoven, Netherlands), Rigaku miniflex 600 x-Ray diffractometer and Perkin-Elmer thermal analyzer TGA 4000, respectively. Details of this characterization had been reported by Delgado *et al.*[6].

Water vapour permeability by sorption experiment: The Sorption experiment was carried out using the method described by Delgado *et al.*[6] with slight modifications. Prior to determination, the sample films were cut into dimensions of 3×3 cm and dried in an oven at 60°C for 4 hrs to obtain a constant weight.

One side of the film was covered with aluminum foil. This is to ensure absorption takes place only on one side and prevent moisture permeation from the other side. The dried films were placed in a desiccator containing saturated solution of NaCl (i.e. 75% RH). The film samples were removed at periodic intervals and weighed in an analytical balance. The experiment was done in triplicates. The sorption behaviour was obtained by plotting a graph of the mass fraction (m_t/m_∞ versus the square root of time divided by the film thickness and fitted to Fickian's diffusion equation[11]:

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \times n^2} \times e^{\frac{-D\ x\ (2n+1)^2\ x\ n^2 xt}{L^2}} \tag{1}$$

Simplified Fickian Equation under short time lapse gives:

$$\frac{m_t}{m_\infty} = \frac{4}{hrs}\sqrt{\frac{Dt}{\pi}} \tag{2}$$

where, $\frac{m_t}{m_\infty}$ is the mass fraction of absorbed water vapour (i.e is the mass absorbed at time t and m_∞ is the mass of moisture absorbed at equilibrium), h is the thickness of the film, $\pi = 3.142$, D is diffusion coefficient and t is time. The application of these equations to these polymer composite materials is a simplification and therefore, D should be interpreted as an effective diffusion coefficient[11,12], (Deff).

The sorption or solubility coefficient was obtained from the mathematical expression based on an assumption of Henry's law that the concentration of absorbed water vapour C_{water} (i.e. $C_{water} = m_\infty \rho$) in the film is linearly dependent on the water vapour partial pressure[13,14] as given in Eq. 3:

$$S_{eff} = \frac{m_\infty}{\Delta p}\rho \tag{3}$$

where, the proportionality constant, (S_{eff}) is the sorption coefficient, ρ is the density of the film and ΔP is the saturation vapour pressure at 75% RH.

The water vapour sorption permeability of the films can obtained using the relationship:

$$P_{eff} = D_{eff}\, x\, S_{eff} \tag{4}$$

Water vapour permeability (experimental or permeation method): The water vapour permeability (WVP) measurements were carried out using the ASTM E96 method as described by Bertuzzi *et al*.[15]. Test films were scaled on cups containing distilled water. The test cups were placed in a desiccator maintained at ambient temperature and 75% RH with saturated NaCl solution. Periodical weightings monitored the weight changes. Weight loss was plotted over time and water vapour permeability was calculated from the linear regression of the plots using the equation.

$$WVP = \frac{G}{A} \times \frac{x}{\Delta p} \tag{5}$$

where, x is the thickness of the film, A is the area of the exposed film and ΔP is the differential water vapour pressure across the film.

Establishment of the mechanism of transport through the film: In order to find the mechanism of transport through the starch-PVA films, the kinetic data were fitted to & Peppas (KP) model[16] as given in Eq. 6:

$$\frac{m_t}{m_\infty} = Kt^n \tag{6}$$

By transformation to linear form, we have Eq. 7:

$$\text{Log}\left[\frac{m_t}{m_\infty}\right] = \log k + n \log t \tag{7}$$

where, k is a constant that depends on the structural characteristics of the polymer matrix and its interaction with the water vapour, n represents the transport mode. The $n \leq 0.5$ indicates quasi-Fickian; Fickian transport, $n \leq 1$ represents anomalous transport mode while n = 1 indicates relaxation-controlled transport while in few cases there are reports on $n > 1$; the so-called case II, relaxation-controlled transport[17]. Thus, the parameter n reveals the extent of deviation from the ideal transport, determining the diffusion mechanism of water through the film[18].

Tools and equipment manufacturers: The instruments used in this study, such as the digital caliper, oven, analytical balance, desiccator and other equipment, were obtained from well-known manufacturers, including Hanna Instruments (Woonsocket, Rhode Island, USA), Thermo Fisher Scientific (Waltham, Massachusetts, USA) and Mettler Toledo (Columbus, Ohio, USA), among others[19-21].

Statistical analysis: The statistical analysis was carried out using the BMDP 2R software for stepwise multiple regression. Data were presented as the mean of three replicate measurements. The findings of the study were considered statistically significant at $p < 0.05$[22-24].

RESULTS AND DISCUSSION

All the films were successfully produced. The thickness and density of the films ranged from 0.30-0.34 mm and 1.23-1.33 $\mu g\ m^{-3}$.

Water vapour sorption kinetics: An important property of packaging materials is its ability to reduce the exchange of water between the packaged product and the environment[11]. The water vapour transport property of films depends on the molecular diffusion coefficient, (D_{eff}) and solubility coefficients, (S_{eff})[18]. Water sorption kinetics provides information on the hydration and mobility of water in the film by determining the solubility (at equilibrium) and diffusion coefficient, respectively. Thus sorption kinetics by %mass uptake is useful in characterizing WVP of hydrophilic films.

Figure 1 showed the plot of water vapour sorption curves versus composition of films (%PVA). The sorption curves were fitted to the Fickian equation (Eq. 2.). The curves were approximately linear at the early parts of the curves (i.e. m_t/m_∞: 0-0.7). It can be seen from the plot, that the slope of each curves decreases with increasing PVA concentration.

In Fig. 1, the X-axis represents the composition of films (%PVA), indicating the percentage of poly(vinyl alcohol) in the starch/PVA blend. The Y-axis represents the water vapour sorption curves (mt/m_∞), which show the ratio of the amount of water vapor absorbed at time (t) to the maximum absorption (∞) by the film. This ratio reflects the water sorption behavior of the films over time and varying PVA concentrations.

Diffusion coefficient (D_{eff}): The Diffusion coefficient, (D_{eff}) was obtained from the slope, S of the initial plot of mass fraction versus square root of time divided by the thickness (as shown from the sorption curve in Fig. 1) using Eq. 2. Figure 2 shows a plot of diffusion coefficient as a function of %PVA. From the result, the diffusion coefficient decreased by 34.5% on the addition of 60%PVA. A remarkable decrease of 28% was obtained on the initial addition of up to 40%PVA while a slow decrease of 6.5% was recorded between 40-60% PVA. The decrease in (D_{eff}) might be due to the stronger intermolecular interaction which creates a more tortuous pathway for the water molecules to migrate (i.e. diffuse) through the polymer matrix[25].

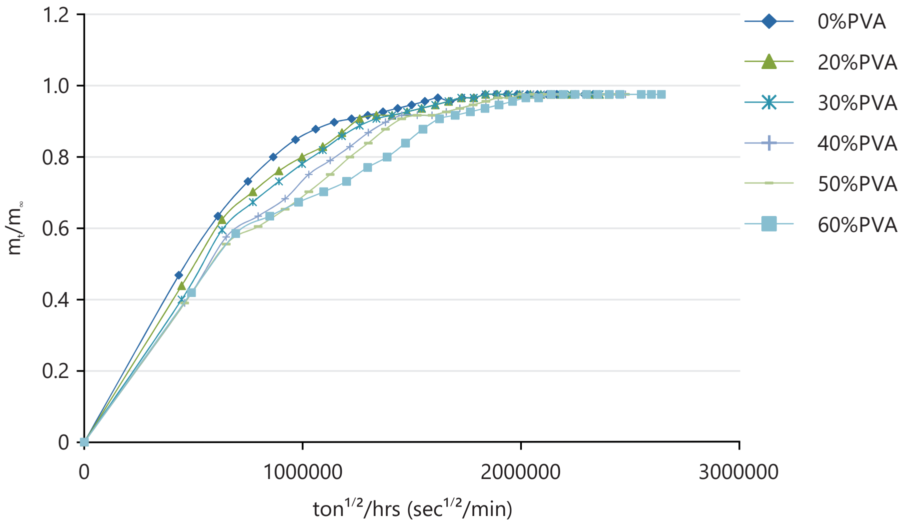

Fig 1: Water vapour sorption curves of starch/PVA films

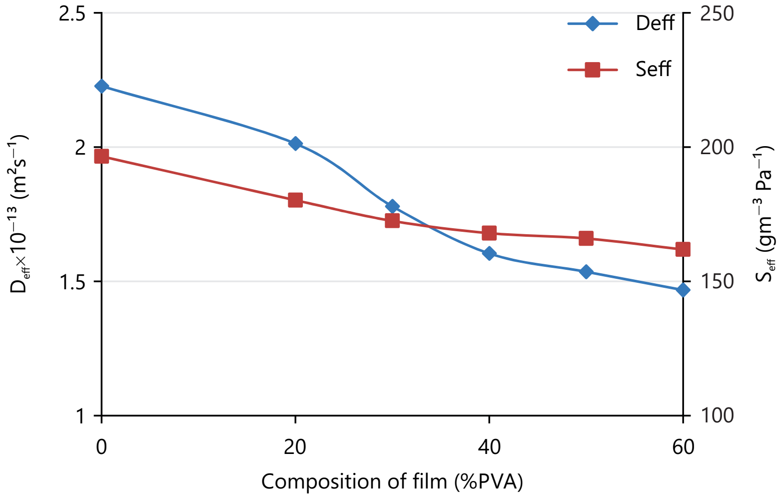

Fig 2: Plot of diffusion coefficient (D_{eff}) and sorption coefficient (S_{eff}) as a function of %PVA

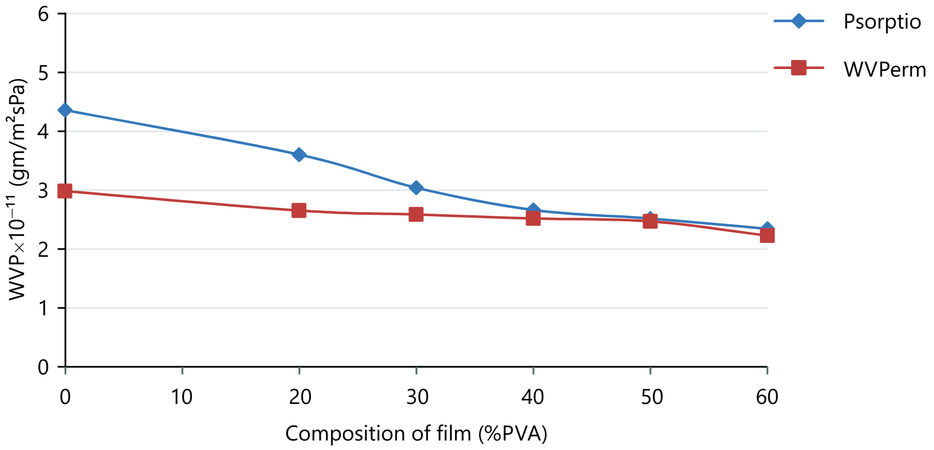

Fig 3: Comparison of $WVP_{sorption}$ and $WVP_{permeation}$ as a function of %PVA

Solubility or sorption coefficient (S_{eff}): he effect of PVA on the sorption coefficients of starch-based films is shown in Fig. 2. The results of sorption coefficient showed that there was 18% decrease in values of sorption coefficient on incorporation of 0-60%PVA. A significant initial decrease of 15% on incorporation of 0-40%PVA while, a slight decrease of 3% was observed from 40-60% PVA incorporation.

Table 1: Data of transport mechanism of films

Films	Concentration (%PVA)	n	K (s^{-1})
Starch/PVA	0	0.22	0.0609
	20	0.25	0.0423
	30	0.28	0.0288
	40	0.28	0.0277
	50	0.30	0.0229
	60	0.27	0.0209

The decrease in sorption coefficient with an increase in PVA concentration might be attributed to an increase in the strength of the intermolecular forces between starch and PVA chains, thereby reducing the intermolecular spaces and therefore decreasing the tendency of the film to interact with water molecules[26]. The PVA function as a crystallizing and reinforcing material in starch-based films.

Water vapour permeability (WVP): The water vapour permeability is a measure of the extent to which water vapour can penetrate through a film at a given humidity condition[27]. Permeability consists of a process of sorption, diffusion and desorption where water vapour dissolves on one side of the film, then diffuse through to the other side where it finally emerges out to the atmosphere[6]. The theoretical WVP obtained from sorption kinetics (non-steady state) was obtained from the product of sorption and diffusion coefficients while the experimental WVP was obtained by permeation experiments (steady-state). Figure 3 compared the results of the WVP values obtained from sorption and permeation measurements.

Both WVPs decreased with an increase in PVA concentration in starch films. Results of WVP from both sorption and permeation showed the same order of magnitude. However, at low PVA content of the film $WVP_{sorption}$ showed a much higher value over $WVP_{permeation}$. This marked difference in values might be attributed to non-ideal behaviour of the films and the difference in experimental conditions[6]. However, at higher PVA content (i.e. 40-60% PVA), the marked difference decreased as both values became approximately the same. The stronger intermolecular interaction between the polymer chains on the incorporation of PVA might have made the film more tortuous for the water molecules to permeate the starch-PVA film hence reducing the water vapour permeability[27].

Establishment of the type of transport mechanism through the films: The values of n and K were given in Table 1. The results of n ($n \leq 0.5$) suggested a quasi-Fickian transport mode for all the films. This result aligned with the study by Delgado *et al.*[6] which showed that thinner films exhibited quasi-Fickian transport mode.

The values of K decrease on incorporation of PVA into starch films indicating a decrease in the level of interaction between the polymer matrix and the water molecules (penetrant)[27]. This result also justifies the decrease in solubility coefficient (S_{eff}), diffusion coefficient (D_{eff}) nd permeability as shown in Fig. 2 and 3.

CONCLUSION

The effect of PVA on the hydration, diffusion and water vapour permeability of plasticized starch-based films was studied. Two different methods, the sorption (i.e. Fickian) method and permeation (i.e. experimental) methods were performed to determine the water vapour permeability of starch-PVA films. Based on the results obtained, both methods gave WVP values of the same order of magnitude. However, WVP values obtained from sorption experiments gave higher values when compared with values of $WVP_{permeation}$. The observed differences could be caused by experimental errors and non-uniform behaviour of the film samples.

SIGNIFICANCE STATEMENT

This study investigates the water vapor transport properties of cassava starch/polyvinyl alcohol (PVA) films, a critical aspect of understanding their potential as packaging materials. By exploring the mechanism and mode of water vapor transmission, determining water vapor permeability through experimental and theoretical methods and examining the impact of PVA on transport properties, this research aims to contribute to the development of biodegradable films with improved barrier properties. The findings will have significant implications for the food packaging industry, as they will provide valuable insights into the design and optimization of cassava starch-based films with enhanced performance, ultimately reducing plastic waste and promoting sustainable practices.

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