

Study of water transport behaviour in polylactide plates filled with rice hulls

Bwire S. Ndazi^{1*}, Sigbritt Karlsson²

¹Department of Mechanical and Industrial Engineering, College of Engineering and Technology, University of Dar es Salaam, P.O. Box 35131, Dar es Salaam, Tanzania

²University of Skövde, P.O. Box 408, SE-541 28 Skövde, Sweden

*Corresponding author. Tel: (+255) 22 2410754; E-mail: bndazi@udsm.ac.tz

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ABSTRACT

The influence of sorption temperatures and rice hull content on diffusion, permeability and solubility of water into PLA has been investigated by theoretical models with the support of experimental data. As expected and experimentally demonstrated water transport rates was higher at higher temperatures. This agrees with the increase in diffusion ($D = 0.67$ to 3.45×10^{-11} m²/s) and permeability ($P = 0.33$ to 0.55×10^{-13} m²/s) obtained by Equation (1). In contrast, the decrease in solubility from $S = 5.0 \times 10^{-3}$ to $S = 0.54 \times 10^{-3}$ as temperature was increased from 23°C ~70°C confirms the reduction of PLA's permeable domains during hydrolysis. Change in molecular weight confirms that hydrolysis was reaction controlled. Furthermore, S, D and P decreased with the increase of rice hull in PLA from 0 to 40 %, contrary to experimental results of **Figs. 2 and 3**. Rice hull was expected to enhance diffusion and permeability of water into PLA on the fact that being hydrophilic, rice hull do not bond perfectly with PLA leading to more permeable products. This leads to the conclusion that the mathematical relations applied need to be modified to account for other factors such as interface properties, type and form of fillers and chemical reaction of the polymer in order to predict reliably water transport behaviour in filled PLA or similar polymers. Copyright © 2016 VBRI Press.

Keywords: Diffusion; permeability; polylactide; rice hull; solubility.

Introduction

Polylactide (PLA) is a bioplastic derived from corn starch, sugar cane or sugar beet (*Beta vulgaris*), which has the potential to replace some of petrochemical plastics [1]. One of the benefits of using products related to PLA is a reduction of solid waste in waste streams due to the capability PLA to biodegrade completely into H₂O, CO₂, and humus when exposed into biochemically active environments [2]. More importantly, degradation products of PLA are biocompatible with the environment and human body. This why there has been a lot of research works directed to develop food packages, consumer commodities [3] and biomedical products such as implants, sutures, clips, and drug delivery systems [4] made of PLA.

PLA is strongly hydrophobic [4] due to methyl (-CH₃) side groups in its main chain [5]. Also it is considered to be comparatively hydrophilic than other traditional polymers, for example poly ε-caprolactone [6], due to cleavage of the labile -C-O-ester linkage next to -CH₃ group (**Fig. 1**) during hydrolysis, which may lead to introduction of hydrophilic groups such as -COOH and OH to PLA [4]. Diffusion or permeation of water into PLA takes place in available permeable sites and free volume, mainly in the amorphous region of unfilled PLA. The diffusion and permeation can continue until equilibrium concentration of the polymer is reached at its maximum solubility [1].

Factors that influence diffusion, permeation and solubility of water or gases into PLA and other plastics have been

investigated [1, 3, 6-13]. Some the factors include temperature, moisture concentration, vapour pressure, crystallinity as well as composition of polymer [1, 10, 13].

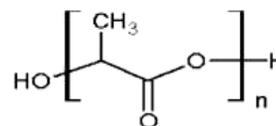


Fig. 1. PLA chemical structure.

The increase in temperature across the glass transition region is expected to increase water vapour and gas transport in some polymers. This has been attributed to the increase in molecular chain movement and vibration, which are induced by thermal expansion of the polymer [11]. A comparative study on permeability of water vapour between PLA and selected commercial petrochemical plastics, namely polyethylene terephthalate (PET) and oriented polystyrene (OPS), revealed a similar mass transport behaviour [17]. In another study reported by Lordanskii *et al.* [18] it was revealed further that the diffusion of water into a linear density polyethylene (LDPE) polymer, which contained polyhydroxyl butyrate (PHB), decreased as the proportion of crystalline phases in LDPE was increased. The decrease in water diffusion with an increase in crystallinity especially in PLA products has been associated with the reduction of initial water diffusion and permeable

sites in PLA that is amorphous domains [15, 19]. Crystallization of amorphous phases in PLA occurs during hydrolysis at higher temperatures [15, 19]. It is possible to deduce from such transformation whether hydrolysis is diffusion or reaction controlled [19]. This has been accomplished by applying the solution-diffusion models developed by Lonsdale in 1965 to study diffusion, permeability and solubility characteristics of water in polymers with respect to change in temperature and structure of polymeric materials [1, 5, 12, 20].

The permeability or diffusion coefficient of water or vapour into polymer with respect to change in temperature can be expressed by Equation (1):

$$A = A_o \exp(-E/RT) \quad (1)$$

where, A_o stands for the pre-exponential factor for permeability (P_o) or diffusion (D_o) and E is the corresponding activation energy of permeation (E_p) or diffusion (E_d), and A stands for the permeability (P) or diffusion coefficient (D).

Solubility of a diffusing mass into a polymeric media has been described theoretically using the solubility coefficient (S) expression given in Equation (2):

$$S = S_o \exp(-\Delta H_s/RT) \quad (2)$$

where, S_o stands for the pre-exponential factor while ΔH_s is the enthalpy of water vapour solution.

Alternatively, the solubility coefficient (S) can also be obtained from the equilibrium vapour content (M_{max}) and partial pressure [1] at STP (cm^3) using Equations (3) and (4) which are similar to the sorption coefficient equation used in Kittikon *et al.*[12] work:

$$S = M_{max}/p \quad (3)$$

where, p is the saturation vapour pressure (Pa) obtained from steam tables and S is expressed in cm^3 (STP)/ cm^3 (Pa).

$$M_{max} = \frac{(M - M_o) \times 22,414p}{18M_o} \quad (4)$$

where, M is the mass of polymer at any time t . M_o stands for initial dry mass of the polymer (g), ρ is the density of the polymer (g/cm^3). The corresponding densities of amorphous and crystalline PLA are .248 and $1.290 \text{ g}/\text{cm}^3$, respectively [20].

The relationship between permeability, solubility and diffusion coefficients has been described by Equation (5):

$$P = SD = S_o D_o \exp[-(E_d + \Delta H_s)/RT] \quad (5)$$

The corresponding relation for activation energies is given in Equation (6) [6, 11]:

$$E_p = E_d + \Delta H_s \quad (6)$$

Activation energies of water vapour transport in PLA have been reported as $E_p = 5 \text{ kJ}/\text{mol}$ [9], $E_d = 49 \text{ kJ}/\text{mol}$ and $\Delta H_s = -40 \text{ kJ}/\text{mol}$ of water (amorphous and semi-crystalline PLA) [1], respectively.

Addition of organic fillers in plastic materials is intended to reduce costs while at the same time enhancing thermal stability, hydrolysis resistance, stiffness and strength of the plastics [4]. However, permeation and diffusion of water into plastic products filled with hydrophilic fillers can be accelerated due to poor bonding at the interfaces of fillers and plastic [11]. Since permeability is a characteristic of both the diffusing fluid and the porous media [21], it is therefore theoretically expected that P and D increase proportionally to the concentration of available free volume in the permeable media. Thus, computation of water transport may be simplified by assuming that the diffusion and permeation processes into permeable plastic products occur through porous interfaces. Mathematical Equations (7) to (9) based on the rule of mixture, which have been modified to account for aspect ratio and orientation of fillers [22, 23], can be used to describe the dependence of solubility, diffusion and permeation of water into the plastic product on its filler concentration.

The solubility and diffusion behaviour have been described by Equations (7) and (8) as follows:

$$S_c = S_m (1 - v_f) \quad (7)$$

$$D_c = \frac{D_m}{1 + \alpha v_f / 2} \quad (8)$$

where, S_m and D_m are solubility and diffusion coefficients, respectively, of unfilled polymer if known and v_f is the volumetric concentration of fillers in the matrix.

Based on Equation (7), the corresponding theoretical model developed by Nielsen for permeability coefficient, which was later modified to account for orientation of fillers and their aspect ratios (α) in the product [22,23] is given by Equation (9).

$$P_c = \frac{D_m S_m}{\left(1 + \frac{\alpha}{3} v_f\right)^2} \quad (9)$$

The volumetric fraction of fillers v_f in Equations (7) to (9) can be obtained from weight fractions of polymers (w_m), density of polymer (ρ_m), and dry bulk density of fillers (ρ_f) as indicated in Equation (10).

$$v_f = \frac{w_f / \rho_f}{w_f / \rho_f + w_m / \rho_m} \quad (10)$$

In this paper, the influence of temperature change and rice hull filler concentration on diffusion, permeation and solubility of water vapour into PLA plates have been investigated using the solution-diffusion model and the modified Nielsen model.

Experimental

Materials

The materials used were PLA plates containing 0, 20, 30 and 40 % rice hull fillers and were designated as PLA-00, PLA-20, PLA-30 and PLA-40, respectively. The plates were prepared as described previously [19].

Measurement of water transport properties

Water transport to the samples was measured according to ASTM D570-98 standard using five specimens of 20 mm × 50 mm × 2 mm as described elsewhere [19]. Mathematical relations for determining the diffusion coefficient (D) of water within an error of 0.1 % assuming a short time diffusion process with M_t/M_{max} ratio being less than 0.5 are given in Equations (11) [24-26].

$$M_t/M_{max} = \frac{2}{h} \left(\frac{D}{\pi} \right)^{0.5} \times t^{0.5} \quad (11)$$

Effect of temperature on water transport behaviour

The effect of temperature on S, D and P at 23 °C ~ 50 °C and ~70°C was determined by Equations (1) to (6) using the density, activation energies and diffusion data of PLA reported previously [1, 6, 19].

Effect of filler content on water transport behaviour

The effect of filler content on S, D and P was determined using Equations (7) to (9) and some of the results of Section 2.3.

Confirmation of hydrolysis by molecular weight distribution analysis

The effect of water transport at different temperatures on the distribution of molecular weight fractions of PLA was studied by TripleSEC size exclusion chromatography (SEC) with GMHxl columns and Tetrahydrofuran (THF) as eluent and solvent. The aim was to understand how the diffusion and permeation process of water vapour influenced the structure and molecular weight of PLA.

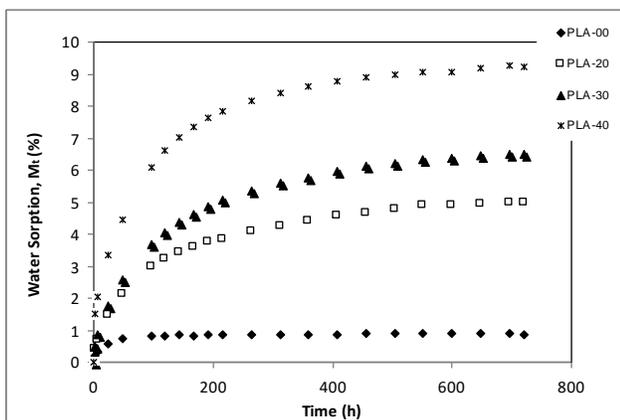


Fig. 2. Water transport rates into PLA plates at 23°C.

Results and discussion

Water transport behaviour in PLA plates

Figs. 2 and 3 show sample graphs of water transport rates into unfilled and filled PLA plates after immersion in water at 23 and ~50 °C temperatures. Addition figure for the temperature of ~70°C is attached in the appendix for further reference. It is shown clearly that the increase in temperature and filler concentration led to significant increase in water transport rates and equilibrium water content ($M_{max,t}$) in the PLA products. A similar observation has been reported previously in polypropylene filled composites [13] as well as in PLA composites [26].

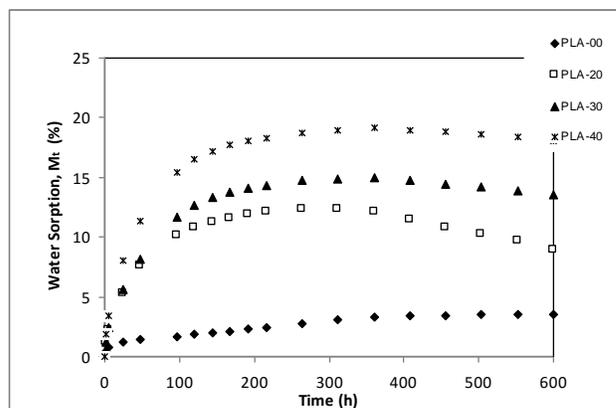


Fig. 3. Water transport rates into PLA plates at ~50°C.

Theoretically a more porous media will allow more diffusion and permeation of mass [21]. As expected therefore the results of M_{max} obtained by Equation (4) confirm that the rates of water sorption into the PLA plates increased with the increase of rice hull concentration in the PLA plates. High porosity in the filled PLA plates is attributed to inadequate interfacial bonding between the hydrophilic rice hull and the strongly hydrophobic PLA despite application of the coupling agent [19]. The porous structure in the filled PLA plates created potential sites through which the diffusion and permeation of water into the material took place. It is important to note that the diffusion coefficient of water into rice hull is $1.16 \times 10^{-8} \text{ m}^2/\text{s}$ [21], which is less than the diffusion of water into PLA ($6.7 \times 10^{-12} \text{ m}^2/\text{s}$) [19]. The difference demonstrates further that the rice hulls are relatively more porous than PLA, which makes it reasonable also to believe that the presence of the rice hull in the PLA plates contributed to the observed higher rates of water sorption into the filled PLA plates.

Effects of temperature on diffusion, permeability and solubility of water

Using activation energies of diffusion ($E_d=49 \text{ kJ/mol}$) and permeation ($E_p=5 \text{ kJ/mol}$) reported previously [6] and the enthalpy of solubility of PLA ($\Delta H_s=-40 \text{ kJ/mol}$) [1], it was possible to theoretically calculate the solubility, diffusion and permeability of water into unfilled PLA. The results presented in Table 1 shows the influence of temperature

change on the coefficients of diffusion (D), permeability (P) and solubility (S) of water into unfilled PLA plates at 23, ~50 and ~70°C based on Equations (1) to (4).

Theoretically, Equation (1) predicts an increase in D with respect to the increase in temperatures. The diffusion coefficient D of water into PLA at 23 °C has been previously reported as $6.7 \times 10^{-12} \text{ m}^2/\text{s}$ [19]. This value was slightly lower than the diffusion coefficient of water $D = 5.0 \times 10^{-10} \text{ m}^2/\text{s}$ in PLA at 30 °C reported by Siparsky *et al.* [1]. The difference in the diffusion coefficients reported in the two studies may be attributed to differences in specimen's geometry, testing procedures for water transport behaviour as well as temperature differences. Siparsky *et al.* [1] used PLA film samples of thicknesses ranging from 0.22 to 0.30 mm tested in an environmental chamber whereas the other study [19] used PLA plate samples of 2 mm thick which were tested in a water bath conditioned at 23, ~50 and ~70°C.

Table 1. Temperature dependence on diffusion, permeation and solubility coefficient of water in PLA.

Product	Temp (K)	Solubility (cm ³ stp/cm ³ s)		Diffusion (m ² /s)		Permeability (m ² /s)	
		S ₀ × 10 ⁻¹⁰	S × 10 ⁻³	D ₀ × 10 ⁻³	D × 10 ⁻¹¹	P ₀ × 10 ⁻¹²	P × 10 ⁻¹³
PLA-00	296		5.0	0.67		0.33	
	~323	4.36	1.28	2.95	1.19	1.29	0.45
	~343		0.54		3.45		0.55

According to the theoretical results in **Table 1** obtained by Equation (1), the diffusion coefficient D is shown to increase from $6.7 \times 10^{-12} \text{ m}^2/\text{s}$ to $3.45 \times 10^{-11} \text{ m}^2/\text{s}$ with the increase of temperatures from 23 °C to ~70 °C, respectively. The experimental result obtained previously confirms this only for filled PLA plates [19]. The increase in D with respect to temperature increase predicted by Equation (1) suggests that the polymer was more permeable at higher temperatures. This is contrary to previous experimental facts that crystallization of the amorphous domain in the PLA leads to reduction in the diffusion sites of water [15, 19, 27]. This is also supported by Lordanskii *et al.* [18] findings that water diffusivity should to lower into a more crystalline polymer. Therefore, the theoretical model in Equation (1) does not account for these unique structural changes that occur in PLA and similar polymers. Unless the chemical and physical changes which occur leaves residual amorphous phases during hydrolysis which may act as water sorption sites [11]. This may need experimental confirmation.

The result in **Table 1** indicates further that the permeability coefficient of water into PLA also increased from $3.3 \times 10^{-14} \text{ m}^2/\text{s}$ to $5.5 \times 10^{-14} \text{ m}^2/\text{s}$ with the increase of temperature from 23°C to ~70 °C. This theoretically implies that a diffusing mass permeates more readily into a more porous and more permeable media at higher temperatures. However, since there are no experimental results for comparison, it is reasonable conclude that the theoretical results in **Table 1** are based on the assumption that permeable sites at higher temperatures in PLA may be attributed to physical changes related to molecular movements and expansion of the polymer other than physical changes associated with chemical changes, namely crystallization of amorphous domains due to hydrolysis.

The results for the solubility of water into PLA with respect to temperature changes as determined by Equations (2) to (4) also are given in **Table 1**. The results were obtained using equilibrium water content $M_{\text{max}} = 13.98\text{g}$ from experimental data, PLA's density of 1.25 g/m^3 , pre-exponential factor (S_0) determined by Equation (2), and solution enthalpy of the penetrant ($\Delta H_s = -40 \text{ kJ/mol}$) [1]. The solubility coefficient S, which describes the equilibrium water (M_{max}) available for hydrolysis, is shown to decrease with the increase of sorption temperatures. According to Duncan *et al.* [11], solubility of polymers at higher pressures (temperature) is dominated by amorphous phases. The decrease in S with respect to increase in temperature as predicted by Equation (2) agrees with previous experimental findings that there was a reduction of amorphous phases in PLA due to crystallization at higher temperatures during hydrolysis [19]. Therefore, this model describes quite reasonably the solubility of water into PLA with respect to temperature increase.

Effects of filler content on water diffusion, permeation and solubility

The influence fillers on water transport into plastic materials have been reported widely [13, 19, 28]. The results in **Table 2** show that diffusion, permeability and solubility coefficients decreased with the increase of filler content and sorption temperature from 23°C to ~70°C. This theoretical a result opposes the trend of the experimental results reported elsewhere [13, 19, 28]. The result implies that the plates became less permeable as more rice hull was added in PLA. They further suggest that there was perfect interface bonding between the rice hull fillers and the polymers, which is not practically true due to differences in the polarity of the two materials. The model also suggests that the diffusion coefficient in rice hull (D_f) may be less than the diffusion coefficient of PLA (D_m) [11]. Previous studies shown that the diffusion coefficient of water into rice hull is relatively higher than that of PLA by $1.18 \times 10^{-8} \text{ m}^2/\text{s}$ [19, 21]. However, the results are in agreement with a study which observed reduction of 43 % in water vapour transport in nano-composites filled with impermeable organo-modified clay [23]. The models therefore cannot be applied directly for studying water transport behaviour in PLA or polymers filled with hydrophilic material unless modifications to include filler type, filler-matrix interaction and possible chemical reactions are incorporated.

Table 2. Influence of filler content on average solubility, diffusion and permeability coefficient of PLA plates.

Product	Temp (K)	Filler content, v _f (%)	S ₀ × 10 ⁻⁵ (cm ³ stp/cm ³ s)	D ₀ × 10 ⁻¹¹ (m ² /s)	P ₀ × 10 ⁻¹⁴ (m ² /s)
PLA-00	296	0.0	499.43	0.67	3.3
PLA-20		0.63	184.79	0.26	0.79
PLA-30		0.75	124.86	0.23	0.65
PLA-40		0.82	89.90	0.22	0.59
PLA-00	~323	0.0	128.35	1.19	4.5
PLA-20		0.63	47.49	0.46	1.07
PLA-30		0.75	32.09	0.42	0.89
PLA-40		0.82	23.10	0.39	0.80
PLA-00	~343	0.0	53.85	3.45	5.5
PLA-20		0.63	19.92	1.34	1.31
PLA-30		0.75	13.46	1.20	1.09
PLA-40		0.82	9.69	1.13	0.98

Effect of water transport temperatures on molecular weight distributions

The results in **Fig. 4** show that the molecular weight distribution shifted slightly to lower molecular weight fractions, implying that the proportion of high molecular weight fractions in the polymer decreased after immersion at higher temperatures. According to previous studies [15, 16, 19] this is associated with hydrolysis and cleavage of the polymer chain to oligomers and monomers.

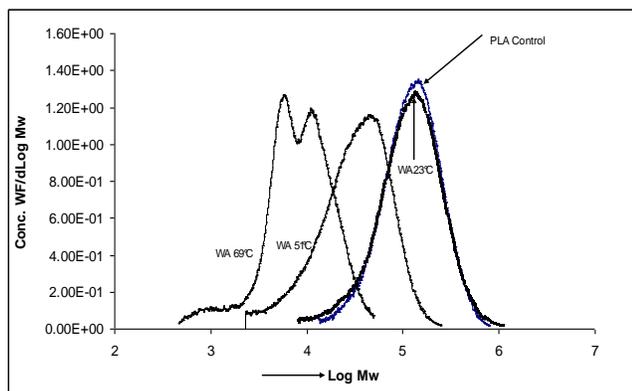


Fig. 4. Effects of sorption temperature on distribution of Mw fractions in PLA.

Conclusion

The results have shown that water transport in PLA plates is strongly affected by temperature and rice hull content. The solubility coefficient (S), which describes equilibrium water available for hydrolysis, decreased from $499.43 \times 10^{-5} \text{ cm}^3/\text{cm}^3$ (stp) to $53.85 \times 10^{-5} \text{ cm}^3/\text{cm}^3$ (stp) with the increase of temperature from 23°C to 70°C . As reported earlier, solubility of polymers at higher pressures (temperature) is dominated by amorphous phases. Therefore, the decrease in S with respect to increase in temperature as predicted by Equation (2) agrees with previous experimental findings that there was a reduction of amorphous phases in PLA due to crystallization during hydrolysis [19]. These changes are also supported by reduction of high molecular weight fractions in the polymer at higher temperatures. Unlike the models for diffusion and solubility, this model describes quite reasonably the solubility of water into PLA with respect to temperature increase.

The results have demonstrated further that an increase in filler content in the PLA plates from 0 to 40 % led to the decrease of S , D and P . This theoretically and practically contradicts previous studies and the facts that presence of the hydrophilic rice hull into the strongly hydrophobic PLA was expected to make the product more porous and more permeable. The diffusion coefficient of water into rice hull is relatively higher than that of PLA by $1.18 \times 10^{-8} \text{ m}^2/\text{s}$. Thus, the models are more applicable to polymers filled with impermeable filler where a reduction of 43 % in water vapour transport has been reported. The models therefore cannot be applied directly for studying water transport behaviour in PLA or polymers filled with hydrophilic material. There is a need to structure the models so that

they can account for filler type, filler-matrix interaction and related chemical reactions.

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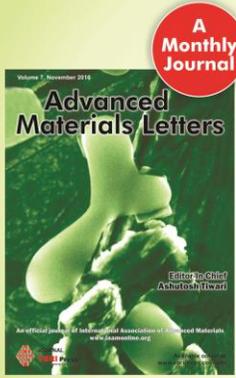
Author's contribution

Conceived the plan: BSN; Performed the experiments: BSN; Data analysis: BSN; Guided the Research: SK; Wrote the paper: BSN; SK. Authors have no competing financial interests.

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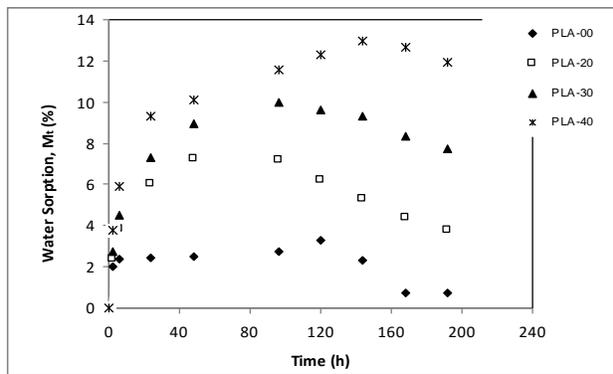
Supplementary Information

Fig. A. Water diffusion rates into PLA plates at $\sim 70^{\circ}\text{C}$.