Research article

Water absorption characteristics of polyester matrix composites reinforced with oil palm ash and oil palm fibre

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Abstract

The water absorption characteristics of polyester matrix hybrid composites reinforced with oil palm ash and oil palm fiber have been investigated. Open moulding method was used to produce polyester hybrid composites of 2, 4, and 6 wt% reinforcement consisting of oil palm ash (OPA) and oil palm fiber (OPF) in weight ratios of 1:0, 3:1, 1:1, 1:3 and 0:1 respectively. Water immersion test was used to study the adsorption behaviour from which the water diffusion mechanisms of the composites were established. The results show that the amount of water absorbed by the composites increases with increase in the fiber weight ratio of the OPA-OPF hybrid reinforcement and also with the increase in the weight percent of the reinforcement phase. The diffusion transport mechanism as predicted from the diffusion exponent (n) shows that the majority of the hybrid reinforced composite compositions and all the composites reinforced only with OPF exhibited super case II or case II diffusion. But all the composite grades reinforced with OPA only and the unreinforced polyester exhibited Fickian and less Fickian diffusion, respectively. It was only the hybrid composition containing 2 wt% reinforcement having weight ratio OPA: OPF of 3:1 that exhibited the intermediate behavior between Fickian and non-Fickian diffusion. Generally, it is observed that the values of the diffusion exponent (n) increase as the amount of water absorbed by the composites increases.

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Keywords: Polyester matrix composites, oil palm fiber, water absorption diffusion mechanism, oil palm ash, Fick's diffusion theory

1. Introduction

The use of natural plant fibers as reinforcement in polymer composites for making low cost engineering materials has generated much interest in recent years. Environmental and economic concerns as well as consumer pressure have forced manufacturing industries (particularly automotive, construction and packaging) to search for new materials that can substitute for conventional non-renewable reinforcing materials such as glass fiber [1, 2]. The use of natural fiber and fillers as reinforcement in polyester composites have increased in many applications, a contributory factor to the above is its environmental friendliness and possession of various desirable properties which include good specific strengths and modulus,

economic viability, low density, reduced tool wear, enhanced energy recovery, and reduced dermal and respiratory irritation and good biodegradability [2-5].

However, the main drawbacks are poor mechanical properties and high moisture absorption. The latter is due to its hydrophilic nature that produces a harmful effect on almost all properties, including the dimensional stability [6]. This problem can be severe if the composite is used in high moisture environments. Moisture uptake in polymer matrix composites has a deleterious effect on their mechanical properties because it leads to degradation of fibre/filler–matrix interface region creating poor stress transfer efficiencies resulting in a reduction of mechanical and dimensional integrity [7]. High moisture resistance and good aging properties are key improvements required for these materials in order to expand their range of applications and compete more efficiently against synthetic fiber composites [8].

Moisture penetration in composites as reported by Lee and Peppas [9] occurs via three mechanisms. The first mechanism involves the diffusion of water molecules inside the micro-gaps between the polymer chains [10-11]. This capillary flow represents the second mechanism for conveying water to the interior part of composites, which tends to occur preferentially along the interface if wetting of the fibres by the matrix is incomplete [12]. Percolating flow and storage of water in micro-cracks possibly present in the matrix constitute a third mechanism of moisture penetration into polymer based composites. Generally, based on these mechanisms, diffusion behaviour of polymeric composites can further be classified according to the relative mobility of the penetrant and of the polymer segments, which is related to either Fickian, non-Fickian or anomalous, and an intermediate behavior between Fickian and non-Fickian [13-14].

A considerable research has been conducted on water absorption of natural fibre composites made of different fiber and resin (thermoplastic or thermoset) [15-18]. From their results, it can be seen that it is necessary to address further the moisture absorption problem associated with natural fibre composites. Many researchers have proposed chemical modifications of the fibres' surface in order to improve the fibre/matrix adhesion, enhanced water resistance, better stability, and reduce the water uptake of the resulting composite [19]. Among the systems studied by researchers, none has presented results helpful in understanding water absorption characteristics of oil palm filler-fibre hybrid reinforced polyester matrix composites.

Recently, oil palm ash-oil palm fibre hybrid reinforced polyester matrix composites were successfully produced in our laboratory using open moulding method. The produced composites showed promising mechanical properties. It is therefore imperative to study the water absorption behaviour of the composites as it is noted that water absorption affects most of the engineering properties of PMCs. In the present study, the water absorption behavior of oil palm ash-oil palm fibre/polyester composites was investigated. Ash and fibre treatments were performed in order to reduce the water uptake with time, and produce composites with a higher dimensional stability.

2. Materials and Methods

2.1. Materials

The polymer selected as the composite matrix for this research is polyester resin as-supplied with stability below 25°C. To cure the polyester resin during the fabrication of the composites, methyl ethyl ketone peroxide (MEKP) and cobalt naphthanate were

selected for use as initiator and catalyst respectively. Oil palm fruit fibers obtained from an oil processing mill were utilized for the preparation of the reinforcements for the composite.

2.2. Reinforcement Preparation

Fiber Preparation

The oil palm fibers were chemically treated to improve wettability between the fibers and the polyester matrix, and reduce the tendency of the fibers to absorb water. The chemical treatment was carried out using 0.1M NaOH in a water bath maintained at a temperature of 50°C for 2-4 h. The fibers were thereafter rinsed with water, and then sun dried. The oil palm fibers before and after chemical treatment are presented in Fig. 1.
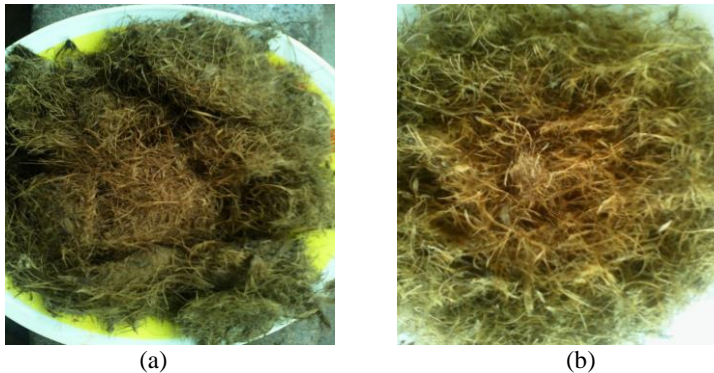

(a)   (b)

Fig. 1 Oil palm fibers (a) before and (b) after chemical treatment

Filler Preparation

The oil palm ash used as reinforcing filler was produced by burning some sun dried oil palm fibers using a metallic drum which served as burner. The fibers were allowed to burn completely in the drum after ignition with charcoal. The ash obtained from the process was thereafter heat-treated (to reduce the carbonaceous and volatile constituents) in a furnace at a temperature of 550°C for 4 hrs. Sieve size analysis was carried out on the heat-treated ash using a digital sieve shaker. Particle sizes below 50 μm were collected and utilized as the reinforcing filler. The nominal chemical composition of the oil palm ash is presented in Table 1. The oil palm ashes before and after the heat-treatment is presented in Fig. 2.

Table 1
Nominal chemical composition of palm oil ash [20]

Chemical constituent	OPA (%)
SiO_2	65.20
Al_2O_3	4.48
Fe_2O_3	5.44
CaO	4.12
MgO	2.25
Na_2O	0.10
K_2O	2.28
SO_3	2.25
Loss on ignition	13.86

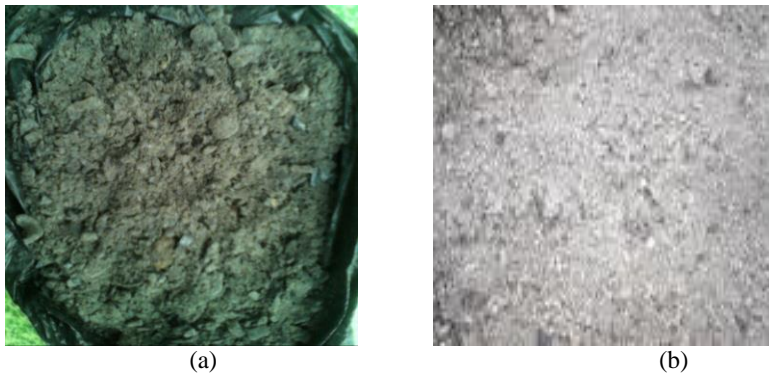(a)   (b)

Fig. 2 Oil plam ash (a) before and (b) after heat treatment

2.3. Composite Fabrication

Open moulding method was used to prepare the oil palm ash-fiber reinforced polyester hybrid composites. The process started with the determination of the quantities of oil palm ash (OPA) and oil palm fiber (OPF) required to produce 2, 4, and 6 wt% reinforcement consisting of OPA and OPF in weight ratios of 0:1, 1:3, 1:1, 3:1 and 1:0, respectively (which amounts to 0, 25, 50, 75 and 100% OPA in the reinforcement phase). The determined quantities of the polyester resin, OPA and OPF particles were measured on an electronic weighing balance. The polyester was poured into a beaker; 2% of cobalt naphthanate (catalyst) and 1% of methyl ethyl ketone peroxide (MEKP, accelerator) were added and stirred with a rod manually to achieve homogenization. Thereafter, the reinforcing phases were added and stirred for few minutes until an even dispersion was achieved. The mixture was then cast into already prepared aluminium moulds which were pre-coated with polyvinyl alcohol (PVA) for easy removal of the cast samples from the moulds. The mixture was left for about one and half hours in the mould to cure before they were removed. This procedure was repeated for all samples preparation. Representative samples produced from the process are presented in Fig. 3.

Fig. 3 Representative produced polyester hybrid composites

2.4. Water Absorption Test

Water absorption tests were carried out following the recommendations specified in ASTM D5229M-12 [21]. Samples of each composite grade were oven dried before weighing in accordance with Osman and Vakhguelt [22], and the weight recorded was reported as the initial weight of the composites. The samples were then placed in distilled water maintained at room temperature (25°C); and at time intervals of 24h, the samples were removed from the water, cleaned using a dry cloth and weighed. The weight measurements were taken periodically at time intervals of 24h for up to 336h which was after water saturation in all the composites had been noticed. The amount of water absorbed by the composites (in percentage) was calculated using the equation:

$$W(\%) = W_t - W_o / W_o \times 100 \tag{2.1}$$

Where W is percent water absorption, W_o and W_t are the oven dry weight, and the weight of the specimen after time t, respectively.

Graphical plots of weight gained–immersion time and percent water absorption–immersion time for all the composites were produced and utilized to study the water absorption behaviour. The mechanism of water diffusion into the composites was studied by analysing the slope and intercepts of the water absorption graphs plotted by using the relations [23]:

$$M_T/M_\infty = kT^n \tag{2.2}$$

$$\log(M_T/M_\infty) = \log(k) + n\log(T) \tag{2.3}$$

where M_T is water absorption at time T, M_∞ is water absorption at saturation point, k is a constant related to the polymer network structure, and n is the release exponent which determines the type of diffusion.

3. Results and Discussion

3.1. Water Absorption Behavior

The water absorption plots of the composites with varied weight percent reinforcement and weight ratio OPA/OPF is presented in Figs. 4-6. It is observed from Fig. 4 (the water absorption plots for the composite grades reinforced with 2 wt% OPA-OPF) that the water absorption by the composites increases with immersion time although the rate of absorption decreases with increased time. It is also observed that the water absorption attains equilibrium after 240h at which stage the composites have attained saturation point as far as water absorption is concerned. Similar trends of water absorption behavior are observed for the composite grades with 4 wt% (Fig. 5) and 6 wt% (Fig. 6) OPA-OPF reinforcements.
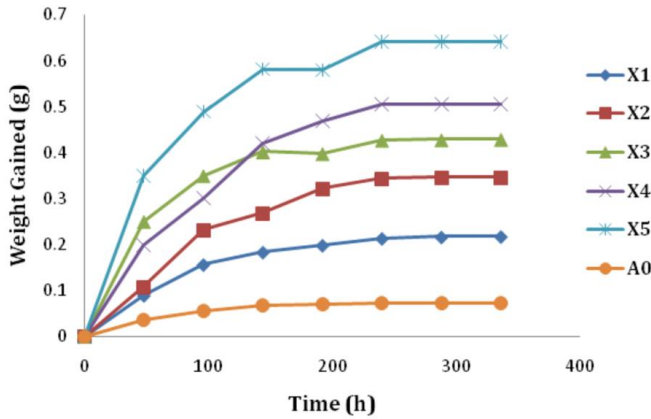
Fig. 4 Water absorption curve for composites containing 2 wt% reinforcement
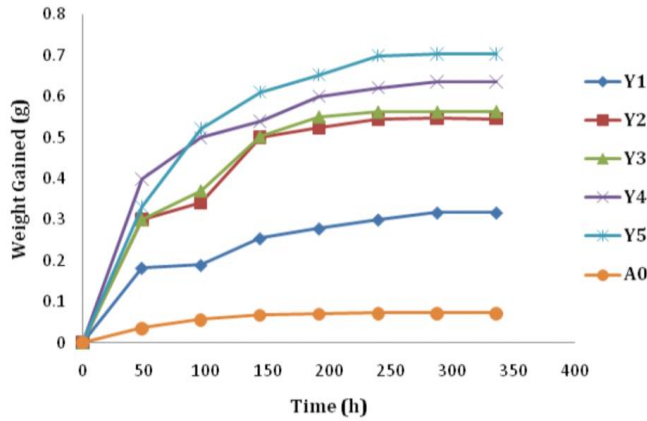

Fig. 5 Water absorption curve for composites containing 4 wt% reinforcement

Fig. 7 shows clearly that irrespective of wt% reinforcement, the amount of water absorbed by the composites increases with the increase in the fibre content of the OPA-OPF hybrid reinforcement phase. This suggests that the OPF is more hydrophilic in comparison with OPA. Also, for a constant weight ratio of OPA and OPF, the amount of water absorbed by the composites increases with increase in the weight percent of the reinforcement phase. Dhakal *et al.* [24] have reported that water absorption property of PMCs reinforced with natural fibres and their derivatives is dependent on the amount of the fibre, fibre orientation, immersion temperature, area of the exposed surface to water; also the permeability of fibres, void content, and hydrophilicity of the individual components (in this case the fibres, ash, and the polyester matrix). In the case of the composites produced, exposure to water makes the highly hydrophilic oil palm fibre to swell. As a result of fibre swelling, micro cracking of the polyester occurs particularly along the fibre/matrix interface which gives room for further water penetration. Bismarck [25] reported that the swelling stresses that develop under these circumstances can result in composite failure.
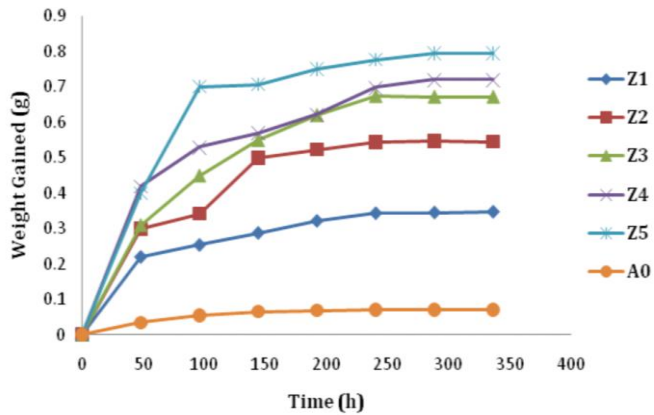
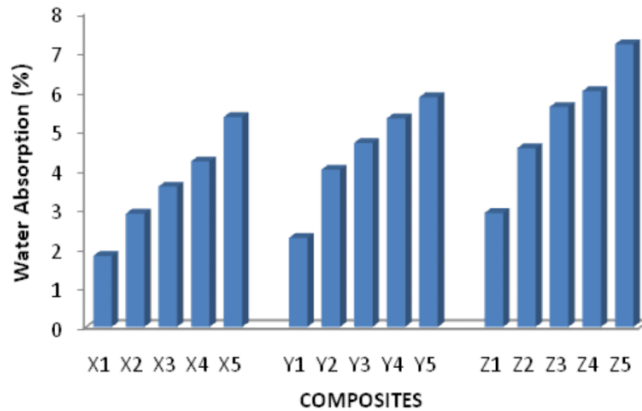**Fig. 6** Water absorption curve for composites containing 6 wt% reinforcement

Fig. 7 Water absorption of the composites for different compositions

3.2. Water Diffusion Mechanism in Composites

The values of the slope n, from the plots of log (M_T/M_∞) versus log (T) presented in Figs. 8-10 can be used in establishing the water diffusion mechanism of the composites produced. The water diffusion behaviour of PMCs obeys Fick's diffusion theory and is reported to be dependent on the relative mobility of the penetrant (water molecules) and the polymer segment [24]. On the basis of the relative mobility of the penetrant and the polymer segments, three classes of diffusion can be distinguished. When the rate of diffusion of the penetrant (in this case water molecules) is much less than that of the polymer composite segment mobility, Fickian diffusion mechanism (Case I) is said to prevail. For this diffusion mechanism the value of $n = 0.5$ and independent of time, the equilibrium inside the polymer composite is rapidly reached and maintained [26]. For Case II, the value of $n = 1.0$ which indicates that the diffusion process is much faster than the relaxation process (R_{diff} » R_{relax}, system controlled by relaxation), this diffusion is characterized by the development of a boundary between the swollen outer part and the inner glassy core of the polymer. The boundary advances at a constant velocity, and the core diminishes in size until an equilibrium penetration concentration is reached in the whole polymer composite [27]. $0.5<n<1.0$ indicates non-Fickian (anomalous) diffusion mechanism, which describes those cases where the diffusion and relaxation rates are

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comparable ($R_{diff} \approx R_{relax}$). In this case, an intermediate behavior between Fickian and non-Fickian diffusion will be observed [28]. Occasionally, values of *n* > 1 have been observed, which are regarded as Super Case II kinetics [29]. When the water penetration rate is much below the polymer chain relaxation rate, it is possible to record the n values below 0.5. This situation, which is classified also as Fickian diffusion, is called as 'Less Fickian' behavior [30]. These three cases of diffusion can be distinguished theoretically by the shape of the sorption curve represented by Sombastsompop and Chaochanchikul [23], and on which basis the graphs presented in Figs. 8-10 were plotted. All types of water transport discussed above are presented in Tables 2 and 3 for the oil palm ash-oil palm fiber polyester composite with the coefficients *n* and *k* calculated from slope and intercept respectively of log plot of M_T/M_∞ versus time which was drawn from experimental data as shown in Figs. 8-10.
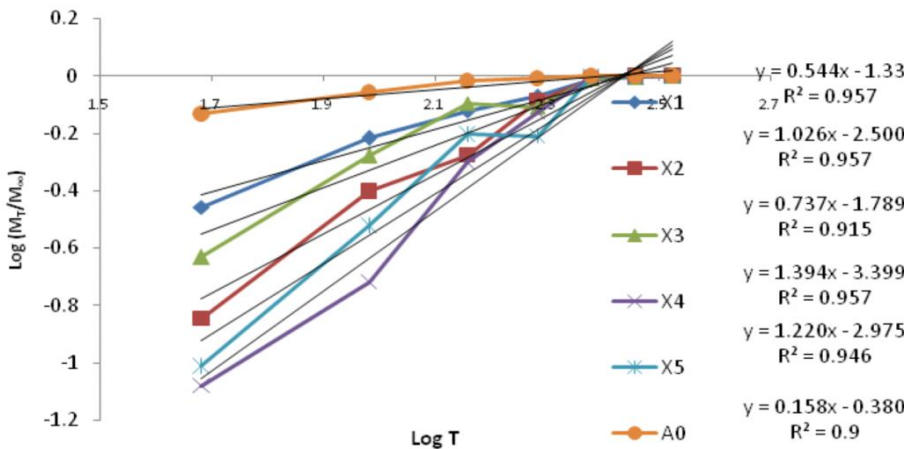

Fig. 8 Diffusion curve fitting for polyester OPA/OPF composites with 2% reinforcement

Figs. 8-10 show the diffusion curve fittings of experimental data for 2 wt%, 4 wt% and 6 wt% reinforcements with varying composition of OPA/OPF of produced hybrid composites. It is observed from Figs. 8-10 that all the composites exhibited line graph shapes which are best fit by linear line graphs in agreement with equation 3. The values of the slope *n* and intercept *k* were calculated from the log plot, and presented in Table 2. The analysis of the modes of water transport for the hybrid composites produced is presented in Table 3.

It can be clearly seen from Table 3 that values of the diffusional exponent range (*n*) between 0.158 and 1.493. For the unreinforced polyester composite A0, the diffusional coefficient (*n*) is far less than 0.5 (0.153) which indicates that the transport mechanism is less Fickian diffusion (the water penetration rate is much below the polymer chain relaxation rate).

The *n* values for the single reinforced composites (X1, Y1, Z1) with weight ration OPA:OPF of 1:0 were found to be close to 0.5, an indication that the rate of diffusion of the water molecules into the composites is much less than that of the polymer composite segment mobility. Hybrid composite (X2) with weight ratio OPA:OPF of 3:1 exhibited the intermediate behavior between Fickian and non-Fickian diffusion where the penetration mobility and the polymer segment relaxation are comparable. For other hybrid composites, the diffusional coefficients (*n*) are higher than 1.0 or close to 1.0 which

indicates that the transport mechanism is Super Case II or Case II (relaxation controlled). Penetration of water molecules is much greater than the relaxation processes. Generally, it is observed that the value of *n* increases as the fiber content of the polymer increases. This is due to the hydrophilic nature of the fibers.

Table 2
Moisture constants for the composites

	Sample Designation	Composition OPA:OPF	Slope (n)	Intercept (k)	R^2
	A0		0.158	0.380	0.900
2 wt%	X1	(1:0)	0.588	1.330	0.957
	X2	(3:1)	0.737	1.789	0.915
	X3	(1:1)	1.026	2.500	0.957
	X4	(1:3)	1.220	2.975	0.946
	X5	(0:1)	1.394	3.339	0.957
4 wt%	Y1	(1:0)	0.588	1.470	0.992
	Y2	(3:1)	1.163	2.831	0.892
	Y3	(1:1)	1.217	2.955	0.922
	Y4	(1:3)	1.021	2.515	0.981
	Y5	(0:1)	1.391	3.396	0.970
6 wt%	Z1	(1:0)	0.593	1.469	0.970
	Z2	(3:1)	1.163	2.469	0.891
	Z3	(1:1)	1.141	4.01	0.972
	Z4	(1:3)	1.214	3.096	0.958
	Z5	(0:1)	1.493	3.396	0.834

Table 3
Water transport mechanism for produced hybrid composites

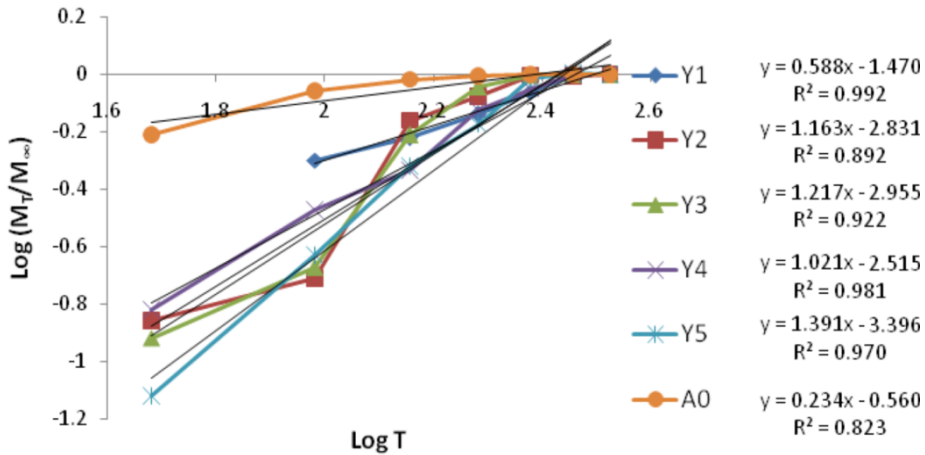| Type of transport	Slope (n)	Time dependence	Composites	Range of water absorption (%)
Less Fickian diffusion	n<0.5	$t^{-1/2}$	A0	0-0.6
Fickian diffusion	n=0.5	$t^{1/2}$	X1, Y1, Z1	1.80-2.90
Non-Fickian (anomalous) diffusion	0.5<n<1.0	t^{n-1}	X2	2.87
Case II transport	n=1.0	Time independent	X3, X4, X5, Y2, Y3, Y4, Y5, Z2, Z3, Z4, Z5	3.5-7.2
Super Case II transport	n>1.0	t^{n-1}	X3, X4, X5, Y2, Y3, Y4, Y5, Z2, Z3, Z4, Z5	3.5-7.2

Fig. 9 Diffusion curve fitting for polyester OPA/OPF composites with 4% reinforcement
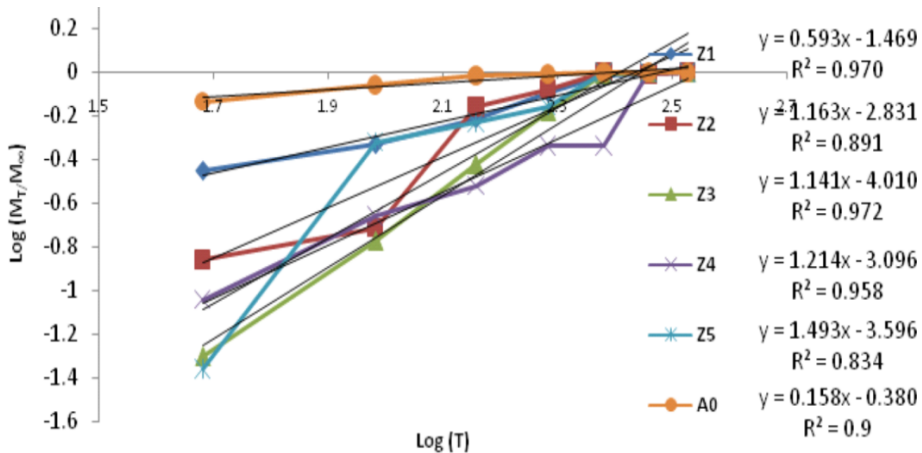

Fig. 10 Diffusion curve fitting for polyester OPA/OPF composites with 6% reinforcement

It is also noted from Table 3 that there is correlation between the percent water absorption and diffusion exponent (n). It is observed that as the water absorption rate increases with the increase in OPF content in the composite, the diffusion exponent value also increases. It can therefore be said that the amount of water absorbed by the composites is directly proportional to the diffusion exponent (n), and hence influences the diffusion transport mechanism.

4. Conclusions

The water absorption characteristics of polyester matrix hybrid composites reinforced with varied weight ratios and weight percent of oil palm ash and oil palm fiber have been investigated. From the results obtained, the following conclusions are drawn:

- The amount of water absorbed by the composites increases with the increase in the fibre weight ratio of the OPA-OPF hybrid reinforcement, and also with the increase in the weight percent of the reinforcement phase.

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- The diffusion transport mechanism as predicted from the diffusion exponent (n) shows that the majority of the hybrid reinforced composite compositions and all the composites reinforced only with OPF exhibited super case II or case II diffusion.
- All the composite grades reinforced with OPA only and the unreinforced polyester exhibited Fickian and less Fickian diffusion, respectively.
- Only the hybrid composition containing 2 wt% reinforcement having weight ratio OPA: OPF of 3:1 exhibited the intermediate behavior between Fickian and non-Fickian diffusion.
- Generally, the values of the diffusion exponent (n) increased as the amount of water absorbed by the composites increases.

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