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# Kinetic Studies on Water Absorption properties of Cocoa-pod Epoxy Composites

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*ABSTRACT*

The kinetic and characteristics of water absorption of cocoa-pod husk filler reinforced epoxy composite by short-term immersion at room temperature was studied. Composite specimen containing 5, 10, 20 and 30% filler volume fraction were prepared. The percentage of moisture uptake increased as the fibre volume fraction increased due to the high cellulose content of cocoa-pod husk. Results indicate that a D value of $105.8 \times 10^{-7}$ $m^2/s$ at 30% volume fraction was obtained.The process of absorption of water was therefore found to follow the kinetics and mechanism described by Fick's law.

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## INTRODUCTION

Due to their favorable performance characteristics, polymer composites are becoming widely used in different facets of human endeavors. However, the mechanical properties of these materials are subjected to deterioration especially when exposed to moisture for a considerable period. Therefore, to harness the potential of such composite material, their response to moisture must be clearly understood. The effect of moisture on epoxy resins has been studied from the point of view of both absorption that brings about degradation and of sorption behavior itself. For example, water absorption has been found to decrease the glass transition temperature, $Tg$ , because of strong hydrogen bonds, and it has been shown that in amine-cured resins, water is homogeneously distributed as a plasticizer and that water clusters are present at microcrack [1].

In recent times, Cocoa-pod husk (CPH), an agricultural harvest residue abundant in southwest Nigeria has been studied in the past, in order to understand its rheological behaviour [2], physicochemical analysis and effect as filler in polymer composites [3, 4].

The poor resistance of filler reinforced composite to water absorption can have undesirable effects on the mechanical properties and the dimensional stability of the resulting composites. Cracking and debonding can also modify the mechanisms of water penetration in the composite by providing new pathways for moisture ingress [5]. Water absorption is primarily measured by weight gain, and Fick's law characterizes the mechanism of its diffusion and this has been shown to be governed by three different mechanisms [6, 7]. The first involves of diffusion of water molecules inside the micro gaps between polymer chains. The second involves capillary transport into the gaps and flaws at the interfaces between fiber and the matrix. This is because of poor wetting and impregnation during the initial manufacturing stage. The third involves transport of micro cracks in the matrix formed during the compounding process [8, 9]. Study of the water absorption characteristic of natural filler reinforced polymer composite is important in order to effectively harness their outdoor utilization and to meet the stringent service requirements of the composite. The

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objective of this work therefore, is to study the kinetic of water absorption characteristic of cocoa-pod husk filler reinforced epoxy composite.

## MATERIAL AND METHODS

Cocoa pod husk was obtained from harvested cocoa during the harvest season in southwestern Nigeria. The pod was first sun dried for three day, after which the sample was ground into powder and sieved with BS/ISO 3310 into particle size of 75 µm. It was oven dried at 80$^0$C until a constant weight was obtained. Epoxy resin 3554A, a bisphenol class of epoxy resin, and 3554B an amine class hardener, were supplied by a local supplier in Lagos Nigeria. Composites with requisite amounts of Cocoa pod husk filler ranging from 5, 10, 20, and 30 wt. % were produced. Water absorption studies were performed following the ASTM D570-98 method. The samples were taken out periodically and weighed immediately, after wiping out the water on the surface of the sample, to determine the amount of water absorbed. The amount of water absorbed in the composites was calculated by the weight difference between the samples exposed to water and the dried samples.

### Kinetics of Water Absorption

The poor resistance of the fibres to water absorption can have undesirable effects on the mechanical properties and the dimensional stability of the composites [10-15]. In general, diffusion behaviour in glassy polymers can be classified according to the relative mobility of the penetrant and of the polymer segments. With this, there are three different categories of diffusion behaviour [9]. Case 1, in which the rate of diffusion is much less than that of the polymer segment mobility. The equilibrium inside the polymer is rapidly reached and it is maintained with independence of time. Case II (and super Case II), in which penetrant mobility is much greater than other relaxation processes. 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 penetrant concentration is reached in the whole polymer. Non-Fickian or anomalous diffusion occurs when the penetrant mobility and the polymer segment relaxation are comparable. It is then, an intermediate behavior between Case I and Case II diffusion. These three cases of diffusion can be distinguished theoretically by the shape of the sorption curve represented by the following equation:

$$\mathrm{M}_t/\mathrm{M}_s = Kt^n \qquad (1)$$

where $\mathrm{M}_t$ is the moisture content at time t; $\mathrm{M}_s$ is the moisture content at the equilibrium; and k and n are constants.

*K* is a constant characteristic of the sample which indicates the interaction between the sample and water and n indicates the mechanism of sorption. The values of n and k were determined by linear regression analysis. The value of coefficient n shows different behaviour between cases; for Fickian diffusion $n = 0.5$; while for Case II $n = 1$ (and for super Case II $n > 1$). For anomalous diffusion, n shows an intermediate value ($0.5 < n < 1$). Natural fibres and fillers reinforced polymer composite moisture absorption processes, often follow the prediction of Fick's law, where the mass of water absorbed increases linearly with square root of time, and then gradually slows until equilibrium plateau. The diffusion coefficient, D, can be determined from the equation expressed below:

$$\mathrm{M}_t/\mathrm{M}_s = (4/h)(D/\pi)^{1/2}t^{1/2} \qquad (2)$$

Where h is thickness of sample

## RESULTS AND DISCUSSION

### Water Absorption Kinetics

It is clear from Figure 1 that the composites absorb water very rapidly at the initial stage, and later a saturation level was attained without any further increase in water absorption. Increase in water absorption as filler volume fraction, may be largely due to high cellulose content of cocoa-pod husk [4], high poor wettability and adhesion between filler and matrix, defects such as voids, which lead to water penetration in the composite thus providing new pathways for moisture ingress [16]

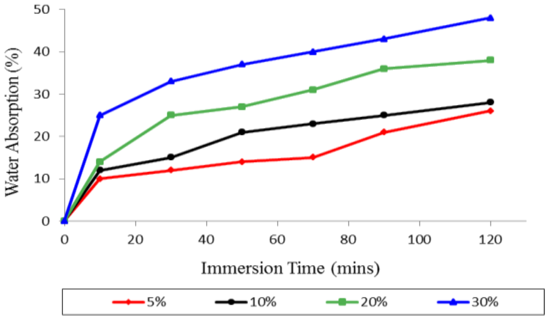

**Figure 1.** Change in water absorption of composites.

Water absorption in polymers is often analyzed in terms of Fickian diffusion, which requires that the results are plotted as weight gain (as a percentage of dry weight) versus square root of time [16]. As shown in Figure 2, percentage moisture absorption increases steadily with $t^{1/2}$ in the initial stage and then tends to level off following the saturation point, indicating a Fickian mode of diffusion.

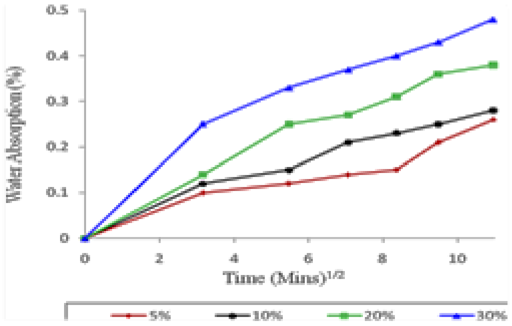

**Figure 2.** Water absorption curve for composite

The analysis of the diffusion mechanism and kinetics were performed based on the Fick's theory. It was considered that the change of weight gain for all samples is a typical Fickian diffusion behaviour. The mechanism of water uptake and hence the study of the kinetic parameters n and k, were analyzed by adjusting the experimental values to the following equation, obtained from Eq. (1) as follows:

$$\log(M_t/M_s) = \log k + n\log(t) \qquad (3)$$

Figures 3(a) to 3(d) show the fitting of the experimental data to Eq. (3). The values of the parameters n and k obtained from the fitting curves of the water absorption of the composites are presented in Table 1. Since the values of n approached 0.5, the implication is that the composites showed a tendency to approach Fickian behaviour. When n lies between 0.5 and 1, the diffusion is anomalous [5], [17]

**TABLE 1.** Moisture Sorption constantand Difission Coefficent of Composite

| Sample | n | k | D x $10^{-7}$ $m^2/s$ |
|---|---|---|---|
| 5% | 0.5587 | 0.58019 | 1.437 |
| 10% | 0.4995 | 0.5334 | 5.446 |
| 20% | 0.2901 | 0.15322 | 9.112 |
| 30% | 0.2540 | 0.11195 | 105.899 |

The diffusion coefficient (D) is the most important parameter of Fick's model, which shows the ability of the water molecules to penetrate inside the polymer matrix. This was calculated using the following equation from the initial slope of the plot of Mt/Mm against $(\text{time})^{1/2}$[5]:

$$M_t/M_S = (4/h)(D/\pi)^{1/2}t^{1/2} \qquad (4)$$

Figure 4 shows the diffusion curve fitting plots for composites for diffusion coefficient. The values of D are also presented in Table 1. Due to the hydrophilic character of natural fillers, the inclusion of water molecules inside the composite material is favoured as demonstrated by the kinetics of the diffusion processes [5]

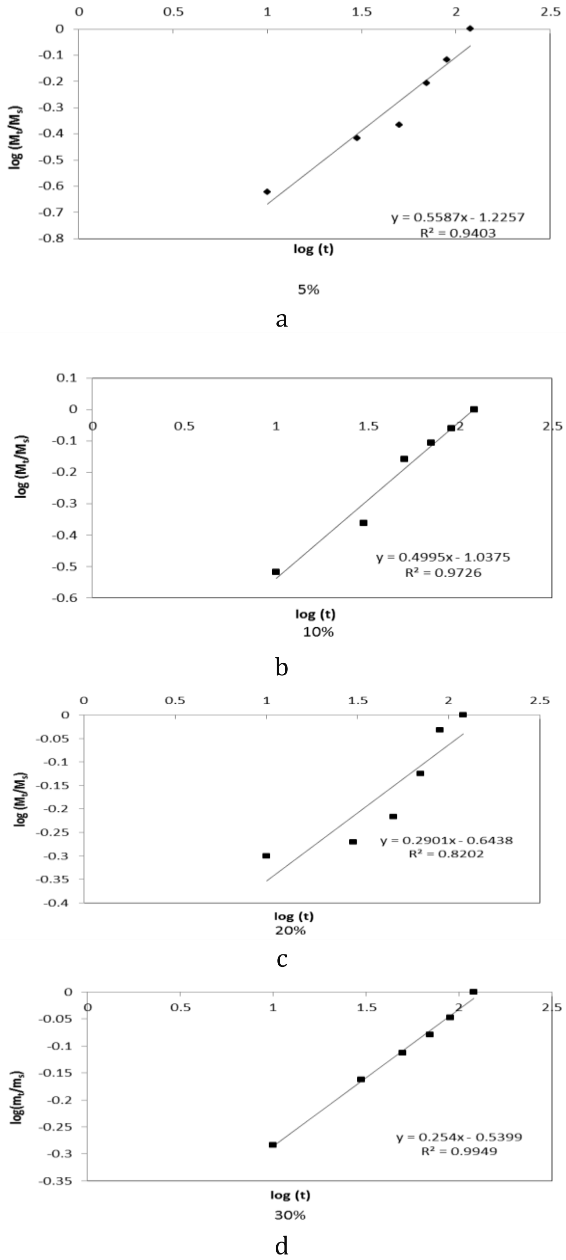

**Figure 3. (a)** Diffusion curve fitting plot of Composite at 5% volume fraction. (b) Diffusion curve fitting plot at 10% volume fraction. (c) Diffusion curve fitting plot at 20% volume fraction. (d) Diffusion curve fitting plot at 30% volume fraction

## CONCLUSION

The kinetic and characteristics of water absorption of cocoa-pod husk filler reinforced epoxy composite has been studied. Results indicate that moisture uptake increase as filler volume fraction increases due to increased voids and cellulose content. Therefore, cocoa pod –epoxy composites indicate a Fickian mode of diffusion and a tendency to approach Fickian behaviour.

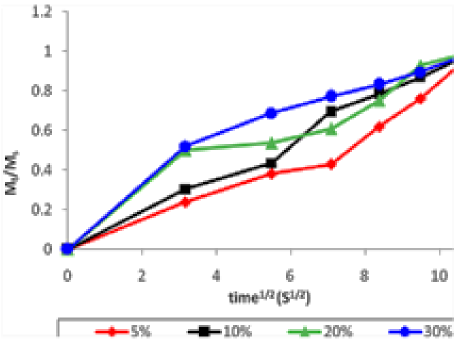

**Figure 4.** Diffusion curve fitting plots for composites for diffusion coefficient

## Competing interests

Authors have declared that no competing interests exist.

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## Persian Abstract

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### چکیده

سینتیک و مشخصات جذب آب برای کمپوزیت فشرده ی فیلتر شده ی پوسته کاکائو توسط غوطه وری کوتاه مدت در دمای اتاق مورد مطالعه قرار گرفت. گونه ی کمپوزیت شامل ۵، ۱۰، ۲۰ و ۳۰ درصد از کسر فیلتر شده آماده شد. درصد جذب رطوبت با افزایش کسر حجمی در اثر افزایش مقدار سلولز افزایش یافت. نتایج نشان می¬دهد که D-value برابر ۱۰۷×۱۰۵,۸ متر مربع بر ثانیه در ۳۰٪ کسر حجمی بدست آمد. با توجه به نتایج سینتیک و مکانیزم فرآیند جذب آب توسط قانون فیک توجیه شد.