

Diffusion Studies of Nanofibril Reinforced Unsaturated Polyester Nanocomposites

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ABSTRACT: This work deals with the water sorption characteristics of isorananofibril reinforced polyester composites with special reference to filler loading as well as temperature. It was found that, the neat polyester resin shows high water absorption at room temperature. The reduction of water absorption of INF filled composites is due to the improved inter-facial adhesion, which prevents the easy penetration of water molecules in the nanofibril composite. The formation of fibrous network of cellulose nanofibrils with the polyester matrix also prevents the swelling of the composite and thus reduces the water penetration. At 90 °C, after the initial capillary uptake of water, as the INF loading increases the water uptake also increases. This is due to the hydrophilic character of INF. At higher temperature, the composite lost all its hydrogen bonding interactions and the neat polyester shows lower water uptake. The mechanism of diffusion was analysed and the effect of INF on the sorption kinetics was studied. Parameters like diffusion, sorption and permeability coefficients of the composites were determined.

I. INTRODUCTION

The use of natural plant fibres as reinforcement in polymer composites for making low cost engineering materials has generated much interest in recent years [1-5]. New environmental legislation as well as consumer pressure has 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 fibre [6]. The advantages of natural plant fibres over traditional glass fibres are acceptable as good specific strengths and modulus, economical viability, low density, reduced tool wear, enhanced energy recovery, and reduced dermal and respiratory irritation and good biodegradability [7]. Furthermore, cellulose fibres are environmentally friendly, non-toxic and renewable materials. Despite the enormous advantages presented by cellulose fibres, their utilization as reinforcement in polymer composites has been limited by their susceptibility to moisture absorption. This makes them susceptible to swelling, resulting in formation of micro-cracks and voids at the fibre-matrix interface region. This in turn reduces the dimensional stability and mechanical properties of composites [8-10]. The hydrophilic nature of cellulose fibres is facilitated by hydroxyl groups which are present in the structure of cellulose that makes them attract and bind with water molecules via hydrogen bonds [11-13]. Moisture diffusion in polymeric composites has shown to be governed by three different mechanisms [14, 15]. The first involves 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 fibre and the matrix. This is a result of poor wetting and impregnation during the initial manufacturing stage.

The third involves transport of micro cracks in the matrix arising from the swelling of fibres (particularly in the case of natural fibre 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 behaviour between Fickian and non-Fickian [16,17]. In general moisture diffusion in a composite depends on factors such as volume fraction of fibre, voids, viscosity of matrix, humidity and temperature [18].

Natural fiber reinforced polyester materials are more or less sensitive to humidity through absorption of water and the differential swelling between the fibers and the resin. The uptake of water can also lead to chemical degradation such as hydrolysis of the matrix. Consequently the fiber-matrix interface is affected, resulting in changes of bulk properties such as dimensional stability and mechanical properties. Water treatment is strongly affected by the nature of fiber/matrix interface. If the interface is strong, it is difficult for the water molecules to diffuse into the composite system. Several investigators have evaluated the sorption properties of composites based on jute, pineapple, oil palm etc in different polymer matrices [19-21]. Bessadoc et al. [22] investigated the water sorption characteristics of alfa fibers. The results revealed that, the treatments reduced the overall water uptake of alfa fibers. The physical mechanism of moisture diffusion into highly hygroscopic fibers

such as wool and cotton can be described by a 2 stage moisture diffusion process, a fast Fickian diffusion with a concentration diffusion coefficient and a slow diffusion with a time dependent diffusion coefficient. Several studies have been reported on the effect of moisture absorption on the mechanical properties of natural fiber reinforced unsaturated polyester and randomly oriented natural fibers/polyester composites [23].

This paper is concerned with the moisture sorption characteristics of isorananofibril reinforced unsaturated polyester nanocomposites. The water sorption of these composites at different temperatures was analysed. The diffusion coefficient, sorption coefficient, permeability coefficient and the kinetic parameters of water diffusion of the composites were calculated. It is important to add that no detailed studies have been reported on the water absorption of nanofibril reinforced unsaturated polyester nanocomposites.

II. EXPERIMENTAL

Materials used:

The resin employed in this study was, unsaturated polyester based on isophthalic acid with 40% of styrene [specific density -1.080 g/cm^3 , at 258°C viscosity is 650 cps]. Methyl ethyl ketone peroxide [MEKP], and cobalt naphthenate were introduced into the system as initiator and accelerator respectively. The resin and the reagents were supplied by Sharon Engineering enterprises, Cochin, India. Isorananofibrils were extracted from the bark of *H. isoraplant* using steam explosion technique. Isorafibers have a diameter of 10–20 μm , density of 1.35 g/cm^3 and a tensile strength of 500–600 MPa. Sodium hydroxide, acetic acid, sodium chlorite and oxalic acid were the chemicals used in the nanofibril preparation and all reagents were of analytical grade.

Preparation of isorananofibrils

Isora fibers were chopped into short length of about 0.5–1 cm and treated with 2 wt% NaOH in an autoclave and kept under 137 Pa pressure for one hour. Then fibers were bleached using a mixture of NaOH and acetic acid and a mixture of 1:3 sodium hypochlorite solution. The steam exploded bleached fibers were treated with 10% oxalic acid in an autoclave under pressure. The fibers were suspended in water and homogenized the solution for 20 min and the suspension was kept in an oven at 90°C till it was fully dried.

Preparation of composites

Isorananofibrils [INFs]–polyester composites were prepared using a three piece stainless steel mold having dimensions of $200 \text{ mm} \times 150 \text{ mm} \times 30 \text{ mm}$. Prior to the composite preparation, the mold surface was polished well and a mold releasing agent was applied to the surface. Isorananofibrils (in powder form) of varying composition [0.5, 1, 3 and 5 wt%] were mixed with 100 g unsaturated polyester resin by homogenization, followed by probe sonication. The quantity of accelerator and catalyst added to resin was 1.5% by volume of resin each and is mixed by mechanical mixing for 2 min. Then the resin mixture was poured evenly on to the mold and air bubbles were removed carefully. The closed mold was cured at room temperature for 12 h under constant pressure (1 MPa). The demolded samples were post cured for a further period of 24 h and cured at 80°C for 6 h. From the sheet, samples were cut for measuring various properties according to ASTM standards.

Diffusion studies

Diffusion studies were used to determine the barrier properties of isorananofibrils on the water absorption behaviour of the polyester composites under specified conditions. For the diffusion tests, round shaped samples of 2 mm thickness and a diameter of 2 cm were used and a minimum of three samples used for each composition. The specimens were dried in an oven at 80°C for 6 hours, and after cooling the specimens were weighed accurately using electronic balance. Then these samples were immersed in water taken in test bottles at room temperature and studied the diffusion rates.

III. RESULTS AND DISCUSSION

Water uptake of INF/unsaturated polyester nanocomposites

Figure 1 shows the molar uptake of INF reinforced unsaturated polyester nanocomposites at different filler loading, as a function of immersion time at 25°C . It was found that, the neat polyester resin shows high water absorption at room temperature. The observed absorption of water in this case could have occurred through the micro cracks present in the material. All the composite samples absorbed water at the initial stage and later a saturation level was attained without any further increase in water sorption. The water absorption curves show a multi stage mechanism. The initial portion of the moisture absorption curve is linear, after which the mechanism changes. Water diffusion in polymers was found to lead to typical phenomena of composite swelling and physical relaxation. According to Flory's two-stage theory [24] the swollen polymer chains induce increased elasticity of chain structure and thus increased chemical potential. The increased chemical potential

inhibits further absorption of water which may be observed as the first equilibrium of water uptake. However the swollen polymer chains start relaxing with time and subsequently reduce chemical potential.

the second equilibrium is attained by the decreased elasticity of the polymer chains. From figure it can be seen that, 0.5 wt% INF reinforced composite shows very low water absorption. These three dimensionally cross-linked nanocomposites has very little absorption at room temperature. All the composite samples absorbed water at the initial stage but resulted in a levelling off at a later stage. This indicates the attainment of equilibrium. The water penetration and diffusion are mainly through the filler/matrix interfacial region and cross sectional portion of the filler by capillary mechanism.

The reduction of water absorption of INF filled composites can be explained by several factors. The improved inter-facial adhesion prevents the easy penetration of water molecules in the nanofibril composite. Another reason is the formation of fibrous network of cellulose nanofibrils with the polyester matrix prevents the swelling of the composite and thus reduces the water penetration [25]. Although the cellulose contains a number of hydrophilic OH groups, the water intake of the nano composites is reduced compared to neat resin indicating a lower availability of free -OH groups and a higher fraction of polymer matrix entrapped within the cellulosic network and on the surface of the nanofibers.

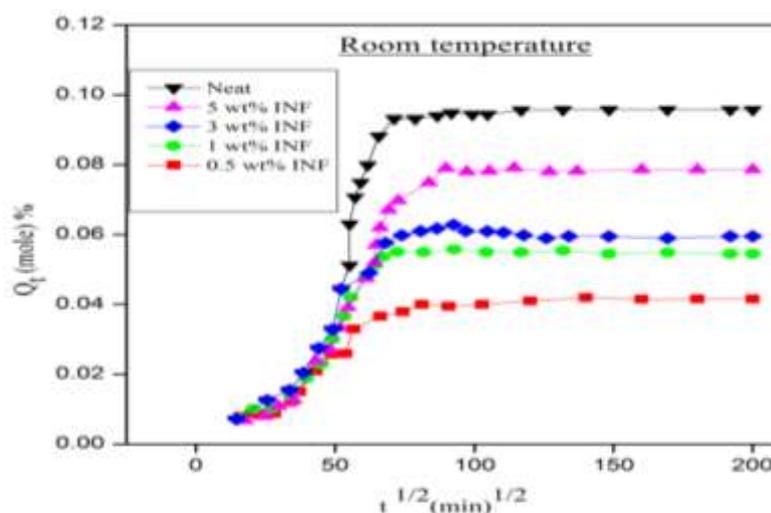


Figure 1: Molar uptake of unsaturated polyester nanocomposites having different INF content as a function of immersion time at 25°C

Due to the hydrogen bonding between nanofibril and polyester, hydroxyl groups available for water absorption is decreased, and it results in lower water intake. The percentage swelling was lowest for 0.5 wt % INF composite compared to the other INF reinforced samples. The water sorption was found in the order neat > 5 > 3 > 1 > 0.5 wt % INF filled nanocomposites. Higher water absorption rate of 3 and 5 wt % INF filled composites can be explained as follows.

At higher concentrations of isorananofibrils, there exists poor filler matrix interaction and which results in vacant spaces in composites, thereby increases the water absorption. Also the addition of nanofibrils at higher concentrations exposes more free hydroxyl groups, which can direct towards water molecule results in more water absorption. Similar trend is observed by Das et al., with biocopolyester reinforced with jute nanofiber [26]. The percentage swelling was lowest in 10 wt % jute nanofiber reinforced composites and they explained it due to the uniform dispersion of the nanofiber in matrix.

Upon reinforcing polyester resin with INF, a large decrease in sorption takes place. The presence of reinforcement modifies the response of the resin to humid environments. The diffused moisture may reduce the bond strength by the breaking of the bonds. The lower water uptake of INF filled composites supports the increased fibril/matrix adhesion observed in the mechanical property measurements. The interaction between nanofibril and water molecule is represented in **figure 2**. Two types of hydrogen bonds are present in the system. Inter molecular hydrogen bonds are formed between the hydroxyl groups in the cellulosic fiber and water, while intramolecular hydrogen bonds are formed with the hydroxyl groups of two cellulosic units in the form of chain.

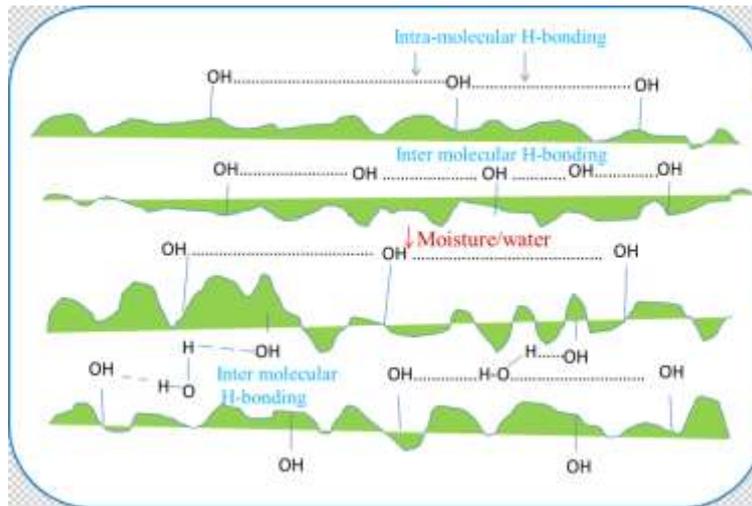


Figure2: Schematic showing the interaction of cellulose with water molecule

possibility of water absorption in composites is through the interfacial region. Several researchers have reported the chances of thermal shrinkage in composites especially in thermosetting resin matrices during curing [27]. By the addition of INF, moisture absorption reduced in composites, thus the durability of UPR composites can be improved by the addition of this nano filler. The water sorption is found to follow the order: 0.5 wt% > 1 wt% > 3 wt% > 5 wt% INF filled composites. As the hydroxyl groups of cellulose become chemically bonded to UPR, by hydrogen bonding interaction, the hydrophilic character of the filler is reduced, which favours a strong interfacial adhesion between INF and UPR matrix.

Effect of temp.on water uptake of INF/unsaturated polyester nanocomposites

Figure 3 shows the molar uptake of INF reinforced unsaturated polyester nanocomposites at different filler loading, as a function of immersion time at 90°C. At 90 °C, after the initial capillary uptake of water, as the INF loading increases, the water uptake also increases. This is due to the hydrophilic character of INF. All the composites showed higher water uptake at 90 °C and the saturation level for the composite is much higher at 90 °C. At this temperature, the water sorption gradually increases with the filler loading. As the fiber loading increases, the composite surface becomes more and more hydrophilic and water can penetrate into the composite, leading to increased water absorption.

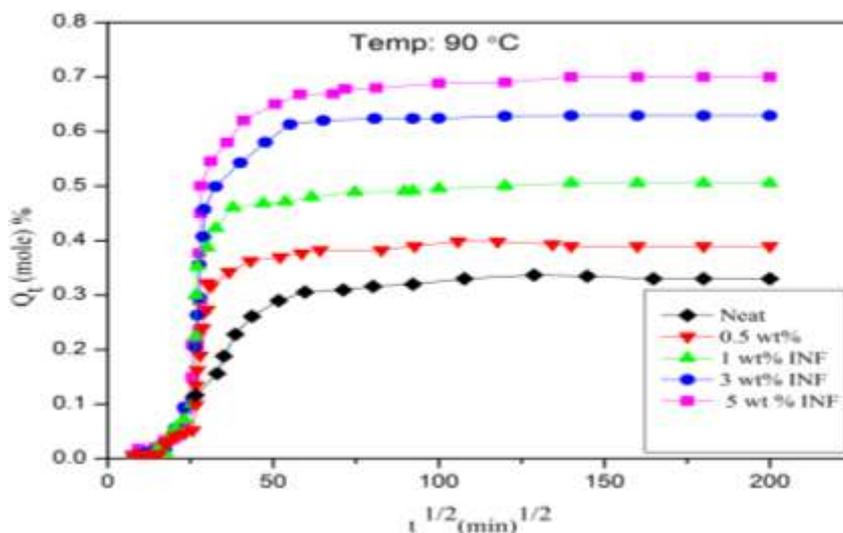


Figure.3: Molar uptake of unsaturated polyester nanocomposites having different INF content as a function of immersion time at 25°C

It is observed that, the initial rate of water sorption and the equilibrium rate of water uptake of INF/polyester nanocomposites increased with increase in temperature because diffusion coefficient (D) is related to the velocity of the diffusing molecules by the equation given below.

$$D = 1/3 \lambda c \dots \dots \dots (1)$$

Where c is the mean velocity of molecules, λ is the mean free path (distance travelled by molecules between two consecutive collisions). Since the mean velocity increases with temperature, the diffusion also increases with temperature.

The effect of INF loading on the Q_α values for the composites at 90 °C is evident from **table2**. The water absorption is found to follow the order, neat < 0.5 wt% < 1 wt% < 3wt% < 5 wt% INF filled nanocomposites. For all composites, the rise of temperature leads to enhanced water uptake at equilibrium. The observed change in Q_α shows that, temperature has a strong effect on the fiber/matrix interaction in these composites. This is associated with the changes that occur in the interface at high temperatures, in composites. At high temperature, the composite lost all its hydrogen bonding interactions and the neat polyester shows lower water uptake. Then further with increase in INF, the water absorption rate increases, leading to a regular increase in water absorption rate with INF loading. The increased water uptake at higher temperature can be due to the relaxation mechanism in the polymer whereby the polymer network is distorted. This inevitably leads to large scale segmental motion, allowing further penetration of water.

At higher temperature, the adhesive bonding is deteriorated. The temperature affects the penetration rate of water to the interface. Bellenger et al. [28] observed that, in crosslinked polyesters the water equilibrium concentration is an increasing function of temperature. With increase of temperature, as a result of the expansion of volume fraction accessible to water molecules is increased and the water uptake got enhanced.

Kinetics of water diffusion:

To study the mechanism of water sorption, the kinetic parameters n and k , diffusion coefficient and permeability coefficient of water absorption in different systems were analysed using the following relationship. $\text{Log}(Q_t/Q_\alpha) = \log K + n \log t$ (2)

Where Q_t is the mole percent uptake at time t , Q_α is the mole percent uptake at equilibrium, t is the time, k is a constant characteristic for the polymer, which indicates the interaction between the polymer and the water. The values of n and k are determined by linear regression analysis. The value of n shows the diffusion process and the constant k indicates the interaction between polymer and the solvent. When the value of $n = 0.5$, diffusion obeys Fick's law and is said to be Fickian. This occurs when the segmental mobility of the polymer chains is faster than the rate of diffusion of permient molecules. When $n > 1$ the diffusion is said to be anomalous. When the value of n is, between 0.5 and 1 the diffusion is non Fickian. The value of n is between 0.5 and 1. The value of n clearly shows that the diffusion process deviates from the Fickian mechanism.

Diffusion, sorption and permeability coefficient

Diffusion coefficient explains the rate at which diffusion process takes place. It is the rate of transfer of the diffusing substance across unit area of section divided by the space gradient of concentration. It characterizes the ability of water molecules to diffuse into the system. The values of diffusion co-efficient were calculated from the relationship and are given in **table3 and4**.

$$D = \pi [h\Theta/4Q_\alpha]^2$$
..... (3)

Where Θ is the slope of the initial linear portion of the sorption curves and h is the thickness of the sample. Q_α is the mole % at equilibrium. The values of diffusion coefficient are given in table. The diffusion coefficient changes with changes in filler loading and with temperature. The diffusion coefficient D which characterizes the ability of water molecules to diffuse into the fiber is increased at higher temperature. At higher temperature, the hydrogen bond formation tends to disappear and the molecular packing controls the diffusion process. At room temperature, the absorption diffusion mechanism with filler loading is slow and especially at 0.5 wt%, because the entrance of water molecules into the crystalline regions is difficult. Diffusion coefficient obeys the activated transition theory and its temperature dependence can be expressed by the Arrhenius equation [29, 30].

$$D = D_0 \exp(-E_a/RT)$$
 (4)

In which E_a is the activation energy of diffusion, D_0 is the pre-exponential factor and R is the gas constant. The exponential correlation of diffusivity with $1/T$ results in a very strong temperature dependence. The permeability of small molecules into a polymer is dependent on diffusivity as well as the sorption or solubility of a liquid in the polymer. Diffusion which is a thermally activated process is very sensitive to temperature. It is a general phenomenon that, low diffusion coefficient of materials in polymers, shows considerable dependence on any change of condition of concentration, temperature etc.

The sorption coefficient (S) or solubility can be calculated from equilibrium swelling using the equation [29],

$$S = M\alpha/M_p$$
 (5)

Where M_a is the mass of water taken up at equilibrium and M_p is the initial mass of the polymer. Solubility is a thermodynamic parameter which depends on the strength of interaction in the polymer penetrant mixture. The obtained values for sorption coefficient are given in table3 and 4. At room temperature maximum sorption coefficient is for neat polyester and least for 0.5 wt % INF filled composites. The reduction of water absorption of INF filled composites is due to the improved inter-facial adhesion, which prevents the easy penetration of water molecules in the nanofibril composite. At 90 °C, maximum sorption is for 5 wt% INF reinforced composites. This is due to the hydrophilic character of INF. At higher temperature, the composite lost all its hydrogen bonding interactions and the neat polyester shows lower water uptake. Permeability coefficient gives an idea about the amount of water permeated through uniform area of the sample per second. Permeability coefficient which could be considered as the total effect of sorption and diffusion can be estimated using the following equation.

$$P = DS \dots \dots \dots (6)$$

Where D is the diffusion coefficient and S is the solubility.

Table3 and4 shows the effect of filler loading on permeability of isorananofibril reinforced unsaturated polyester nanocomposites at different temperatures. The calculated P values are shown in table. The P values also increased with increase in temperature and the D with filler loading (90°C). It is due to the inherent hydrophilic nature of filler. As the temperature increases, the D value increases in all composites. At room temperature D value is maximum for neat and least for 0.5 wt% INF reinforced composites. At higher concentrations of isorananofibrils, there exists poor filler matrix interaction and which results in vacant spaces in composites, thereby increases the water absorption. Also the addition of nanofibril at higher loadings exposes more free hydroxyl groups, which can direct towards water molecule results in more water absorption. The sorption and permeability coefficient vary with filler temperature. At 90 °C, the permeability value increases as a function of filler loading and is maximum for 5 wt% INF filled composites. Because at 90 °C, the interactions get deteriorated and with the addition of hydrophilic nanofibrils, permeability coefficient increases.

Table.1: Effect of filler loading on the Q_a , n and k values of isorananofibril reinforced unsaturated polyester nanocomposites at 25 °C.

Sample	Q_a (mole/g)%	n	K (g/g/min ²)
neat polyester	0.095	0.82	3.15
0.5 wt% INF	0.04	0.59	2.25
1 wt% INF	0.05	0.70	2.64
3 wt% INF	0.05	0.69	2.60
5 wt% INF	0.08	0.93	3.53

Table 6 : Effect of filler loading on the Q_a , n and k values of isorananofibril reinforced unsaturated polyester nanocomposites at 90 °C.

Sample	Q_a (mole/g)%	n	K (g/g/min ²)
neat polyester	0.33	0.62	2.18
0.5 wt% INF	0.39	0.88	3.5
1 wt% INF	0.51	0.73	3.7
3 wt% INF	0.63	0.73	3.1
5 wt% INF	0.7	1.11	3.79

Table 3: Transport properties of isorananofibril reinforced unsaturated polyester nanocomposites at 25 °C (D, diffusion coefficient, S and P, sorption and permeation coefficient).

Sample	D (*10 ⁻⁹) (cm ² sec ⁻¹)	S (g/g)	P (*10 ⁻¹⁰) (cm ² sec ⁻¹)
neat polyester	2.04	0.28	0.57
0.5 wt% INF	0.65	0.08	0.05
1 wt% INF	0.81	0.10	0.08
3 wt% INF	1.2	0.12	0.14
5 wt% INF	1.4	0.20	0.28

Table4: Transport properties of isorananofibril reinforced unsaturated polyester nanocomposites at 90 °C

Sample	D (*10 ⁻⁹) (cm ² sec ⁻¹)	S (g/g)	P (*10 ⁻¹⁰) (cm ² sec ⁻¹)
neat polyester	0.68	0.21	0.14
0.5 wt% INF	0.90	0.40	0.36
1 wt% INF	1.5	0.45	0.68
3 wt% INF	1.8	0.52	0.94
5 wt% INF	2.4	0.60	1.4

IV. CONCLUSIONS

The water absorption kinetics of isorananofibril reinforced unsaturated polyester nanocomposites were analysed at two different temperatures 25°C and 90 °C. The effect of filler loading on the water absorption of composites was valuated. It was observed that, the neat polyester resin shows high water absorption at room temperature. The reduction of water absorption of INF filled composites is due to the improved inter-facial adhesion, which prevents the easy penetration of water molecules in the nanofibril composite. At 90 °C, after the initial capillary uptake of water, as the INF loading increases the water uptake also increases. This is due to the hydrophilic character of INF. At higher temperature, the composite lost all its hydrogen bonding interactions and the neat polyester shows lower water uptake. The values of diffusion coefficient, sorption coefficient and permeability coefficient at equilibrium of nanocomposites were also studied. Diffusion studies revealed that the interfacial adhesion plays a vital role in the water transport process. Fickian model was used to study the diffusion process in nanocomposites and showed some deviations from Fickian behaviour. Finally it is highly relevant to add that, water transport studies could be used as a probe to evaluate the strength of the interfacial adhesion in nanofibril reinforced polymer composites.

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