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NON-FICKIAN TRANSPORT MECHANISM IN GLASSY POLYMERS, CROSSLINKED POLYMERS AND FIBER REINFORCED POLYMERIC COMPOSITES

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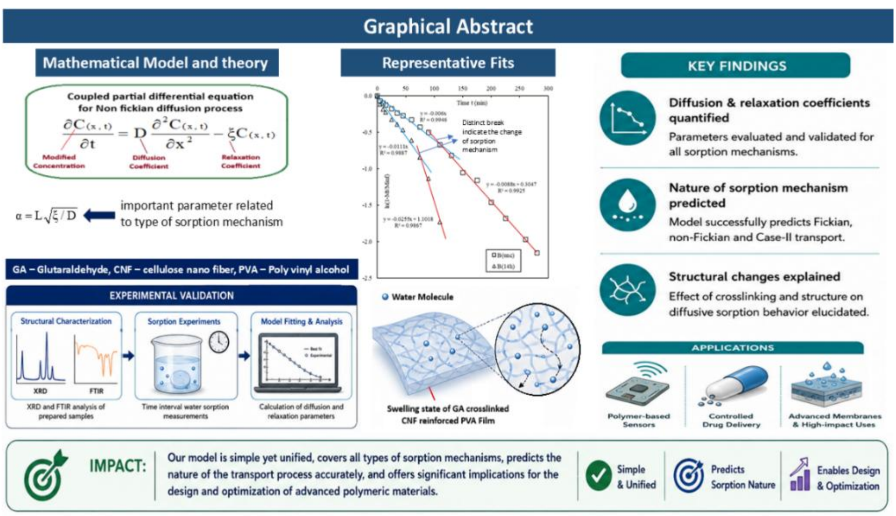
Abstract

This study presents a mathematical theory for non-fickian transport mechanism for glassy polymers, crosslinked polymeric system and fiber reinforced polymeric composites system; same was examined on cellulose nanofiber (CNF) reinforced and glutaraldehyde (GA) crosslinked poly vinyl alcohol (PVA) samples, having varying crosslinking density. XRD and FTIR characterization of CNF/PVA composite film gives the structural information about the reinforcement of CNF in crosslinked PVA matrix. Proposed mathematical model for non-fickian transport mechanism very well explains the effect of crosslinking in PVA and structural changes in polymeric system due to chain flexibility and mobility, while XRD and FTIR characterization cofirms structural changes. Quantitatively this model determines the diffusion coefficient (D), relaxation constant (ξ), and relaxation contribution parameter (α) from sorption data. The estimated D values 10−6 cm^2/min (~10^{-8} cm²/s) agrees well for glassy polymers Evaluated diffusion coefficients and relaxation coefficients, justified the real sorption process observed in non-fickian transport mechanism. This model is novel in a sense that it explains all type of transport mechanism and is capable of predicting nature of sorption process.

Keywords: *Non-fickian transport mechanism, Cellulose fiber reinforced PVA composite, anomalous diffusion model.*



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Introduction

Diffusion is the process involving transportation of from one part of a system to another because of random molecular motions[1]. Transport phenomena in polymeric systems, whether for drug delivery [2], membrane separation, or sensing applications [3] are governed by the mechanisms through which penetrant molecules move within the polymer matrix. Over the decades, a series of mathematical model have been proposed that explained the transport kinematics in polymeric diffusive systems (e.g., hydrogels). These models are categorized as: Fickian diffusion models, Collective diffusion models and non-Fickian diffusion models (anomalous) diffusion [4-9]. Polymeric systems—especially those that are glassy, semi-crystalline, or cross-linked—often deviate from classical Fickian behavior[6] due to viscoelastic nature of their matrix, chain relaxation, and penetrant–polymer interactions. These complexities of polymeric systems led to the recognition and classification of non-Fickian transport phenomena, which cannot be fully explained by Fick's laws alone. To account for these anomalies, Berens, and Hoffenberg (1978) [10] proposed a two-stage model, for Case II transport by coupling Fick's second law with a moving boundary to describe the advancing front of solvent into the polymer. A significant advance in modelling non-fickian behavior came from the work of Tanaka and Fillmore (1979) [11], they applied time-dependent diffusion coefficients to capture swelling-controlled transport in gels. In 1980 Frisch and coworkers [12] had developed a series of mechanistic models incorporating relaxation effects; in which the polymer was treated as a viscoelastic medium. Peppas and Ritger (1987)[8] developed semi-empirical models (power function model) to characterize solute release from polymers; in this power function model water uptake is a time dependent phenomenon [9] and fractional water uptake m_t/m_∞ is proportional to nth power of time. i.e. , where m_t and m_∞ are the masses of the water uptake at time t and at equilibrium respectively, n is the swelling exponent and k refers to the characteristic constant related to the swelling networks such as hydrogel[[5], [7], [8]]. This model can be applied only to initial sorption process i.e. up to 60% initial swelling. Based on the relative rates of diffusion and polymer relaxation[[8], [9], [13], [14], [15]]; value of swelling exponent "n" gives information about the diffusion mechanism. Although this power-law model provided a convenient and widely used framework, it lacked a mechanistic basis and was limited to the early stages of release. To overcome these limitations, more rigorous models were developed based on partial differential equations that couple diffusion with polymer relaxation dynamics.

In another important contribution, Amsden (1998) [16] proposed models for solute transport in hydrogels which accounts for the obstruction effect of polymer chains.Metzler and Klafter (2000) [17] introduced fractional diffusion equations to describe anomalous sub diffusive and super diffusive behavior observed in many biological and polymeric systems. In the context of controlled drug delivery, Siepmann and Peppas (2001) [18] integrated Fickian diffusion with polymer dissolution and degradation processes. Their model allowed simultaneous consideration of drug diffusion, matrix swelling, and erosion, which are common in biodegradable delivery systems.Yu et al., (2023) [19] proposed A two-stage moisture non fickian diffusion model based on the moisture diffusion mechanics of both neat resin and 3D woven composites, which describes the initial fast diffusion and the long-term slow diffusion stages. The moisture diffusion behavior of 3D woven composites exhibits non-Fickian properties. Lyu et al., (2024) [20] proposed a Unified Model for Non-Fickian Diffusion and Anomalous Swelling of Glassy Polymer Gels by extending the previous theory for swelling of soft gels. They assumed that the polymer network is a viscoelastic gel of glassy polymers and its relaxation time depends strongly on solvent concentration. Their theory predicts how the permeation speed of solvent and the characteristic times of the swelling process depend on material parameters and experimental conditions. Although the model successfully predicts anomalous swelling and solvent-front propagation, its validation is mainly limited to the conditions and systems considered in the study also this model has high computational complexity so determining multiple material parameters experimentally is very difficult in this model.

Maike A.F. dos Santos (2019) [21] presented a review to stress and reunite some of the analytic formalism of the anomalous diffusive processes. In this paper a fact was emphasised that there are many possible ways of modelling the anomalous diffusive processes. Another recent review work presented by Zhokh and Strizhak, (2026) [22] reviewed the non-Fickian reaction-diffusion equations arising from various microscopic models of the diffusive transport accompanied by a chemical transformation including continuous time random walks (CTRW), Levy flights, and diffusion in a fractal environment. They discussed the steady-state problem and related issues concerning the utilization of non-Fickian reaction-diffusion equations in chemical engineering.

These reported models discussed earlier, provide important theoretical advancements, their practical application often require simplifications or numerical methods due to their mathematical complexity. With the rise of smart materials, responsive hydrogels, hybrid composites, and chemiresistive thin film semi-conducting gas sensor [23] there is an increasing need for robust mathematical models that can predict behaviour under non-ideal and dynamic conditions. The development of such models remains an active area of research, particularly in fields like drug delivery, sensor design, and membrane technology.

In our study, in comparison to previously proposed complex models we have introduced a very simple and easily applicable new non-Fickian transport model which integrates relaxation dynamics with Fickian diffusion. This model explains all types of transport mechanism and is capable of predicting nature of sorption process.

We have applied this model to glutaraldehyde cross-linked CNF/PVA composites to determine diffusion and relaxation coefficients; which provides insights into how structural heterogeneity, crosslinking and nanoparticle dispersion affects transport. Proposed mathematical model for non-Fickian transport mechanism very well explains the effect of crosslinking in PVA and structural changes in polymeric system due to chain flexibility and mobility. Evaluated diffusion coefficients and relaxation coefficients, justified the real sorption process observed in the non-Fickian transport mechanism. Unlike conventional empirical models, the proposed model not only classifies the transport mechanism but also quantitatively determines the individual contributions of diffusion and relaxation processes

Materials and Methods

Materials-Poly Vinyl Alcohol (PVA) CH2CHOH, hot water soluble, M.W. 60,000 - 1,25,000; degree of hydrolysis 98 - 100.00 mol % and dialysis membrane-150 LA401-1MT (Capacity 5.07ml/cm) were obtained from Hi Media Chemicals Mumbai, India. Microcrystalline cellulose Powder (MCC) (AR Grade); pH 5 - 7.5 (100 g/l, H_2O, 20 °C) (slurry) and Sulfuric Acid (SA) 98% for analysis were obtained from Merck Chemical Industry, Mumbai, India. Glutaraldehyde (GA) (AR Grade) Assay 25% Aquas Sol., with water, density 1.06 gm/cm^3 was obtained from Loba Chemicals India and used as received. Hydrochloric Acid (N/10) 500ml were obtained from Fisher Scientific (AR Grade) was used as received. Acetone (Assay 99.0%, FW 58.08,500ml, (AR Grade) was obtained from Advent Chembio Pvt. Ltd., and was used as received. The Double Distilled Deionized CO_2 free water was used for the synthesis of various solutions.

Preparation of Cellulose Nano Fiber (CNF) suspension from Micro crystalline cellulose (MCC)- The cellulose Nano Fiber (CNF) suspension was obtained from acid hydrolysis of MCC by using (64% w/v) H_2SO_4 solution, followed the method described elsewhere [[30], [31]]. 2% w/v suspension of CNF in water was prepared[32].

Preparation of CNF reinforced PVA Film [32]- At first preparation of 0.1 w/v crystal clear 95 ml solution of PVA with D.I. water, was done. Thereafter, at 45°C temperature, 25 ml of CNF suspension (2 w/v) (pre ultrasonicated for 10 minutes for achieving homogeneous suspension) poured into the PVA solution and stirring on hot plate with stirrer at speed 600-700 rpm to ensure complete mixing of CNF into the PVA matrix and homogeneous suspension of CNF in PVA solution obtained. Whole mixture of PVA and CNF transferred onto the clean glass mold for film casting. For obtaining films drying was done in hot air oven at 45°C temperature for 24 hours. Dried CNF reinforced PVA films were peeled out from glass mold.

Crosslinking of CNF reinforced PVA film by Glutaraldehyde (GA)-The CNF Reinforced PVA film was first cut into 5 pieces of 1x1 cm^2 dimension and then we put them into the 50 ml crosslinking solution of Glutaraldehyde (5 v/v GA (25% solution), 0.12 v/v HCl (35-38%) and 94.88v/v of Acetone)[33] for different time at temperature 15-20°C (winter season). The immersed film samples were taken out from crosslinking solution, one by one at desired time interval of 14 h, 25 h, 37 h and 49 h, then they are dried in hot air oven at 45°C for 6 hours before performing required characterization and time interval sorption experiments.

Time interval sorption experiment- Water absorption of GA crosslinked PVA/CNF films was studied by gravimetric time interval sorption method by using high precision (A&D Japan) digital Balance. Distilled water with pH 7.1 is used as a swelling medium. First, we measured the thickness L (in cm) of all film samples , thereafter, a pre-weighed film samples (Labeled 14 h, 25 h, 37 h and 49 h) were placed in 100 mL of distilled water (pH 7.1) at 27°C separately. As according to labeling they are taken out regularly at different time intervals of 14 h, 25 h, 37 h and 49 h. After this they are gently wiped with tissue paper to remove loosely bound surface water and then dried; afterwards they are accurately weighed on a digital balance. The sample is then again placed in the swelling medium. The swelling ratio (SR) calculated by using the expression, $SR = (M_t-M_0)/M_0$, where, M_t is the mass of swelled film sample at time t and M_0 is the initial mass of film sample in dry state(Awasthi et al., 2016; Bajpai et al., 2014)[[7], [34]].

XRD and FTIR Characterization-The XRD spectra for our GA crosslinked CNF reinforced PVA film sample were recorded by XRD Spectrometer (Rigaku Mini Flex 600) and FTIR spectrum was recorded on FTIR-spectrophotometer (Shimadzu, 8400S) from central instrument facilities in Govt. Science College Jabalpur. FTIR scans recorded were the average of 100 scans and spectral range selected was 400 to 4000 cm^{-1}.

Proposed Model and related theory- Non-fickian diffusion (anomalous) process in glassy polymeric systems involves two equally probable and comparable transport mechanisms, fickian diffusion and relaxation mechanism [[5], [6], [7], [8], [9], [13]].While the Fickian diffusion is governed by Fick's I & II laws[[1], [24], [25], [26]] the relaxation mechanism is governed by exponential solute uptake from solution by diffusive system. Relaxation mechanism of solute uptake depends only on the present concentration difference from equilibrium solute uptake by system and is characterized by relaxation constant ξ (min^{-1} or sec^{-1}). For the development of our non-fickian diffusion model, we made following assumptions:

(1) Relaxation mechanism is caused because of free space created by polymeric chain readjustment due to swelling of polymeric system by diffusion mechanism [27].

(2) Both mechanisms are inter-dependent or correlated for both solute uptake scenario and swelling of crosslinked polymeric networks. i.e., in the time interval solute sorption experiment or swelling of polymeric system, equilibrium solute uptake concentration c_∞ is the sum of two separate contributions $c_{\infty,d}$ (fickian mechanism) and $c_{\infty,r}$ (relaxation mechanism), and these contributions affects each other.

(3) Relaxation constant ξ and diffusion coefficient D are independent of position x & time t for a particular period of sorption process.

(4) Solute uptake through edges is negligible, as area of thin planner sheet is considered too negligible.

Based on above assumptions, we have derived a second order partial differential equation representing the non-Fickian diffusion process –

$$\frac{\partial C_{(x,t)}}{\partial t} = D\frac{\partial^2 C_{(x,t)}}{\partial x^2} - \xi C_{(x,t)} \qquad \ldots (1)$$

Here, $C_{(x,t)} = c - c_\infty$ is modified concentration at time t and position x. For the solution of this partial differential equation, we assumed that, a finite sheet of unit cross section (A=1) and thickness L is placed in a well stirred solute solution or water for allowing solute or water diffuse into it. The sheet occupies the space $0 \le x \le L$, and solute solution (or water in the case of swelling) occupies the space $L \le x \le h$. The concentration of the solute in the solution is always uniform and is initially c_0, and sheet is free from solute (see fig. 1.). Again, we assume that the thickness of film is so small and the solute uptake through edges is negligible; as area of sheet is considered too negligible. Here x=0 and x=h are impermeable boundaries for solute uptake by sheet. Across these boundaries there is no net change of solute concentration with x.

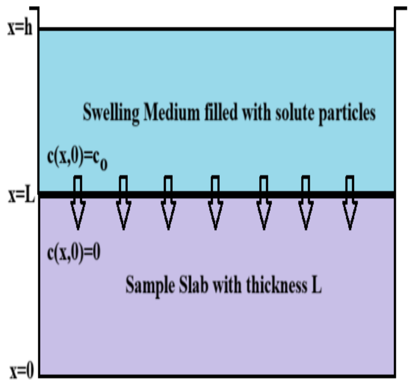

Fig. 1. Finite sheet of unit cross section (A=1) and thickness L is in a well stirred solute solution at time t=0

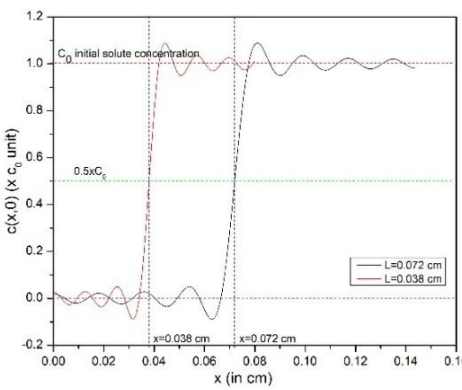

Fig. 2. Initial concentration profile c(x,0) vs position x theoretical plot
(for sample slab thickness L=0.072 cm and 0.038 cm)

Based on above considerations which is similar to the situation of solute uptake or swelling of polymeric membrane in water, the initial condition for modified concentration $C(x,t)$ is given by –

$$C(x,t) = \begin{cases} c_0 - c_\infty & \text{for L<x<h, t=0} \\ -c_\infty & \text{for 0<x<L, t=0} \end{cases} \tag{2}$$

And boundary condition[26] is given by –

$$\mathrm{grad}_x C(x,t) = \frac{\partial C(x,t)}{\partial x} = 0 \text{ for x=0 and x=h } \forall\ t \geq 0 \tag{3}$$

By using separation of variable method and applying initial and boundary conditions eq. (2) and (3), the solution $c(x,t)$ of our coupled partial differential equation (1) is –

$$c(x,t) = c_\infty + \left(c_0 \frac{(h-L)}{h} - c_\infty \right) e^{-\xi t} - \frac{2c_0}{\pi} \sum_{n=1}^{\infty} \left[\frac{1}{n} \sin \frac{n\pi L}{h} \cos \frac{n\pi x}{h}\right] e^{-\left(\frac{n^2\pi^2 D}{h^2} + \xi\right)t} \tag{4}$$

This is the required solute concentration profile for the complete span [0, h] of coordinate x and time t. At initial time t=0, and at arbitrary position x the concentration profile c(x,0) vs position x, theoretical plot (for sample slab thickness L=0.072 cm and 0.038 cm) is shown in fig. 2. From this plot, it is clear that the initial solute concentration at interface (x=L) of sample slab and solute medium is $c_0/2$.

Generally, time interval sorption experiments can be used to evaluate diffusion constant D. In our case we have used experimental data to evaluate required parameters for non-fickian (anomalous) mechanism they are; diffusion coefficient D and relaxation constants ξ. Total solute diffused per unit cross section area across the boundary into thin slab from solute solution due to fickian diffusion and relaxation mechanism m_t is given as: -

$$m_t = m_i + (D + \xi L^2) \int_0^t \left(\frac{\partial c(x,t)}{\partial x} \right)_{x=L} dt \tag{5}$$

Where, m_i is the solute mass uptake correction term for the mid and late diffusion process due to initial sorption (initial 50-60%) process, at the time where the relaxation assumes to start, stop or change into another relaxation mechanism and contribute to subsequent sorption process along with diffusion process. This behavior of sorption process seen as distinct break in $\ln(1-m_t/m_\infty)$ vs time t curve[28], [29]; which can be easily evaluated by using the point of intersection "A" of $\ln(1-m_t/m_\infty)$ vs time t straight line with $\ln(1-m_t/m_\infty)$ axis for mid and later sorption data. For initial sorption process $m_i = 0$, value of m_i is given by –

$$m_i = m_\infty (1 - e^A) \tag{6}$$

On solving the equation (5) (assuming h=2L in simple case), we have–

$$m_t - m_i = \frac{c_0(D+\xi L^2)}{L}\sum_{m=0}^{\infty}\left(\frac{1-e^{-\left(\frac{(2m+1)^2\pi^2 D}{4L^2}+\xi\right)t}}{\frac{(2m+1)^2\pi^2 D}{4L^2}+\xi}\right) \tag{7}$$

It is easily seen that, in the case of pure fickian diffusion mechanism, where the relaxation mechanism is not responsible for solute uptake or swelling of diffusive sample. i.e., $\xi = 0$. Equation (7) is converted into the following form –

$$\frac{m_t - m_i}{m_\infty} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}e^{-\frac{(2m+1)^2\pi^2 D}{4L^2}t} \tag{8}$$

Here, $m_\infty = c_0 L/2$ equilibrium mass of solute uptake by sample due to **pure fickian diffusion mechanism**[27]. Equation (8) is well known result for the evaluation of diffusion coefficient D from time interval sorption experimental data[1], [25], [27].

For the case of anomalous diffusion mechanism, as sorption time t approaches infinity, the equilibrium solute uptake by diffusive system due to non fickian diffusion mechanism is given by –

$$\frac{2m_\infty e^A}{c_0 L} = \sqrt{\frac{D}{L^2\xi}}\tanh\left(L\sqrt{\frac{\xi}{D}}\right) + \sqrt{\frac{L^2\xi}{D}}\tanh\left(L\sqrt{\frac{\xi}{D}}\right) \tag{9}$$

For further analysis, we must find the root of this equation by using either graphical method (see fig. 3.) or numerical analysis method. For required solution of this equation, we find the point of intersection of straight line $y = 2m_\infty e^A / c_0 L$ and curve $y = (1/z + z)\tanh z$ where, $z = L\sqrt{\xi / D}$. Let the root of equation (9) obtained from graphical method is α, then $\xi = (\alpha / L)^2 D$.

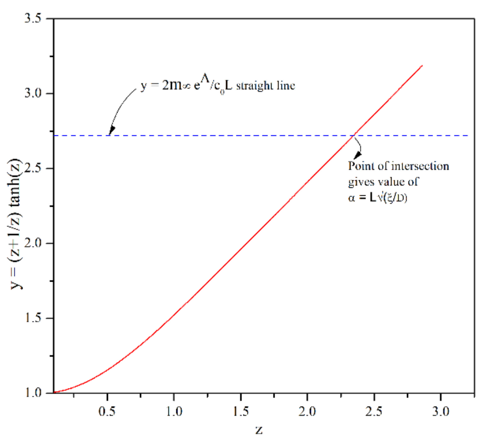

Fig. 3. Graphical method for solving transcendental equation $2m_\infty e^A/c_0L=(z+1/z)\tanh(z)$

Evaluation of various parameters related to non-fickian diffusion from time interval sorption experiment of glassy polymeric system. Equation (7), contains infinite series which is rapidly convergence for large value of t ≥ 0, and for large time t, the successive terms of this infinite series rapidly decreases with increasing index m. hence we consider only first terms (m=0) of infinite series expansion in equation (7) for mid or later sorption process, which is sufficient to calculate various parameters. Thus, after straight forward mathematical manipulations equation (7) can be converted into the below equation of straight line –

$$\ln\left(1-\frac{m_t}{m_\infty}\right)=\ln\left(\frac{4c_0L(1+\alpha^2)}{m_\infty(\pi^2+4\alpha^2)}\right)-\left(\frac{\pi^2 D}{4L^2}+\xi\right)t \tag{10}$$

If we plot the time interval sorption data for $\ln\left(1-m_t/m_\infty\right)$ v/s time t and fitted straight-line $\ln\left(1-m_t/m_\infty\right)=A-Bt$ for mid and late time sorption data and roughly initial sorption data, then the coefficients of fitted straight line contains, information about the nature of swelling network and inherent transport mechanism. Hence, we obtain following desired parameters representing non-fickian diffusion mechanism of sorption.

$$D=\frac{4L^2}{\pi^2+4\alpha^2}B\ ,\ \ \xi=\left(\frac{\alpha}{L}\right)^2 D\ \&\ m_\infty(\text{theo.})=\frac{c_0L}{2}\left(\frac{1}{\alpha_i}+\alpha_i\right)\tanh\alpha_i \tag{11}$$

Here α_i is root of eq. (9) for initial sorption (A=0). An important finding of our above analysis is that "the equilibrium solute mass uptake due to relaxation mechanism $m_\infty(r)$is α_i^2 times the equilibrium solute mass uptake due to diffusion mechanism $m_\infty(d)$ for initial sorption data(50-60%)".i.e., $m_\infty(r)=\alpha_i^2 m_\infty(d)$ .Here, $m_\infty(d)=c_0L\tanh\alpha_i/2\alpha_i$ and $m_\infty(r)=c_0L\alpha_i\tanh\alpha_i/2$.

Thus, our mathematical model can predict about the nature of or type of release mechanism same as well-established Korsmeyer and Peppas semi-empirical model [[5], [8], [9], [13]].If the value of $\alpha_i\approx 0$, then it represents pure fickian diffusion mechanism, if the value of $\alpha_i\approx 1$ then it represents super case II release or swelling mechanism. Other value of α represents the non-fickian behavior of release or swelling mechanism.

For the case, where whole sorption process is governed by pure fickian diffusion mechanism. In such cases value of α=0 and ξ=0. Thus, $A=\ln\left(4c_0L/m_\infty\pi^2\right)$ and $m_\infty=c_0L/2$ and equation (10) can be converted into the below form –

$$\ln\left(1-\frac{m_t}{m_\infty}\right)=\ln\left(\frac{8}{\pi^2}\right)-\frac{\pi^2 D_L}{4L^2}t \tag{12}$$

Where, D_L is known as late time diffusion coefficient [28], [29]. After finding the slope of this straight line by using list square fitting method later time diffusion coefficient D_L is given by[6] –

$$D_L=-\frac{4L^2}{\pi^2}(\text{slop of fitted straight line for late time sorption data}) \tag{13}$$

Results and Discussions

XRD and FTIR spectral analysis-X-ray diffraction (XRD) pattern depicted in fig. 4. indicate the essential structural information about CNF reinforced GA cross-linked$_{(14h)}$ PVA film. In XRD pattern, a large broad diffraction peak found at 19.87° (with FWHM 2.21°) and small extra broad peak found at 41.3°(with FWHM 6.8°)due to intra and intermolecular hydrogen bonds in PVA,suggests a semi-crystalline nature of PVA[[35], [36], [37], [38], [39]].The broadness and intensity of the peak gives clear indication about the disruption of the crystalline structure of PVA due to the CNF reinforcement in PVA matrix and cross-linking with GA. The smaller “shoulder” peaks found at around 16°, 22.4° are the characteristics peaks of CNF indicated the presence of CNF in PVA matrix, these were corresponded to (010), (002) crystalline plane of cellulose crystal[40]. Its low intensity and broad shape confirms the crosslinking process has reduced the size and order of the crystallites. On the other hands, the lack of sharp crystalline peaks in the XRD pattern, shows good dispersion of the CNF particles in the PVA matrix and no formation of large crystalline aggregates.

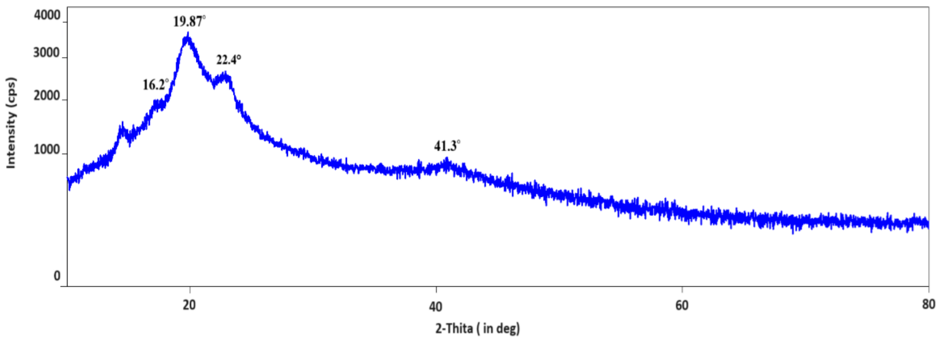

Fig. 4. XRD pattern for CNF reinforced GA cross-linked PVA film

FTIR spectra for CNF reinforced GA crosslinked$_{(14h)}$ PVA is given in fig. 5. an O-H Stretching broad peak observed in near 3533.71 cm^{-1}due to the stretching vibration of hydroxyl (-OH) groups[39] from PVA and CNC. its extra loosely bound OH groups peaks 3639.80 cm^{-1} also observed due to moisture uptake characteristics of PVA. Also, too reduced peak intensity around 3300 cm^{-1}suggests cross-linking due to OH groups was consumed during the crosslinking reaction[41], [42]. C-H stretching peaks occurrence around 2958.90 cm^{-1} from alkyl (-CH2, -CH3) groups present in PVA[40] and CNC. Two very intense C=O stretching peaks 1751.42 cm^{-1} and 1668.48 cm^{-1} in the FTIR spectra indicate the formation of acetal (-C-O-C) linkages due to aldehyde (-CHO) groups from glutaraldehyde after cross-linking.CH_2 Wagging intense peaks1386.86 cm^{-1} and 1473.66 cm^{-1} were observed due to the characteristic of PVA and cross-linking interactions. C-O-C and C-OH vibrations (1020.38,1147.68, 1282.71 cm^{-1}) These peaks confirms acetal bond formation[41] and correspond to the ether and hydroxyl groups in CNC and PVA.

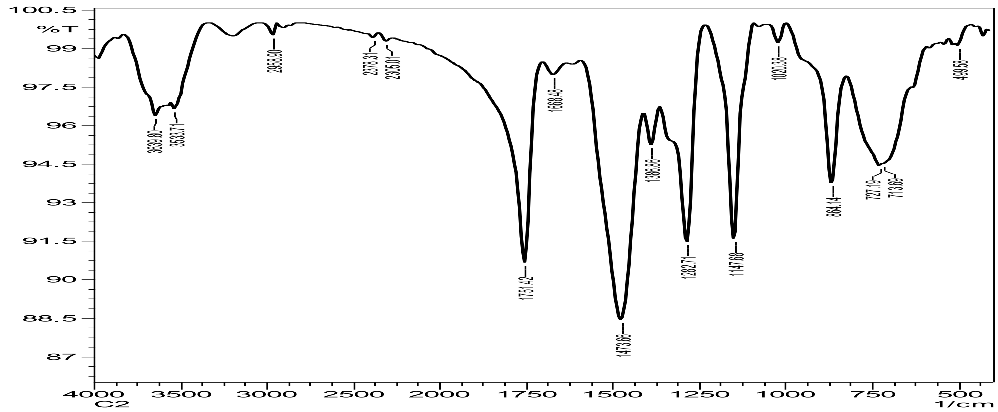

Fig. 5. FTIRSpectra for CNF reinforced GA cross-linked PVA film

Water uptake behavior of GA crosslinked CNF reinforced PVA Film-We have investigated the water uptake of PVA/CNF with varying GA crosslinking time 0 h(un-crosslinked) and 14h, 25h, 37h & 49h film samples at 27°C buffer medium of pH 7.1.Obtained water sorption data with time was plotted in term of SR value (gm/gm) along y-axis and sorption time t (min) along x axis (see fig 6.(a)). These swelling curves clearly indicate that the GA crosslinking time considerably affect the swelling capacity and swelling rates of our PVA/CNF composite Film. Swelling rate decreases as increasing crosslinking time and also, we can say from fig. 6.(b) that the equilibrium swelling ratio (ESR) values will reduce with increasing crosslinking time. From this we conclude that crosslinking of GA forms a rigid strong network via hydrogen bonding between PVA polymeric chains which reduces the overall flexibility and available free space.

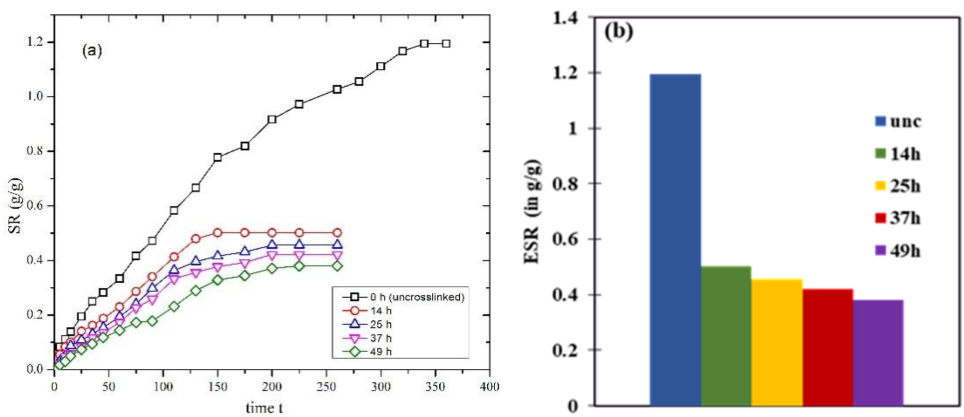

Fig. 6. (a) Plot for variation of swelling ratio (SR) vs time t curve for GA crosslinked CNF reinforced PVA film and (b) Plot for equilibrium swelling ratio variation with crosslinking time.

Fig. 7. Plots between $\ln(m_t/m_\infty)$ vs sorption time ln t for various crosslinkingtime (a) for 0 h (uncrosslinked), 14h, 25h, and (b) for 37h and 49h of CNF reinforced PVA film with GA.

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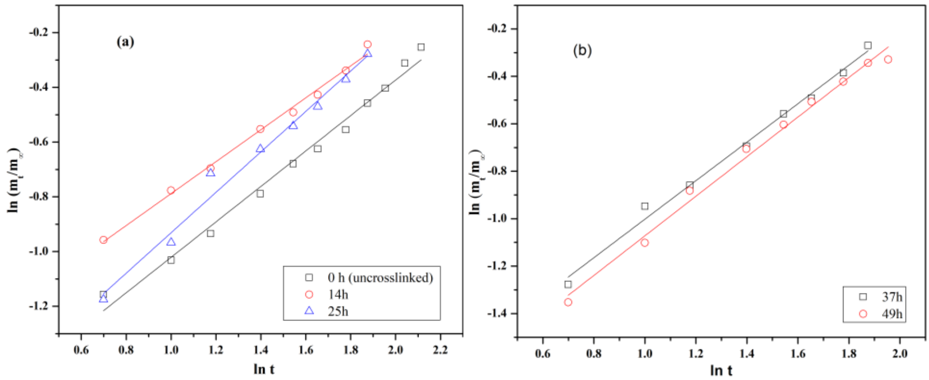

Fig. 7. Plots between $\ln(m_t/m_\infty)$ vs sorption time ln t for various crosslinkingtime (a) for 0 h (uncrosslinked), 14h, 25h, and (b) for 37h and 49h of CNF reinforced PVA film with GA.

Power Function Model Analysis-We have analyzed the water swelling mechanism of PVA/CNF film with GA crosslinking by applying power function model[[5], [7], [8], [34]]. It is the most frequently useful mathematical model to find the mechanism of sorption process in many swellable networks, hydrogels etc. We have plotted $\ln(m_t/m_\infty)$ vs lntgraphs for our film samples shown in fig. 7.(a) and 7.(b). By fitting a straight line, we obtain power function parameters n and k values given in table 1.On observing value of swelling exponent n, all the values is in the range 0.5 to 1, thus we can say that this represents the non-fickian diffusion mechanism.

Table 1. Power Function Model Parameters

Sample Code	n	k	R^2	M_∞ (Exp) (in g/g)	Type of mechanism
0 h (uncrosslinked)	0.647	0.02148	0.987	1.194	Non-fickian
14h	0.583	0.04256	0.994	0.502	Non-fickian
25h	0.738	0.02138	0.984	0.456	Non-fickian
37h	0.817	0.01489	0.994	0.431	Non-fickian
49h	0.83	0.01164	0.993	0.41	Non-fickian

Water uptake analysis by Our mathematical model-Our model is capable to find the value of diffusion coefficients D and relaxation constant ξ for whole sorption data. During the sorption process in non-fickian mechanism neither a single relaxation mechanism nor a single diffusion mechanism is responsible for whole sorption process but instead many different mechanisms of both types are playing their part in whole sorption process. Therefore, we divided the whole sorption process in different sections determined by sorption rate changes due to change in relaxation rates. If relaxation rates change then diffusion rates will also change.

Table 2. Diffusion coefficient and relaxation constant calculated from our model

Sample code	**For initial (50-60%) swelling**	**For late time swelling**	**Sample code**	**For initial (50-60%) swelling**	**For late time swelling**
0 h (uncrosslinked)	**D_i (in cm^2/min)**	**ξ_i (in min^{-1})**	0.987	**D_i (in cm^2/min)**	**ξ_i (in min^{-1})**
0 h(uncrosslinked)	4.21×10^{-6}	3.88×10^{-3}	0 h(uncrosslinked)	4.21×10^{-6}	3.88×10^{-3}
14h	18.6×10^{-6}	8.87×10^{-4}	14h	18.6×10^{-6}	8.87×10^{-4}
25h	14.9×10^{-6}	5.40×10^{-4}	25h	14.9×10^{-6}	5.40×10^{-4}
37h	14.0×10^{-6}	7.35×10^{-5}	37h	14.0×10^{-6}	7.35×10^{-5}

To determine the non-fickian transport parameters diffusion coefficient D (in cm^2/min), relaxation coefficient ξ (in min^{-1}), we have plotted the time interval sorption data for $\ln(1 - m_t / m_\infty)$ vs sorption time t (in min) and fitted a straight line according to eq. (10) for mid and later sorption data for different crosslinking time 0h (un-crosslinked), 14h, 25h, 37h and 49h (see fig. 8(a, b, c)). On inspecting these fitted straight lines, we can say that they are all of higher order of list square fitting factor R^2 above 0.98. Thus, our theoretical model shows excellent degree of correspondence with experimental time interval sorption data. These plots clearly indicate the distinct break in the slope as observed by Shankar, 1979[28]; Yoshizawa et al., 1997[29]. These slope changes occur due to accelerated or de-accelerated diffusion process by interfering relaxation mechanism of polymers chains originating by swelling and start contributing subsequent sorption phenomenon and overall equilibrium swelling ratio (ESR).

Non-fickian diffusion parameters obtain from these plots are given in table 2. Comparison of these values across various samples helps us to understand the effect of crosslinking time on the swelling properties. For the initial stage of sorption, the diffusion coefficient generally decreases with increasing cross-linking time, from 18.6×10^{-6} cm^2/min for 14h to 9.98×10^{-6} cm^2/min for 49h.

This is because more cross-links create a tighter network, making harder for water molecules to diffuse in. 0 h(uncrosslinked) is an exception, having a lower value than the crosslinked samples. On the other hand, the relaxation constant also generally decreases with longer crosslinking times, indicating that the polymer chains become less mobile and relax more slowly due to the increased cross-linking. The late-time diffusion coefficient values show a less clear trend but are generally higher than the initial diffusion coefficients for the highly cross-linked samples (37h and 49h) and lower than the initial diffusion coefficients for the un-crosslinked and lesser crosslinked samples 0 h(uncrosslinked), 14h & 25h. This suggests that as the hydrogel swells and the network expands, it becomes easier for water to diffuse further into the core. The relaxation constant is consistently higher in this phase compared to the initial phase, indicating that once a significant amount of water has entered, the polymer chains can relax and rearrange more quickly. Chain relaxation mechanism, de-accelerate the diffusion process in later stage of sorption and take over the responsibility to subsequent stage sorption process where it is prominently relaxation-controlled process for samples 0 h(uncrosslinked), 14h & 25h. For the highly cross-linked samples (37h and 49h) chain relaxation accelerates the diffusion process as well as relaxation process. Value of α_i is not equals to 0 or 1, which indicates the non-fickian mechanism of sorption behavior of our samples according to our proposed model.

The ESR values are larger for un-crosslinked sample 0 h(uncrosslinked) and they are smaller for other crosslinked samples with increasing crosslinking time. This result clearly indicates the fact that crosslinked samples possess more rigid and strong network than un-crosslinked samples and chain relaxation is prohibited for higher degree of crosslinking, this leads to brittleness properties when immersed in water or other solvent (see fig.8(d)). This shows the brittleness property of PVA/CNF film due to excess crosslinking with GA; crosslinking time is 90 hours.

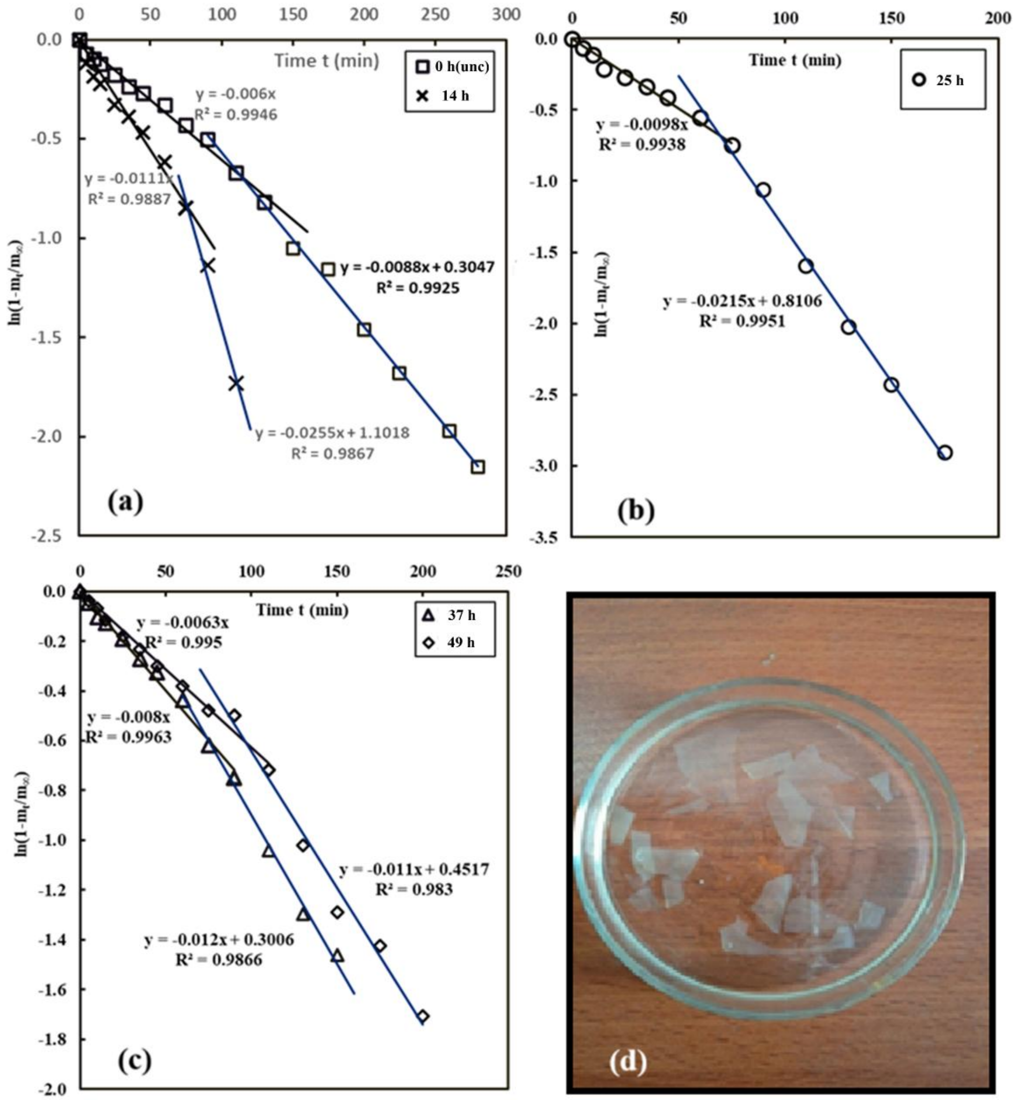

Fig. 9. (a), (b) & (c) depicted various plots between $\ln(1-m_t/m_\infty)$ Vs sorption time t for crosslinking time 0h (un-crosslinked), 14h, 25h, 37h and 49h and obtain the slops A and point of intersection B by fitting a straight-line using list square method according to our mathematical model for non-fickian diffusion (fitted equation of straight line displayed in the plots).(d) PVA/CNF film shows brittleness property due to over crosslinking with Glutaraldehyde (GA) tested it with crosslinking reaction solution (5 v/v GA (25% solution), 0.12 v/v HCl (35-38%) and 94.88v/v of Acetone) immersing time is 90 hours

Conclusions

In view of results obtained we can conclude that in our study, a novel mathematical model was developed to describe non-Fickian transport phenomena and was rigorously validated using Glutaraldehyde cross-linked CNF/PVA composites films. This model successfully accounted for the complex diffusion-relaxation dynamics characteristic of such cross-linked polymer systems and exhibited superior predictive capability compared to previously established models [1], [9]. By incorporating the specific physicochemical interactions of the composite matrix, the model provides a more comprehensive framework for analyzing anomalous transport behavior. Its strong agreement with experimental data underscores its reliability and potential utility. Importantly, the model offers significant implications for the design and optimization of advanced materials in high-impact application areas, such as conducting polymer-based sensors [43] and controlled drug delivery systems [17], where accurate transport modeling is essential for functional performance.

The developed non-Fickian transport model is highly relevant for gas sensors based on biocompatible CNF/PVA with incorporating conducting polymers like poly pyrrole (PPy), poly aniline (PA), PEDOT, PSS etc. Such composite materials are excellent for fabrication of various types of electronic sensors. Traditional Fickian models fail to account for the coupled diffusion–relaxation behaviour often observed in cross-linked or viscoelastic polymer films. Our model can explain these dynamics, enabling more accurate prediction of solute (liquid, gas etc) uptake, response time, and recovery behaviour.

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CRediT author statement

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