Sorption Characterization of Crab Shell Chitin Whisker Reinforced Phenol Formaldehyde Nanocomposites

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Abstract

The crab shell chitin diffusion characteristics are studied for their characterization [1].Solvent absorption of chitin reinforced composites is one major concern in the field biomedical applications, especially in tissue engineering for drug delivery. Traditionally diffusion characteristics of chitin whisker embedded in Phenolic matrix are studied to understand their mechanism of solvent absorption and to find the relationship between the microscopic structure and the solvent absorption of the composites. The purpose of this study is to facilitate for understanding the behavior of nano chitin loading into the polymer like phenolic composites. The solvent absorption behavior of composites with different fiber loadings percentage by weight was investigated. At a critical chitin fiber loading is reported where the diffusion process is found to be dominant.

Keywords: Chitin,nano-fiber, Absorption behavior, Phenolic Plastics, Diffusion.

1. Introduction

Nanomaterials are used fortissue regeneration for the drug delivery which has resultedin providing new reason to study these polymers which provide more opportunity for better treatment of diseases at a molecular level, thus improving the efficiency of drug delivery in treating diseases and reducing their side effects is somehow related to chitin particle loading in composite material prepared by Phenol formaldehyde as matrix and chitin nanoparticle reinforcement. In this chapter, natural nano chitin particles will be discussed, summarizingand analyzing their diffusion, solvent kinematics properties of the composites.

2. Solvent Sorption Experiment.

2.1. Water Absorption Test

Studies on the kinetics of solvent diffusing into the composite material werecarriedto find thesolvent absorption of the phenolic composites prepared by blending with nano chitin as per the standards of ASTM D 570-98 test method for solvent absorption of plastics [2]. The specimens used were thin circular disks and thick. The thickness of the film was therefore supposed to be thin enough so that the molecular diffusion was considered to be one- dimensional. The weights of the samples were taken and then dipped them in three different solvents water, petrol and kerosene. After every10 min., the samples were taken out from the solvent environment and all surface solvent was cleaned with the help of a neat, clean anddry cloth or tissue paper. Then the samples are weighed within 1 min of removing them from the solvent chamber. The samples are weighed for120 min. regularly at intervals of 10 min., initially and the time was increased as the weight reached equilibrium. Later they were weighed for every 1hr and slowly after 12hr time was further increased to 6hr and so on. Such testing was done for 2 days i.e. 48 hrs. respectively. The solvent absorption was calculated by the weightdifference. The weight gain percentage of the composite samples was measured at regular time intervalof time by using the following[3]:

The thin phenolic nanocomposite disks samples were first weighed (M_0) and then immersed in solvents like water, kerosene and petrol. The samples were removed at specific intervals (t) and weighed (M_t) up to an equilibrium value (M_∞). The swelling rate of the samples was determined from the initial slope of the plot of ($M_t - M_0$)/M_∞ as a function of (t)$^{1/2}$.

2.2. Effect of filler loading on sorption properties

The liquids considered for the present investigation were water, petrol, and kerosene. The results of the diffusion experiments have been expressed as weight percentage uptake vs the square root of time.

Figures 2.1 show the liquid sorption curves of unfilled and nano chitin filled phenol formaldehyde at room temperature in petrol, kerosene, and water. It can be seen from Figures 2.1 and 2.2 that the loading of PF with chitin reduces the mole percent (Qt) solvent uptake till the loading percentage is one percent and later increased on further loading. Reinforcement restrains the long range movements of polymer molecule but leaves their local segmental mobility high [4]. The fillers form chemical as well as physical crosslinks with the polymer chains, because of immobilization. This complex crosslink clusters prevent the rearrangement of the polymer chains during solvent ingression and reduces the free volume in the composite thereby causing resistance to the path of penetrants. Later the solvent uptake increased after 1% chitin. The lowest liquid uptake is seen in the case of the composite with 1% chitin loading. The solvent absorption for 1.5 and 2 % loading remained same but increased compared to that of 1% chitin loading as shown in the figure which is attributed to the increase in the cross-links between along with agglomeration of chitin particles which show the slight sensitivity towards the solvents. However in thepresence of water, a normal trend of solvent uptake is observed. Figure 2.3 shows the mole percent uptake of water. In this case, PF resin loaded with 0% chitin takes the highest amount of water. A further increase in chitin loading by 0.5% reduces the water uptake of the
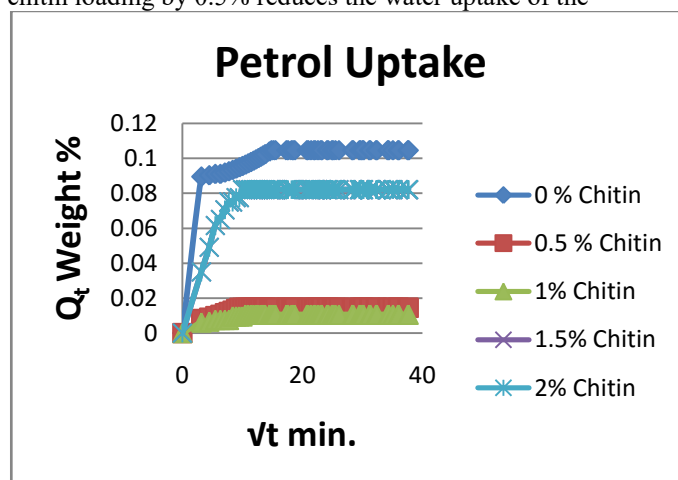

Fig 2.1Q_t of petrol Vs Square root of time

composites. This can be attributed to the reduction of free volume in the composite Similar reports exist in theliterature [5]. On further increasing the chitin loading to 1% by weight slight increase in water uptake is observed afurther increase in loading again decreased the water uptake which leads to anomalous diffusion phenomena.

2.3. Crosslink density

The crosslink density (v) of the present system has been estimated by using the equation :

$$V = \frac{1}{2 M_c}$$

Where M_c is the molar mass between crosslinks in the composites, given by the equation
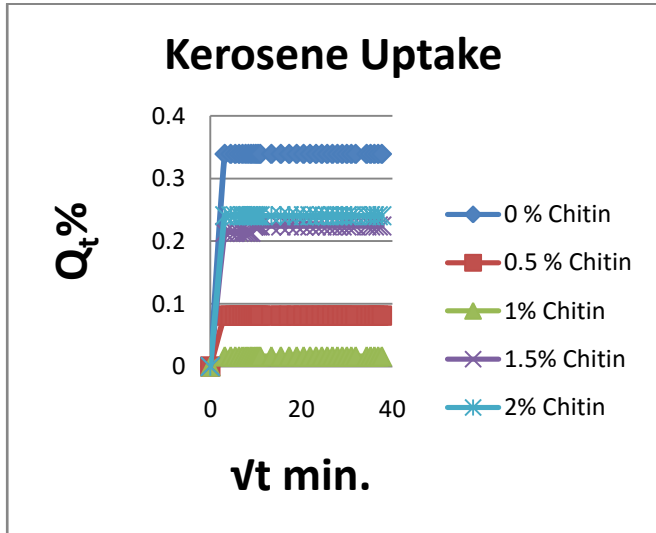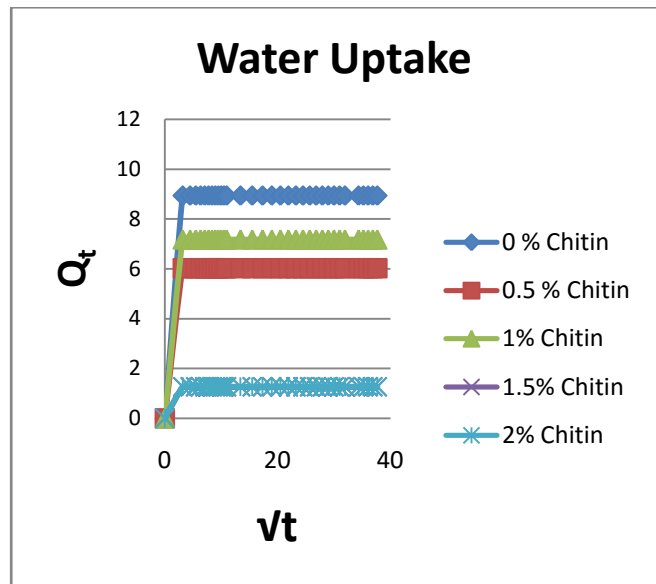

Fig 2.2 Q_t of kerosene vs square root of time

Fig 2.3 Q_t of water vs square root of time

$$M_c = \frac{-\rho_p V_s V_{rf}^{1/3}}{[\ln(1 - V_{rf}) + V_{rf} + \chi V_{rf}^2]}$$

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where V_s is the molar volume of the solvent used, ρ_p is the density of the polymer and χ is the polymer-solvent interaction parameter. V_{rf} is the volume fraction of polymer in the solvent swollen filled composite sample, given by the equation [5]

$$V_{rf} = \frac{(d-f_w) \rho_p^{-1}}{(d-f_w) \rho_p^{-1} + A_s \rho_s^{-1}}$$

.....................2.3

Where d is the deswollen weight of the sample, f is the volume fraction of the filler in the dry composite sample, w is the initial weight of the composite sample, ρ_s is the density of the solvent and A_s the weight of solvent in the swollen sample. Figure 2.4 shows the effect of filler loading on the apparent cross-linking values. As filler loading increases the cross-link density increases. The calculated values of the M_c are given in Table 2.1. M_c values are highest for PFC1, which contains a uniform distribution of fillers and hence has higher crosslink density; this is due to the increased interaction between the filler and the matrix. The M_c values regularly decrease with increase in filler loading and correspondingly crosslink density increases.
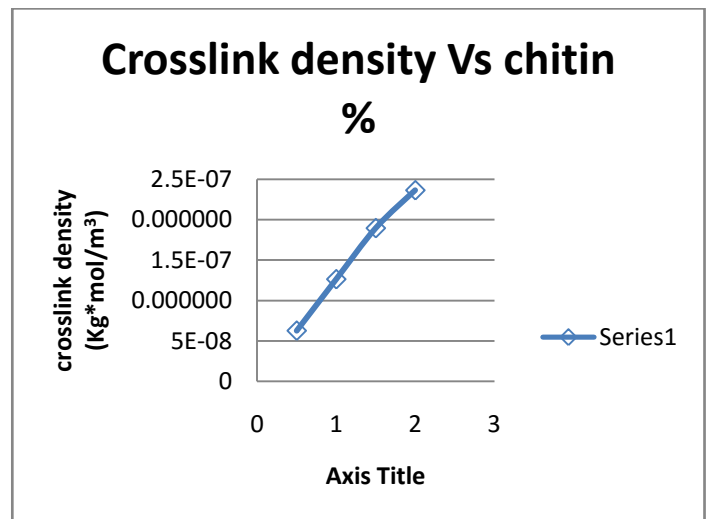

Figure 2.4 Crosslink densities as a function of percentage loading (solvent petrol)

Table 2.1 Effect of filler loading on cross link density

Mixes	M_c	Apparent cross linking (1/ Q) (E-08)
PFC0	13185484	1.18
PFC0.5	19939025	2.5
PFC1	42284483	3.79
PFC1.5	9889113	3.05
PFC2	8456897	3.51

2.4 Diffusion coefficient

The diffusion coefficient is a kinetic parameter related to the polymer segmental mobility, penetrant and to the different crosslinks present in a polymer matrix. The diffusion coefficient of a polymeric material immersed in solvent can be calculated using the equation [6]

$$\frac{Q_t}{Q_\infty} = 1 - 8/\Pi^2 \sum_{m=0}^{m=\infty} \left[\frac{1}{(2m+1)^2} \right] \times e^{-(2m+1)^2 \Pi Dt/h^2}$$

...........................2.4

Where Qt and Q∞ are the mole % uptake at time t and at equilibrium respectively and m is an integer. D is the diffusion coefficient and h is the initial thickness of the sample. The above equation for short time limiting as:

$$\frac{Q_t}{Q_\infty} = 4\left[\frac{D \times t}{\Pi \times h^2}\right]^{1/2}$$

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A plot of Qt versus $\sqrt{t}$ is the linear at short times. By rearranging Equation (2.5), the overall diffusion coefficient can be calculated using the equation [7]:

$$D = \Pi\left[\frac{h \times \theta_D}{4 \times Q_\infty}\right]$$

…………………………. 2.6

Where θ_D is the slope of the initial portion of the plots of Q_t versus $\sqrt{t}$. The values of D at 28 °C for 0, 0.5, 1, 1.5 and 2 percent filler loaded system are given in Table 2.2. It is seen that the solvent uptake tendency reduces with increase in the filler loading. This is due to the higher reinforcement and high filler–matrix interaction in the composites. The theoretical values of D are following the diffusion trend seen practically.

Table2.2 Diffusion coefficient of PF/chitin composite system

Sample	D x 10^{-4} (m^2/s)		
	Water	**Kerosene**	**Petrol**
PFC0	2	1.8	2
PFC0.5	1.7	1.3	1
PFC1	1.9	1	1.2
PFC1.5	1.5	1.6	1.8
PFC2	1.6	1.7	1.8

Conclusions.

Absorption experiment using Water, kerosene and petrol provided additional insight regarding the existence of a chitin network in a composite sample prepared by solvent casting method.The extent of swelling was different for solvent cast samples compared to compression molded samples. It was observed that the samples are more resistive to the organic solvents compared to water because of the tendency of chitin to absorb water easily. It was also observed that increase in whisker content diminished the degree of solvent uptake and swelling of samples in organic solvents. The filler-matrix interaction, chitin network, and the solvent network are all reasons for low degree of swelling in the case of organic solventswhich indicates the rigidity of chitin network towards the organic solvents

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