

**Swelling Kinetics of Unsaturated Polyester-layered Silicate Nanocomposite
Depending on the Fabrication Method**

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Abstract

Kinetics of swelling and sorption behavior of unsaturated polyester nanocomposite (based on glycolyzed PET, maleic anhydride, styrene, and montmorillonite) synthesized by two different mixing methods, simultaneous and sequential is studied in acetic acid at different temperatures. The values of n in the transport equation are found to be below 0.5, showing non-Fickian or pseudo-Fickian transport in the polymers. The dependence of diffusion coefficient on the mixing methods and temperature has also been studied for the unsaturated polyester nanocomposite. The diffusion coefficients in simultaneous mixing samples decrease with an increase in the mixing time in the samples. In case of the sequential mixing samples, the diffusion coefficient increases with an increase in mixing time. The diffusion coefficient increases with an increase in temperature for all the unsaturated polyester nanocomposite samples. The sorption coefficient increases with an increase in the

mixing time for all the samples synthesized by in-situ mixing method. The crosslink density (calculated from the CH₃COOH swelling) ranges from 5.014 to 7.092×10^2 mol/cm³ for simultaneous mixed samples and 5.212 to 7.192×10^2 mol/cm³ for sequentially mixed samples.

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1 Introduction

Polymer nano-composites are the future of the global industries [1]. The polymer nano-composites are prepared by dispersing a nano-filler into the polymer [2-3]. These platelets are then distributed into a polymer matrix creating multiple parallel layers, which force flow of gases and liquids through the polymer in a torturous path, forming a complex barrier [4]. Different types of fillers are utilized for the preparation of nano-composites. Amongst these, the most common is a nano-clay called montmorillonite - a layered smectite clay [5-10]. Additional nano-fillers include carbon nano-tubes, graphite platelets, carbon nano-fibers, etc [8, 11-13]. The barrier properties of the nano-composites are supposed to increase due to nano-clay loading [4, 14].

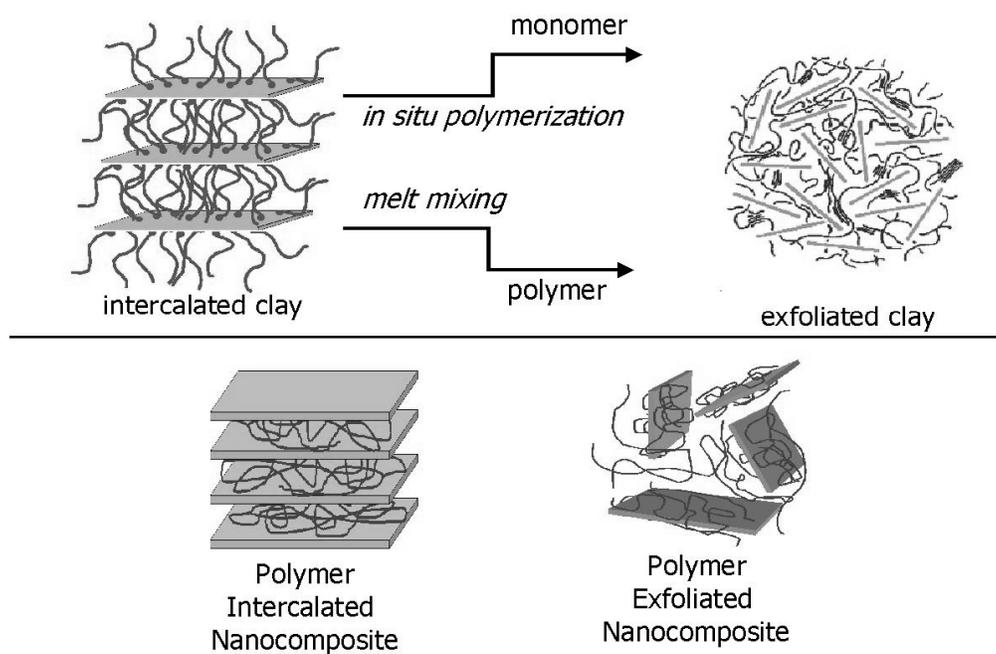
Sorption and diffusion of the solvents in and through polymers have been widely investigated from both theoretical as well as experimental point of view [15–18]. The swelling technique is a commonly used method to determine various coefficients such as diffusion, sorption, and permeability coefficient [18–22]. In swelling experiments, the polymer of known dimension is dispersed in a solvent, and the solvent mass uptake

versus time is recorded and the data is used to calculate the various coefficients. These coefficients give an idea about the use of polymers in various applications such as membranes, ion-exchangers, controlled release systems, packaging, microchip manufacturing, etc.

Sorption kinetics in polymers exhibit a variety of deviations from normal Fickian behavior, attributable to (a) slow viscous relaxations of the swelling polymer or (b) differential swelling stresses generated by the constraints imposed on local swelling during sorption. Several models have been proposed for the study of swelling behavior of the polymers [23-25]. In situ study by FTIR-ATR is also carried out by many researchers for the prediction the sorption behavior of the polymers [26-28].

The properties of unsaturated polyester (UP)/montmorillonite (MMT) nanocomposite greatly depend on the preparation procedure because of the chemical reactions and physical interactions involved. In general, there are two methods of making nanocomposites, melt intercalation and in situ intercalative polymerization of monomers (scheme 1). The nanocomposite of thermoset polymer can be prepared by the in situ intercalative polymerization method [29]; phenol resins, epoxy resins [30,31] and unsaturated polyester resins are included in this category. These thermosetting nanocomposite materials are prepared by first swelling the various organo-modified montmorillonite (MMT) with the proper polymerizable monomers, followed by crosslinking reactions.

Montmorillonite Nanocomposites



Scheme 1. The methods of making nanocomposites, melt intercalation and in situ intercalative polymerization of monomers

In this study, a new system of unsaturated polyester-layered silicate nanocomposite synthesized from glycolyzed PET with two different mixing methods is studied for sorption kinetics in acetic acid. The variation in sorption is studied with respect to time and temperature. The objective of this work is to study the swelling kinetics of the nanocomposite synthesized by two different methods with an alteration in the mixing time. The mechanism of the sorption is studied from the data by a linear fit of the equation of the transport phenomena. The crosslink density and molecular weight between two crosslinks are also calculated from the sorption data using Flory-Rehner equation.

2 Experimental

2.1 Materials

Discarded PET bottles from soft drinks were procured from scrapers, cleaned thoroughly and cut in to small pieces (6 mm x 6 mm). Zinc acetate, minimum assay 99%, Ethylene glycol, diethylene glycol and styrene were procured from E. Merck (India) Pvt. Ltd, Bombay. Phthalic anhydride (PA), Maleic anhydride, benzoyl peroxide and Hydroquinone obtained from CDH (India), montmorillonite (K-10) having surface area 270 m²/g and pH 3-4, dodecyltrimethylammonium bromide (DTAB) C₁₅H₃₄BrN, are purchased from Aldrich Chemical Company (Milwaukee, MI) and are used as received.

2.2 Synthetic Work

2.2.1 Modification of Montmorillonite

Montmorillonite Clays are dispersed in DI water by stirring. Dodecyl trimethyl ammonium bromide (DTAB) is added to dispersion. The whole dispersion is heated at 80 °C for 6 hr with vigorous stirring. A white precipitate formed, which was isolated by filtration and washed several times with hot water/ethanol 50:50 by volume mixture until no trace of chloride was detected in the filtrate by one drop of 0.1 N AgNO₃ solution. The treated clay was dried at 100 °C in the vacuum oven for 24 h until all moisture was removed and a constant weight was obtained.

2.2.2 Glycolysis of PET Waste

Glycolysis of PET scrap has been done in a five necked reaction glass kettle with mechanical agitator assembly. Molar ratio of PET to glycol has been taken 1:2 respectively. The mixture of diols DEG:EG are charged in the ratio 80:20 respectively. Zn(CH₃COO)₂ used as trans-esterification catalyst. The reactants are heated in the

temperature range 120-140 °C for first three hours and then at 180 °C for subsequent 5 hours. The whole reaction is carried out in inert atmosphere (nitrogen atmosphere) under reflux with constant stirring. After 8 h the contents in the reactor were allowed to cool to room temperature.

2.2.3 Synthesis of Unsaturated Polyester from Glycolized PET

Unsaturated polyester synthesized from glycolized PET by reacting glycolized PET with maleic anhydride in presence of p-toluenesulphonic acid. The desired amount of reactants is charged in a reaction kettle. The temperature is maintained in the range of 120-150 °C for first five hours and then to 170 °C for subsequent 3 hours. Distillation is done through reaction to ensure water removal. 30ppm hydroquinone is added to prevent premature gelation of resin. Then prepolymer is dissolved in 35% wt styrene. It is mechanically mixed for 3 hours. Constant stirring is done throughout the reaction. To initiate polymerization, 1 wt% of a free-radical peroxide initiator, benzoyl peroxide (BPO) is added at 60 °C.

2.2.4 Synthesis of Unsaturated Polyester Nanocomposite (Simultaneous Mixing)

The desired amount of monomers (glycolized PET, maleic anhydride) was fed together to the five necked glass reactor having mechanical agitator assembly. The whole reaction is carried out 8 hours with constant stirring at temperature up to 180 °C. Hydroquinone is added to prevent premature gelation of resin. Then, the prepolymer and modified clay is dissolved in 35% wt. styrene with varying mixing times of 15, 30, 60, 120 and 180 min at 60 °C. It is mechanically mixed for 3 hours. The curing is done by initiator at 2%. The initiator is thoroughly dispersed in unsaturated polyester matrix in a glass vial. Materials are cured for 6 h at 60 °C. The temperature is gradually increased

from room temperature to 60 °C at the beginning and then cooled from 60 °C to room temperature at the end of the curing stage in order to prevent craze and cracks due to sudden crosslinking and cooling. The detailed conditions are reported in Table 1. The nomenclature used in this work is based on the original composition of reactants (shown in Table 1).

Table 1: Nomenclature of samples depend upon mixing time of styrene and clay

Sample ID	Mixing Time (min)	Clay Montmorillonite [#] (K-10) (%)
100UP0	0	0
Simultaneous100UP5-15	15	5
Simultaneous100UP5-30	30	5
Simultaneous100UP5-60	60	5
Simultaneous100UP5-120	120	5
Simultaneous100UP5-180	180	5
Sequential100UP5-15	15	5
Sequential100UP5-30	30	5
Sequential100UP5-60	60	5
Sequential100UP5-120	120	5
Sequential100UP5-180	180	5

[#]The clay is modified by using dodecyl trimethyl ammonium bromide (DTAB)

2.2.5 Synthesis of Unsaturated Polyester Nanocomposite (Sequential Mixing)

Sequential mixing is a new approach for preparing unsaturated polyester-layered silicate nanocomposites. In the first step, pre-intercalates of the unsaturated polyester and MMT nanocomposites are prepared. In other words, the mixture of the UP and organophilic-treated MMT are prepared in the first step; then the styrene monomer is added to these pre-intercalates of UP/MMT, varying mixing times of 15, 30, 60 and 180 min at 60 °C. All UP–MMT–styrene mixtures contained 0.01 wt% hydroquinone as an inhibitor to prevent reaction in the mixing stage. Finally, all mixtures are cured at 80 °C

for 3 h and post-cured for 4 h at 120 °C. All UP/MMT nanocomposites contained UP of 60 wt%, styrene monomer of 35 wt% and MMT 5 wt%.

2.3 Swelling Experiments

The samples are cut into circular form, using a die of 12 mm diameter. The thickness of the samples is measured by means of a screw gauge. The dry samples are weighed on an electronic balance and then kept in the solvent in screwed bottles. The samples are taken out of the solvent at specific intervals and the excess solvent is rubbed off. The samples are then weighed and again immersed in the solvent, till equilibrium is attained (i.e. 144 h). The time for measuring weight of the sample is kept minimal (about 30 sec), so that the escape of solvent from the sample is negligible. Equilibrium swelling experiments at different temperature are carried out at 20, 30, 40 and 50 °C (± 1 °C) to study the effect of temperature on swelling. For temperatures higher than room temperature, the samples are kept in a microprocessor controlled hot air oven. The mole percent uptake (Q_t) at each time interval is calculated by using equation 1 [32].

$$Q_t = \frac{M_t}{M_r} \times \frac{100}{M_i} \quad (1)$$

where M_t is the mass of solvent taken up at time interval t , M_r is the relative molar mass of the solvent and M_i is the mass of the dry sample. Equilibrium swelling experiments are also performed at 20 ± 1 °C to determine the solubility parameter of samples of unsaturated polyester and their nano-composites. The swelling is carried out in various solvents ranging from 8.85 to 23.5 (cal/cm³)^{1/2}. From the plots of mole percent uptake (Q_t) versus solubility parameter (δ), acetic acid gives the maximum value of Q in all the samples and hence is used for further kinetic studies. Figure 1 shows the representative plot of mole percent uptake versus solubility parameter for unsaturated polyester samples.

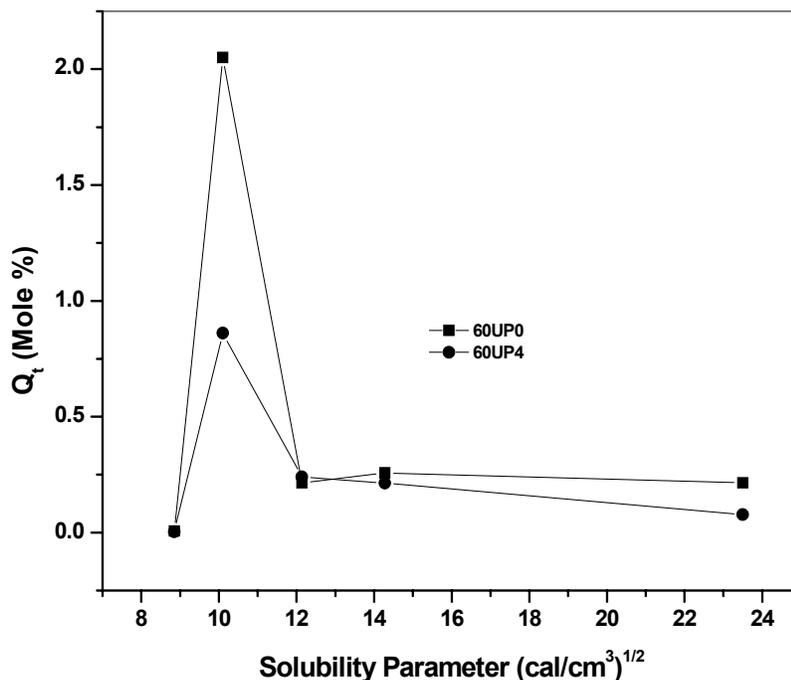


Figure 1. Plot of volume equilibrium of swelling (Q) versus solubility parameter (δ) for simultaneous 100UP5-15 and Sequential 100UP5-180 at 20 °C. The (δ) values in (cal/cm^3)^{1/2} of the used solvents are 8.85 (xylene), 10.1 (acetic acid), 12.14 (dimethyl formamide), 14.28 (methanol).and 23.5 (water).

3. Results and Discussion

3.1 Effect of Simultaneous Mixing Method with Varying Mixing Time

The mole percent uptake of the solvent is plotted against square root of time. The plots for the mole percent uptake are shown in Figure 2 for the nano-composite polymer (5% modified clay) synthesized by in-situ method with varying mixing time 15, 30, 60, 120, 180 min at a temperature of 20 ± 1 °C. It is observed that on increasing the mixing time the solvent uptake increases in the matrix. The solvent uptake is minimum for sample 100UP0 a pure cured unsaturated polyester and maximum for in-situ 100UP5-180 nanocomposite having maximum mixing time. It is further noteworthy that in-situ

samples the solvent uptake has lowest value for 100UP5-15 and increase with increasing mixing time. The sorption curves for all the samples are almost asymptotic with very little increase in the swelling after 64 h except for 100UP0. In the present case, the increase in the solvent uptake with an increase in the mixing time can be explained on the basis of following assumption.

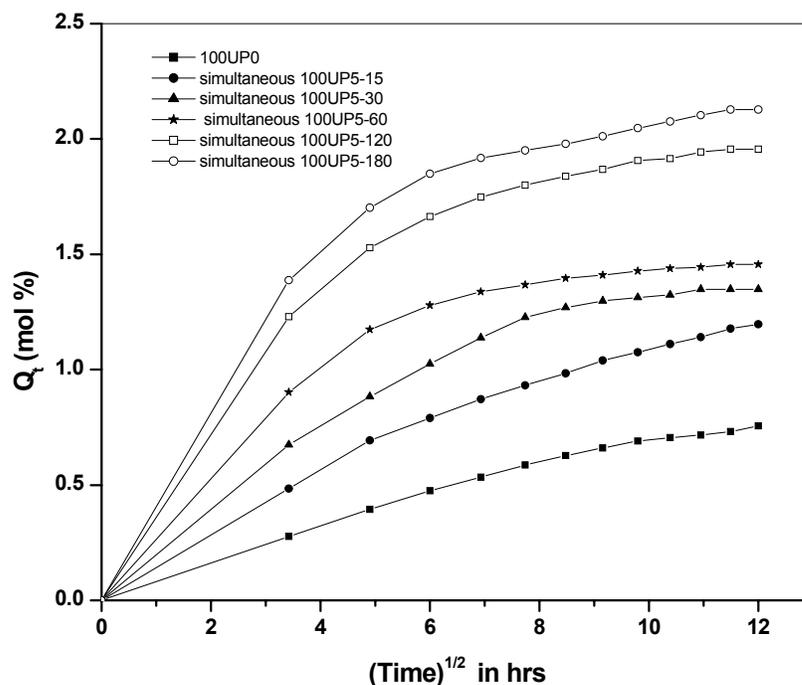


Figure 2. Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varying mixing time (fixed clay 5 %) at 20 °C (Synthesized by simultaneous method).

UP chains, styrene monomers and organic organophilic MMT (O-MMT) coexist in the mixing medium. The styrene monomers diffuse into the gallery of the O-MMTs much faster than the UP chains. Solvents and monomers have diffusion coefficients on the order of 10^{-5} (cm^2/s), while polymers have the diffusion coefficient on the order of 10^{-7} (cm^2/s) [33,34]. If the curing reaction starts in these conditions, the styrene homo-

polymer is produced primarily in the interlayer of the O-MMT and the crosslinking density decreases inside and outside of the O-MMT, because the styrene monomers are concentrated on the interlayer and styrene monomers are insufficient for the crosslinking the reactive double bonds of the unsaturated polyester. For this reason, the UP/MMT nanocomposite manufactured by the in-situ mixing method (conventional) method has a lower T_g and lower crosslinking density than that of the pure cured UP [35]. Thus, with increase in the mixing time the rate of diffusion of styrene in-to the silicate gallery goes on increasing leads to decrease in crosslinking density. The decrease in the crosslink density is confirmed latter during its calculation from the Flory-Rehner equation. In Figure 3, the solvent mole percent uptake is plotted against square root of time for different samples with varying mixing time at fixed modified clay (5 %) at 30 °C.

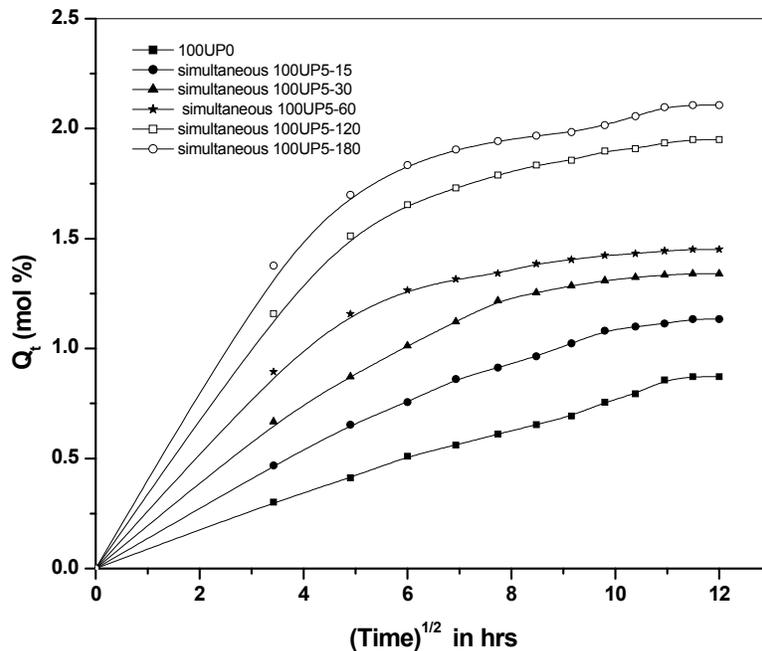


Figure 3. Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varying mixing time (fixed clay 5 %) at 30 °C (Synthesized by simultaneous method).

The sample 100UP0 shows the lowest solvent uptake followed by in-situ100UP5-15. The same trend is also observed in Figure 4 and 5. The sample with 30, 60, and 120 min shows intermediate swelling. All the samples show regular increase in swelling with time. The rate of uptake increases at first as sorption proceeds, but later decreases as the final equilibrium is approached. These curves are often referred to as sigmoid sorption curves [36]. They are generated because of the reason that the surface equilibrium conditions are not established instantaneously.

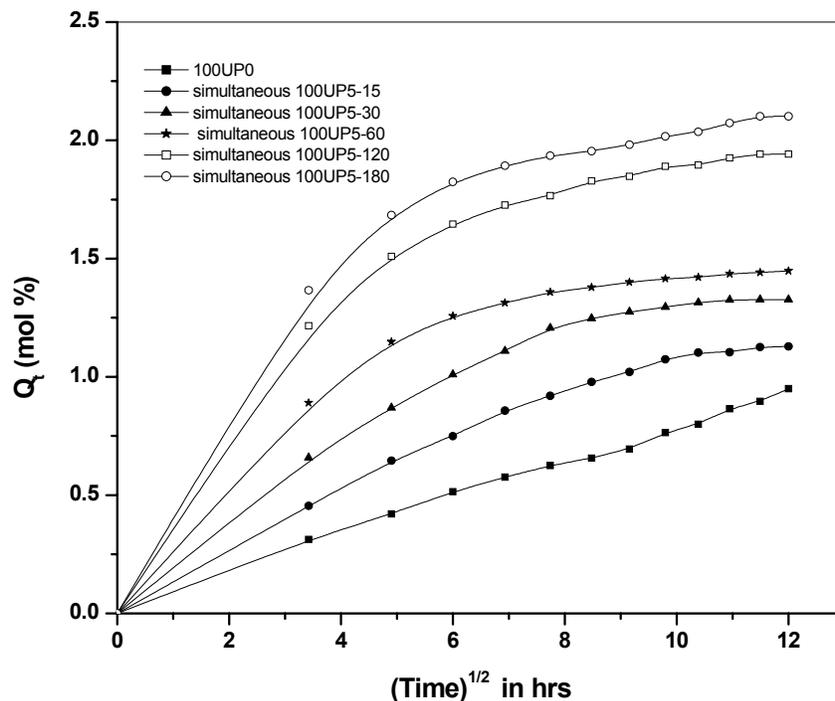


Figure 4. Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varying mixing time (fixed clay 5 %) at 40 °C (Synthesized by simultaneous method).

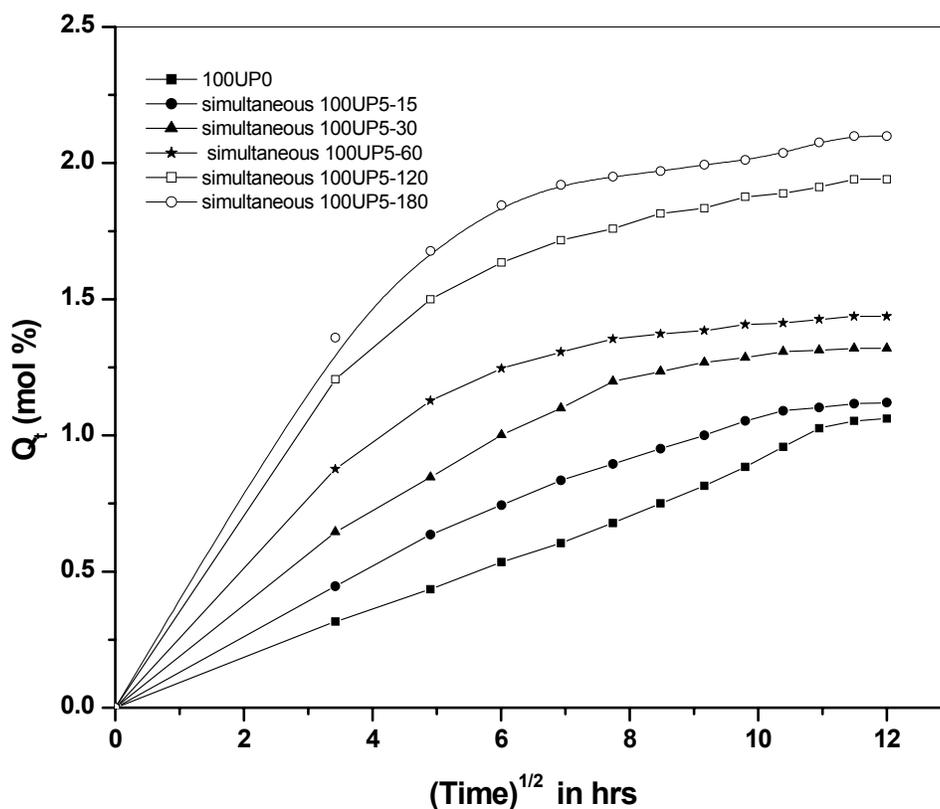


Figure 5. Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varying mixing time (fixed clay 5 %) at 50 °C (Synthesized by simultaneous method).

3.2 Effect of Sequential Mixing Method with Varying Mixing Time

The plots for the mole percent uptake are shown in Figures 6-9 for the nanocomposite polymer (5% modified clay) synthesized by sequential method with varying mixing time at a temperature of 20±1 °C. The solvent uptake order is quite reverse as compare to samples synthesized by in-situ method. It is observed that on increasing mixing time the solvent uptake decrease. The solvent uptake is a minimum for sample Seq100UP5-180 and maximum for seq100UP5-15. The solvent uptake value for 100UP5 “a pure cured UP” is close to Seq100UP5-180. This is to be expected by diffusion of

styrene monomer into the gallery of the MMT intercalated with UP to an extent as time goes on. Therefore, it is thought that crosslinking density and T_g of UP–silicate nanocomposite increase to some extent [35]. Hence, the styrene monomers, which act as a curing agent, are much more dispersed inside and outside of the silicate layers as mixing time increases. Therefore, the crosslinking reaction takes place homogeneously inside and outside of the silicate layers, and crosslinking density reaches the degree of crosslinking density of the cured pure UP at mixing time 180 min.

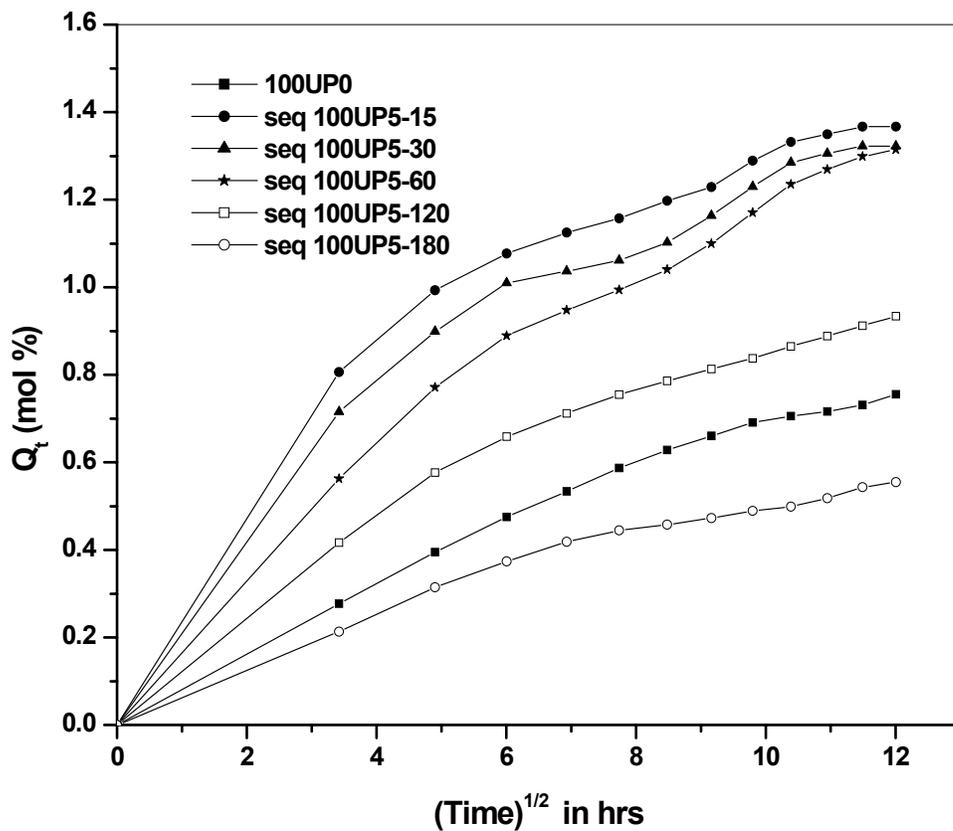


Figure 6. Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varying mixing time (fixed clay 5 %) at 20 °C (Synthesized by sequential method).

The increase in the crosslink density is confirmed latter during its calculation from the Flory-Rehner equation. In Figure 6, the solvent mole percent uptake is plotted against square root of time for different samples with varying mixing time at fixed modified clay (5 %) at 20 °C. The samples with 100UP0 and Seq100UP5-180 show lowest and lower solvent uptake, respectively. The same trend is also observed in Figures 7, 8 and 9. The sample with 30, 60 and 120 min shows intermediate swelling. All the samples show regular increase in swelling with time.

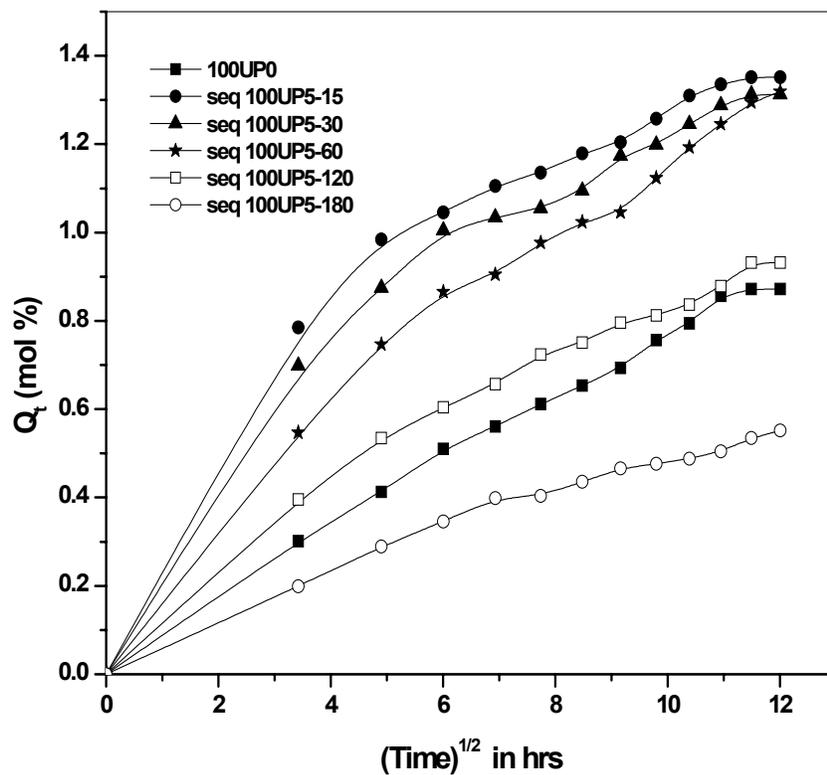


Figure 7. Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varying mixing time (fixed clay 5 %) at 30 °C (Synthesized by sequential method).

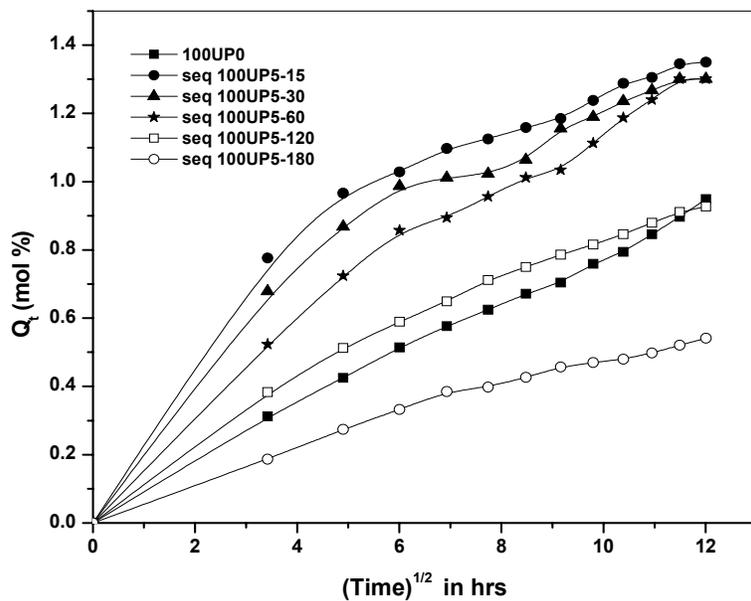


Figure 8. Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varying mixing time (fixed clay 5 %) at 40 °C (Synthesized by sequential method).

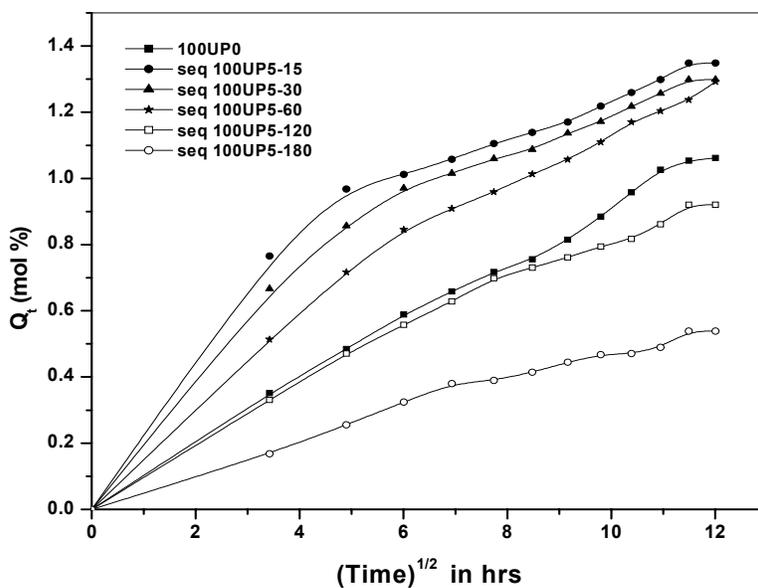
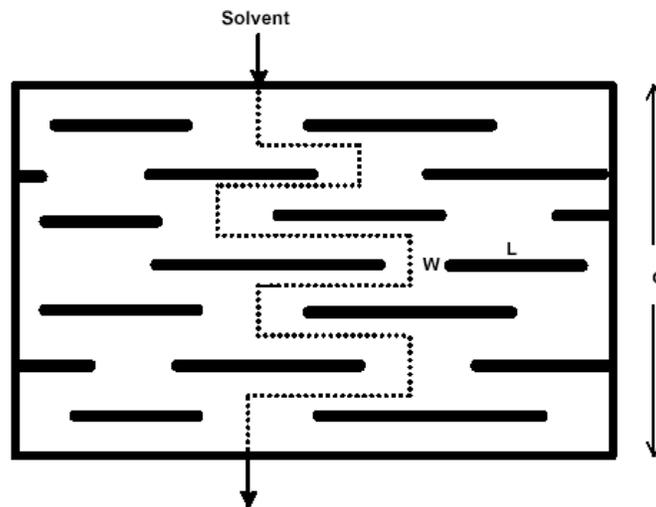


Figure 9. Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varying mixing time (fixed clay 5 %) at 50 °C (Synthesized by sequential method).

3.3 Effect of Temperature

The samples are also studied for the change in diffusion and sorption due to the change in temperature (20, 30, 40 and 50 °C) and are shown in Figures 2-9. It is observed for the samples via simultaneous mixing (Figures 2-5), solvent uptake decreases with an increase in temperature. It is known that the layered nano-fillers have platelet like structure, which improves the barrier properties of the polymer [4]. The platelets due to the rise in temperature are then evenly distributed into the polymer matrix, creating multiple parallel layers. These layers force the solvent molecules to flow through the polymer in a “torturous path”, forming complex barriers to the solvent molecules. The detailed process is shown in Scheme 2. The filler platelets are impenetrable for the diffusing solvent molecules.



Scheme 2. The schematic representation of tortuosity-based model to describe the solvent diffusion in the nano-clay filled polymer composite. (W is the width or thickness and L is the length of the filler platelet. d is the thickness of the polymer matrix, through which the solvent molecules diffuse).

Therefore, when compared to the parent polymer, a decrease in the diffusion of the solvent in the nano-composites is observed. It has reverse order for 100UP0 sample

(neat polymer) with temperature. It is due to an increase in the solvent penetration with increase in temperature, resulting in higher swelling of the polymer. For the samples obtained by sequential mixing (Figures 6-9), the similar trend is observed as that for the samples obtained by simultaneous mixing. The solvent uptake is a maximum for simultaneous mixing samples. It is observed that at 50 °C for simultaneous100UP5-180 the solvent uptake is four fold as compare to seq100UP5-180.

Diffusion Kinetics

In order to find out the mechanism of swelling, the diffusion data is fitted into an empirical equation (eq. 3) [37] derived from equation of transport phenomena (eq. 2) [32]

$$\frac{Q_t}{Q_\infty} = kt^n \quad (2)$$

$$\ln \frac{Q_t}{Q_\infty} = \ln k + n \ln t \quad (3)$$

where Q_t and Q_∞ are the mole percent uptake of solvent at time ‘ t ’ and at infinity or equilibrium. ‘ k ’ is a constant, which depends upon both on the polymer-solvent interaction between and on the structure of polymer. The regression coefficient (r) varies between 0.86 and 0.99 for samples synthesized by in-situ method. The value of (r) lies between 0.94 and 0.99 for samples obtained by sequential method. The values of constant ‘ k ’ and ‘ n ’ obtained from the equation (3) and Q_∞ are represented in Tables 2a and 2b. The value of ‘ n ’ gives an idea of the mechanism of sorption [38]. When the value of n is 0.5, the mechanism of swelling is termed as Fickian transport. This occurs, when the rate of diffusion of solvent is less than that of polymer segmental mobility. The transport is considered as a non-Fickian, if the value of ‘ n ’ is not ‘0.5’. In particular, if ‘ $n = 1$ ’, the transport is called ‘case II’ transport [38]. It is a special case, where the solvent

front moves with constant velocity. If ‘ n ’ lies between ‘0.5’ and ‘1’, then it is called anomalous transport [38]. For non-Fickian transport, the diffusion is more rapid than the polymer relaxation rate. For anomalous transport, the diffusion and relaxation rates are comparable [38]. From Tables 2a and 2b, the values of ‘ n ’ fall below ‘0.5’, indicating the transport as pseudo-Fickian

Table 2a. Values of mole percent uptake at infinite time (Q_{∞}), n , k and standard deviation (SD) for unsaturated polyester nano-composites samples at different temperatures

Temperature (°C)	Sample ID	Q_{∞} (mol%)	N	K	SD
20	100UP0	0.755	0.061	0.070	0.040
	Simultaneous100UP5-15	1.197	0.094	0.149	0.071
	Simultaneous100UP5-30	1.348	0.104	0.279	0.139
	Simultaneous100UP5-60	1.456	0.100	0.453	0.204
	Simultaneous100UP5-120	1.955	0.135	0.585	0.135
	Simultaneous100UP5-180	2.127	0.143	0.670	0.293
	Sequential100UP5-15	1.366	0.097	0.339	0.146
	Sequential100UP5-30	1.322	0.097	0.275	0.120
	Sequential100UP5-60	1.319	0.102	0.171	0.078
	Sequential100UP5-120	0.933	0.070	0.151	0.070
Sequential100UP5-180	0.554	0.043	0.070	0.037	
30	100UP0	0.872	0.072	0.040	0.022
	Simultaneous100UP5-15	1.134	0.092	0.143	0.074
	Simultaneous100UP5-30	1.340	0.104	0.272	0.135
	Simultaneous100UP5-60	1.450	0.100	0.441	0.198
	Simultaneous100UP5-120	1.950	0.137	0.557	0.251
	Simultaneous100UP5-180	2.107	0.142	0.669	0.292
	Sequential100UP5-15	1.352	0.096	0.327	0.141
	Sequential100UP5-30	1.319	0.096	0.270	0.118
	Sequential100UP5-60	1.312	0.101	0.155	0.070
	Sequential100UP5-120	0.932	0.072	0.116	0.053
	Sequential100UP5-180	0.552	0.043	0.052	0.028

Table 2b. Values of mole percent uptake at infinite time (Q_{∞}), n , k and standard deviation (SD) for unsaturated polyester nano-composites samples at different temperatures.

Temperature (°C)	Sample ID	Q_{∞} (mol%)	n	K	SD
40	100UP0	0.949	0.075	0.034	0.020
	Simultaneous100UP5-15	1.128	0.092	0.139	0.075
	Simultaneous100UP5-30	1.326	0.103	0.271	0.135
	Simultaneous100UP5-60	1.447	0.100	0.440	0.198
	Simultaneous100UP5-120	1.941	0.134	0.574	0.253
	Simultaneous100UP5-180	2.102	0.141	0.662	0.290
	Sequential100UP5-15	1.350	0.095	0.320	0.138
	Sequential100UP5-30	1.301	0.095	0.258	0.114
	Sequential100UP5-60	1.301	0.101	0.140	0.066
	Sequential100UP5-120	0.921	0.072	0.106	0.048
Sequential100UP5-180	0.541	0.043	0.045	0.025	
50	100UP0	1.061	0.091	-0.008	0.018
	Simultaneous100UP5-15	1.120	0.091	0.131	0.069
	Simultaneous100UP5-30	1.320	0.103	0.261	0.132
	Simultaneous100UP5-60	1.437	0.100	0.431	0.882
	Simultaneous100UP5-120	1.939	0.134	0.567	0.250
	Simultaneous100UP5-180	2.098	0.141	0.668	0.295
	Sequential100UP5-15	1.348	0.095	0.310	0.133
	Sequential100UP5-30	1.298	0.095	0.257	0.113
	Sequential100UP5-60	1.291	0.099	0.149	0.069
	Sequential100UP5-120	.920	0.074	0.074	0.038
	Sequential100UP5-180	.538	0.044	0.031	0.022

The swelling data is used to calculate diffusion coefficient (D), which is a measure of the ability of solvent molecules to move into the polymer. The sorption coefficient (S), which gives an idea about the equilibrium sorption, is also calculated from the swelling data.

The diffusion coefficient (D) is calculated as [39]

$$D = \pi \left(\frac{h\theta}{4Q_\infty} \right)^2 \quad (4)$$

where $\pi = 3.14$; h is the thickness of the dry sample and θ is the slope of the initial linear portion of the curve Q_t versus \sqrt{t} ; and Q_∞ is the mole percent uptake of the solvent at infinite time. The sorption coefficient (S) is calculated as [39]

$$S = \frac{M_\infty}{M_p} \quad (5)$$

where M_∞ is the mass of solvent uptake at equilibrium and M_p is the mass of dry sample. The sorption and diffusion coefficients are used to calculate permeability coefficient (P) of samples, which is given by [39]

$$P = D \times S \quad (6)$$

Values of these coefficients are reported in Tables 3a and 3b. The data in Tables 3a and 3b indicates that the mixing methods and mixing time influence the diffusion behavior of nanocomposites. The properties of unsaturated polyester (UP)/montmorillonite (MMT) nanocomposite greatly depend on the preparation procedure because of the chemical reactions and physical interactions involved. In case of in-situ mixing, Simultaneous100UP5-15 sample with 15 min mixing time has maximum and Simultaneous100UP5-180 sample with 180 min shows a minimum diffusion coefficient. It is noteworthy that neat polymer (100UP0) shows maximum diffusion coefficient as compare to all samples synthesized by in-situ mixing method. The diffusion coefficient is inversely proportional to the mole percent uptake of the solvent (equation 4). The experimental results indicate that the diffusion of the solvent through nano-composite increases with increase in the mixing time. The diffusion

coefficient shows an increase with an increase in the temperature for all samples obtained by in-situ mixing with 5% clay, while for neat polymer diffusion coefficient decreases.

Table 3a. Diffusion coefficient (D), Sorption coefficient (S) and permeability coefficient (P) in acetic acid medium for the samples at different temperatures

Temperature (°C)	Sample ID	$D \times 10^4$ (cm ² /sec)	S (g/g)	$P \times 10^4$ (cm ² /sec)
20	100UP0	4.943	0.453	2.239
	Simultaneous100UP5-15	4.427	0.718	3.178
	Simultaneous100UP5-30	4.065	0.809	3.288
	Simultaneous100UP5-60	3.766	0.873	3.287
	Simultaneous100UP5-120	3.462	1.173	4.060
	Simultaneous100UP5-180	3.157	1.276	4.028
	Sequential100UP5-15	2.725	0.820	2.234
	Sequential100UP5-30	3.049	0.793	2.418
	Sequential100UP5-60	3.242	0.791	2.564
	Sequential100UP5-120	3.698	0.560	2.071
Sequential100UP5-180	4.382	0.332	1.454	
30	100UP0	3.247	0.484	1.571
	Simultaneous100UP5-15	4.992	0.680	3.394
	Simultaneous100UP5-30	4.634	0.804	3.726
	Simultaneous100UP5-60	4.416	0.870	3.842
	Simultaneous100UP5-120	3.665	1.170	4.288
	Simultaneous100UP5-180	3.160	1.264	3.994
	Sequential100UP5-15	3.252	0.811	2.638
	Sequential100UP5-30	3.631	0.791	2.872
	Sequential100UP5-60	3.848	0.787	3.029
	Sequential100UP5-120	3.846	0.559	2.150
Sequential100UP5-180	4.395	0.331	1.454	

In case of neat polymer (100UP0), the diffusion coefficient is the highest at 20 °C, which keeps on decreasing with temperature and decreases almost two fold at 50 °C. In case of samples obtained by sequential mixing, Seq100UP5-15 sample (with 15 min mixing time) shows a minimum and Seq100UP5-180 sample (with 180 min mixing time) shows a maximum diffusion coefficient. The neat polymer (100UP0) shows maximum

diffusion coefficient in all samples synthesized by in-situ mixing method. The experimental results indicate that the diffusion of the solvent through nano-composite decreases with an increase in the mixing time. Other samples show intermediate diffusion coefficients.

Table 3b. Diffusion coefficient (D), Sorption coefficient (S) and permeability coefficient (P) in acetic acid medium for the samples at different temperatures

Temperature (°C)	Sample ID	$D \times 10^4$ (cm ² /sec)	S (g/g)	$P \times 10^4$ (cm ² /sec)
40	100UP0	2.853	0.569	1.623
	Simultaneous100UP5-15	5.091	0.676	3.441
	Simultaneous100UP5-30	4.663	0.795	3.707
	Simultaneous100UP5-60	4.479	0.868	3.887
	Simultaneous100UP5-120	3.775	1.164	4.394
	Simultaneous100UP5-180	3.165	1.261	3.991
	Sequential100UP5-15	3.808	0.810	3.084
	Sequential100UP5-30	3.854	0.780	3.006
	Sequential100UP5-60	4.182	0.780	3.262
	Sequential100UP5-120	4.298	0.553	2.376
	Sequential100UP5-180	4.310	0.324	1.396
50	100UP0	2.627	0.721	1.894
	Simultaneous100UP5-15	5.210	0.672	3.501
	Simultaneous100UP5-30	4.794	0.792	3.797
	Simultaneous100UP5-60	4.514	0.862	3.891
	Simultaneous100UP5-120	3.952	0.808	3.193
	Simultaneous100UP5-180	3.257	1.1639	3.791
	Sequential100UP5-15	4.256	1.259	5.359
	Sequential100UP5-30	4.365	0.778	3.396
	Sequential100UP5-60	4.425	0.775	3.429
	Sequential100UP5-120	4.571	0.552	2.523
	Sequential100UP5-180	4.664	0.323	1.506

In case of sorption by the samples, no particular trend is observed and it is quite difficult to explain this behavior. For in-situ samples at 25 and 30 °C, the sorption coefficient increases with an increase in the mixing time. The samples with mixing time

30 min and 180 min show a minimum and a maximum sorption coefficient, respectively. On comparison with neat polymer it is found that sorption coefficient has minimum value for 100UP0 and maximum for Simultaneous100UP-180. A small decrease in the sorption coefficient with an increase in the temperature is observed. In case of sequential mixing method, the order is reverse. At 20 to 50 °C, the samples show a decrease in the sorption coefficients with an increase in the mixing time.

A small decrease in the sorption coefficient with an increase in the temperature is observed. The sorption coefficient is a maximum and a minimum for the samples with mixing time 15 min and 180 min, respectively. The value of sorption coefficient is found to be a minimum for sample Seq100UP5-180 even on comparison with sample 100UP0. This shows a decrease in sorption with an increase in mixing time. Other samples show intermediate sorption coefficients. The sorption coefficient is a direct indicator of the absorbed solvent in the polymer. The decrease in the sorption coefficient with temperature indicates the decrease in the solvent absorption capacity of the nano-composite material.

In all of the systems, it is observed that the sorption and diffusion coefficients decrease with an increase in the temperature. It is reported elsewhere [40] for natural rubber that these coefficients show an increase with a rise in the temperature. But in our case, these coefficients decrease with temperature. This can be explained by the dual mode model for diffusion in the polymers below glass transitions [41]. According to this model, glassy polymers contain a distribution of microvoids frozen into a structure as the polymer is cooled through its glass transition temperature. The free segmental rotations of the polymer chains in the glassy state are restricted, which results in the fixed

microvoids throughout the polymer. The microvoids in the glassy polymer network immobilize the solvent molecules by entrapment. These entrapments increase the size of the polymer, resulting in the enlargement of the microvoids. The enlargement of microvoids further leads to initiate the macro-fractures in the polymer.

The permeability coefficients of the samples are the product of diffusion and sorption coefficients. For in-situ samples the permeability coefficients show an increase with the increasing in mixing time. The permeability coefficient also increases with an increase in temperature. For neat polymer the sorption coefficient decreases with an increase in temperature. At 25 °C, the permeability coefficient is observed to be minimum and maximum for the sample 100UP5-15 (neat polymer) and 100UP5-120, respectively.

On comparison with virgin polymer the sample without clay shows a minimum and the sample with 100UP-120 shows a maximum permeability coefficient. The same order is follow for all samples from 20 to 40 °C. At 50 °C, the permeability coefficient is observed to be maximum and minimum for 100UP5-180 and 100UP5-15, respectively. For the samples synthesized by sequential mixing, the permeability coefficient increases with an increase in temperature. The value of permeability coefficient increases with mixing time up to 60 min after that coefficient values decrease.

Crosslink Density and Molecular Weight

The sorption data is also used to calculate the crosslink density of the polymer networks using Flory-Rehner's equation [42]

$$\nu = -\frac{\ln(1-V_p) + V_p + \chi V_p^2}{V(V_p^{1/3} - 0.5V_p)} \quad (7)$$

where V_p is the volume fraction of the polymer in the mixture, χ is the polymer-solvent interaction parameter and V_l is the molar volume of the solvent. V_p and χ are obtained by the following equations [42]

$$V_p = \frac{\text{Weight of polymer} / \text{Density of polymer}}{\text{Weight of polymer} / \text{Density of polymer} + \text{Weight of solvent} / \text{Density of solvent}} \quad (8)$$

$$\chi = \chi_H + \chi_s = \frac{V_l(\delta_p - \delta_s)^2}{RT} + 0.34 \quad (9)$$

Where χ_H and χ_s are the enthalpic and entropic components of χ , δ_1 and δ_2 are the solubility parameters of polymer and solvent, respectively. The solubility parameter of the polymer is obtained by fitting the swelling coefficients of the polymer in various solvents. The results are reported in Table 6. The molecular weight between two crosslinks (\overline{M}_c) is also calculated for all the samples by the following equation [40]

$$\overline{M}_c = \frac{l}{2\nu} \quad (10)$$

The values of the crosslink density and \overline{M}_c are reported in Table 4. The crosslinking density ranges from 5.014 to 7.092×10^2 mol/cm³ for the simultaneous mixed samples and 5.212 to 7.192×10^2 mol/cm³ for the sequential mixed samples. The crosslink density for in-situ sample is the highest for 100UP5-15 and the lowest for

100UP5-180 samples. It is observed that the crosslink density decreases with an increase in mixing time. This is because the styrene monomer moves more easily than uncured UP chains. This may generate higher styrene monomer concentration in the MMT gallery than in any other part in a simultaneous mixing system. If polymerization occurs in these conditions, the total crosslinking density of the sample decreases due to the low concentration of styrene in uncured UP linear chains. Thus with increase in the mixing time the rate of diffusion of styrene in-to the silicate gallery goes on increasing leads to decrease in crosslinking density. This is the reason for showing a minimum solvent uptake for sample having minimum mixing time, hence sample shows maximum diffusion coefficient, which indicates that the sample present a maximum resistance to the solvent molecules.

Table 4. Volume fraction of polymer (V_p), crosslink density (ν) and molecular weight between two crosslinks (M_c) for different unsaturated polyester nano-composites at 30 °C

Sample ID	V_p	$\nu \times 10^2$ (mol/cm ³)	$M_c \times 10^{-2}$ (cm ³ /mol)
100UP0	0.36	7.540	0.066
Simultaneous100UP5-15	0.34	7.092	0.070
Simultaneous100UP5-30	0.31	6.443	0.077
Simultaneous100UP5-60	0.29	6.023	0.083
Simultaneous100UP5-120	0.26	5.411	0.092
Simultaneous100UP5-180	0.24	5.014	0.099
Sequential100UP5-15	0.25	5.212	0.095
Sequential100UP5-30	0.26	5.411	0.092
Sequential100UP5-60	0.28	5.817	0.085
Sequential100UP5-120	0.31	6.443	0.077
Sequential100UP5-180	0.34	7.192	0.070

On comparing with neat polymer it is observed that crosslinking density is highest for neat polymer sample. In case of samples synthesized by sequential mixing method

this order is reversed. The crosslink density increases with an increase in mixing time. It is the highest for 100UP5-180 and lowest for the sample 100UP5-15. The increase in crosslink density decreases the solvent uptake. This explains the solvent uptake trends for the sequential mixing samples, which is in good agreement with sorption kinetics. With increase in the mixing time the crosslinking density increases because the styrene monomer diffuses to the gallery of the MMT intercalated with UP to an extent as time goes on. Therefore, it is thought that crosslinking density and T_g of UP–silicate nanocomposite increase to some extent. Hence, the styrene monomers, which act as a curing agent, are much more dispersed inside and outside of the silicate layers as mixing time increases. Therefore, the crosslinking reaction takes place homogeneously inside and outside of the silicate layers, and crosslinking density reaches the degree of crosslinking density of the cured pure UP. It is noteworthy that crosslinking density for the sample 100UP5-180 is even highest for neat polymer.

Conclusion

A new system of unsaturated polyester nanocomposite depending upon fabrication method is investigated for the sorption and diffusion studies. The kinetics of the sorption is studied by using the equation of transport phenomena. The solvent resistance properties of the montmorillonite filled unsaturated polyester nanocomposite based on glycolized PET are studied in acetic acid medium for food packaging application point of view. The values of ‘n’ in the transport equation are found to be below ‘0.5’, showing the non-Fickian diffusion in the polymer. The dependence of the diffusion coefficient on the mixing time and temperature has been studied for the nanocomposite samples. The diffusion coefficient increases with an increase in mixing

time and temperature for all of the unsaturated polyester nanocomposite synthesized by sequential mixing method, while decrease for simultaneous samples. The crosslink density shows decreasing trend with an increase in mixing time for all simultaneous samples. For sequential mixing samples, the cross linking density increases with increase in the mixing time. The crosslinking density (calculated from the CH₃COOH swelling) ranges from 5.014 to 7.092×10^2 mol/cm³ for the simultaneous mixed samples and 5.212 to 7.192×10^2 mol/cm³ for the sequential mixed samples.

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