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Swelling kinetics of unsaturated polyester and their montmorillonite filled nanocomposite synthesized from glycolyzed PET

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Abstract

The solvent resistance properties of the unsaturated polyester and their montmorillonite filled nanocomposites are studied in acetic acid through equilibrium swelling method at different temperatures. The kinetics of sorption is studied by using the equation of transport phenomena. The values of 'n' in solvent transport equation are found to be below '0.5', showing the non-Fickian or pseudo-Fickian transport in the polymer. The dependence of diffusion coefficient on composition and temperature has been studied for all polymeric samples. The diffusion coefficient of unsaturated polyester samples decreases with an increase in unsaturated acid content. The nanocomposite samples show low diffusion coefficient than corresponding pristine polymers. The diffusion coefficient, sorption coefficient and permeation coefficient increase with an increase in temperature for all the samples. The crosslink density for neat polymer with varied unsaturated acid content ranges from 2.98 to 3.52 ×10^5 mol/cm^3. For the nanocomposite samples it ranges from 3.70 to 5.72 × 10^5 mol/cm^3.

Keywords: Unsaturated polyester, nanocomposite, montmorillonite, sorption, non-Fickian diffusion.

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Introduction

Today, PET bottles have become one of the most valuable and successfully recyclable materials.[1] Waste PET can be depolymerized by glycolysis to obtain oligomeric diols such as BHET dependent on process conditions. The PET glycolysis products were used for the synthesis of saturated and unsaturated polyesters[2–4], polyurethanes[5, 6], coating materials[7, 8], and additives[9]. Unsaturated polyester resins (UPRs) are one of the most important thermoset materials used in composites industry for the preparation of molding compounds, laminates, coatings, and adhesives. UPRs have made significant structural and performance advances[10, 11], which resulted in their broader application in automotive, building, construction, and marine industries. Toyota research group[12-14] demonstrated that nanoscopic dispersion of platelets like structure such as aluminosilicates in a polymer matrix results in remarkable property enhancements. For example improved solvent resistance [15-16] and reduction in permeability to gases have been reported.[17-19] The barrier properties of the nanocomposites are supposed to increase due to nano-clay loading.[20, 21]

The swelling technique is commonly used method to determine various coefficients, such as, diffusion, sorption and permeability coefficients.[22-25] In swelling experiments, the polymer of known dimension is dispersed in a solvent, 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 manufacture, etc.

In the present study, the unsaturated polyester and their nanocomposites are studied using Fickian model. The variation in sorption is studied with respect to time and temperature. The objective of the present work is to study the sorption and diffusion kinetics of the unsaturated polyester based from glycolzed PET (GPET) and their nanocomposites with an alteration in the unsaturated acid and clay contents. The mechanism of the sorption is studied from the data by the linear fit of the equation of the transport phenomena. The effect of unsaturated acid and nano-filler on the barrier properties of the nanocomposites is also studied. The crosslink density and molecular weight between two crosslinks are also calculated from the sorption data using Flory-Rehner equation.

Experimental

Materials

Discarded PET bottles from soft drinks were procured from scrapers, cleaned thoroughly and cut into small pieces (6 mm × 6 mm). Zinc acetate, minimum assay 99%, Ethylene glycol (EG), diethylene glycol (DEG) and styrene were procured from E. Merck (India) Pvt. Ltd, Bombay, Maleic anhydride (MA), Phthalic anhydride (PA) and hydroquinone were obtained from CDH (India). Montmorillonite (K-10), dodecyl trimethyl ammonium bromide (DTAB), were purchased from Aldrich Chemical Company (Milwaukee, MI) and used as received.

Synthetic Work

Modification of Montmorillonite

Montmorillonite Clays are dispersed in DI water by stirring. DTAB is added to dispersion. The whole dispersion is heated at 80 ^{o}C for 6 h 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 $AgNO_3$ solution. The treated clay was dried at 100 °C in the vacuum oven for 24 h, by which time all moisture was removed and a constant weight was obtained.

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 repeating unit to glycol has been taken 1:2 respectively. The mixture of diols DEG:EG was charged in the ratio 80:20 respectively. $Zn(CH_3COO)_2$ was used as trans-esterification catalyst. Initially the temperature gradually increased to 180 °C and the recycled PET flakes started melting. The temperature was slowly raised by increments of twenty, until a temperature of 220 °C was reached. After seven hours at cook temperature of 220 °C, all of the PET particles were visibly digested**.** The whole reaction was carried out in inert atmosphere (argon atmosphere) under reflux with constant stirring.

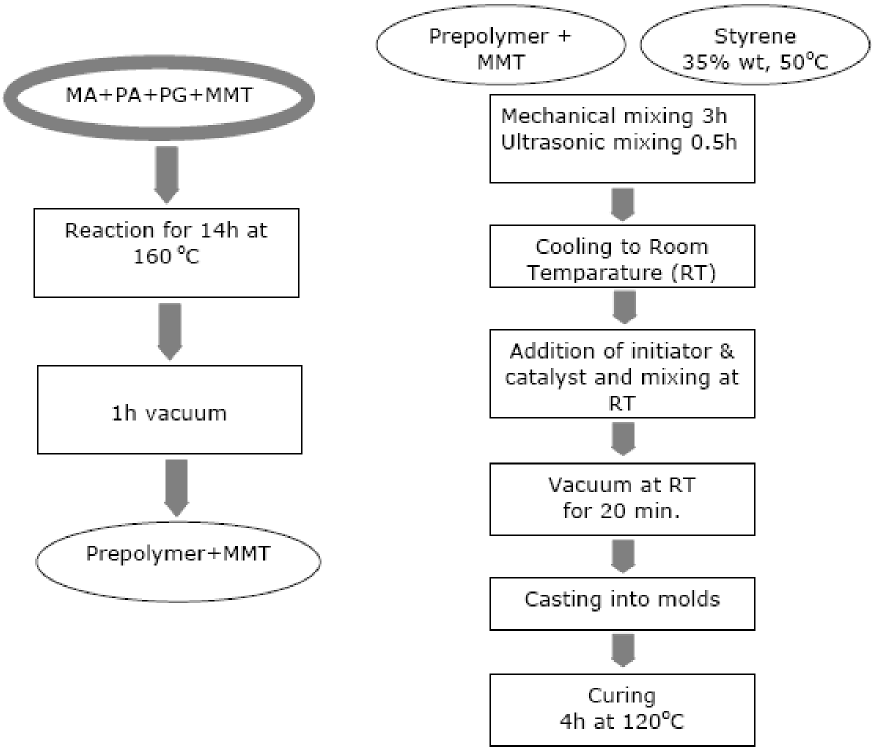
Synthesis of Unsaturated Polyester from Glycolyzed PET

Unsaturated polyester was synthesized by reacting GPET with MA in presence of p-toluenesulphonic acid. The desired amount of reactants was charged in to a reaction kettle. Since there must be a balance between diacids and glycols, the only way to control crosslink density is by introducing different diacids, or to a lesser extent by the use of higher molecular weight glycols. Consequently, dilution of the maleic concentration with another diacid is generally necessary. Subsequently, MA was replaced by PA by 100:0, 90:10, 80:20, 70:30 and 60:40 (wt %) respectively. The temperature is maintained in the range of 120-150 °C for first five hours and then to 170 °C for subsequent 3 hours. Water is distilled throughout the reaction. 30 ppm hydroquinone is added to prevent premature gelation of resin. Then, prepolymer is dissolved in 40 wt % styrene. It is mechanically mixed for 3 hours. Constant stirring is done throughout the reaction. To initiate polymerization, 1 wt % of BPO is added at 60 °C.

Synthesis of Unsaturated Polyester-layered Silicate nanocomposites

The flowchart of the specimen preparation procedure by the in-situ method is shown in Scheme 1.

In the in-situ method, the organoclay is added to the reaction medium simultaneously with the monomers. The penetration of the monomers into the clay layers is followed by polymerization. The nanocomposites contained 0 to 5 % wt. organoclay with DTAB modifier. These reactants were fed together to the five necked glass reactor having mechanical agitator assembly. P-toluenesulphonic acid was used as catalyst. The whole reaction was carried out about 8 h with constant stirring at temperature up to 180 °C. The mixture was then cooled down to 90-100 °C and hydroquinone was added to prevent premature gelation of resin. Then, the prepolymer and clay was dissolved in 40 wt % styrene. The reaction mixture was mechanically stirred for 3 h and then, curing was done by initiator at 1 %.



Scheme 1: Flowchart of specimen preparation by the in-situ method

The initiator was thoroughly dispersed in unsaturated polyester matrix in a glass vial. Materials were cured for 6 h at 60 °C. The temperature was 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 cool. The detailed compositions 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: Detailed feed composition of the unsaturated polyester and nanocomposites with varied acid and clay content

Sample ID	Maleic anhydride (%)	Phthalic anhydride (%)	Clay Montmorillonite (K-10) (%)*
60UP0	60	40	0
70UP0	70	30	0
80UP0	80	20	0
90UP0	90	10	0
100UP4	100	0	4
60UP4	60	40	4
70UP4	70	30	4
80UP4	80	20	4
90UP4	90	10	4
100UP4	100	0	4
90UP2	90	10	2
90UP3	90	10	3
90UP5	90	10	5

* The clay is modified by using dodecyl trimethyl ammonium bromide (DTAB).

Swelling Experiments

The procedure adopted for swelling study of polymeric samples is discussed in our previous manuscript.[26] Equilibrium swelling experiments at different temperature were carried out at 20, 30, 40 and 50 ^{o}C (±1 ^{o}C) to study the effect of temperature on swelling. For temperatures higher than room temperature, the samples were kept in a microprocessor controlled hot air oven. The mole percent uptake (Q_t) at each time interval was calculated by using equation 1[27]

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

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 were also performed at 20 ±1 ^{o}C to determine the solubility parameter of samples of unsaturated polyester and their nanocomposites. The swelling was carried out in various solvents with different solubility parameters ranging from 8.85 to 23.5 (cal/cm^3)$^{1/2}$. From the plots of equilibrium swelling volume (Q_t) versus solubility parameter (δ), acetic acid gives the highest value of Q_t in all the samples and hence is used for further kinetic studies. Figure 1 shows the representative plot of volume equilibrium swelling versus solubility parameter for unsaturated polyester samples.

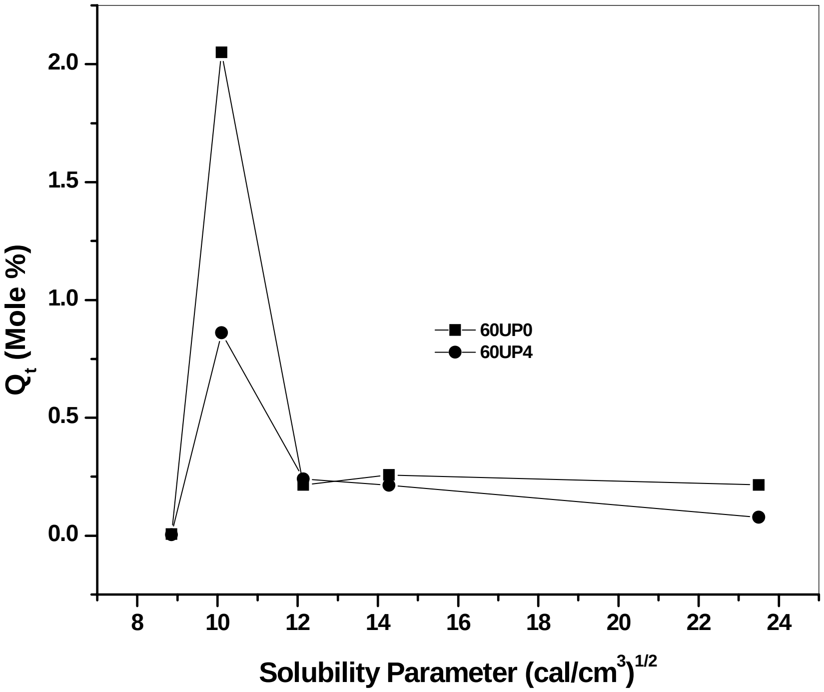


Figure 1: Plot of volume equilibrium of swelling (Q) versus solubility parameter (δ) for 60UP0 and 60UP4 samples at 20 ^{o}C. The (δ) values in (cal/cm^3)$^{1/2}$ of the used solvents are 8.85 (xylene), 10.1 (acetic acid), 12.14 (dimethyl formamide), 14.28 (methanol).and 23.5 water).

Results and Discussion

Swelling of polymer samples

The mole percent uptake of the solvent is plotted against square root of time for neat polyester samples with varied acid content is shown in Figure 2. These samples are studied at a temperature of 20±1 °C. It is observed that unsaturated acid content is varied from 100 to 60 wt % in the polymer matrix.

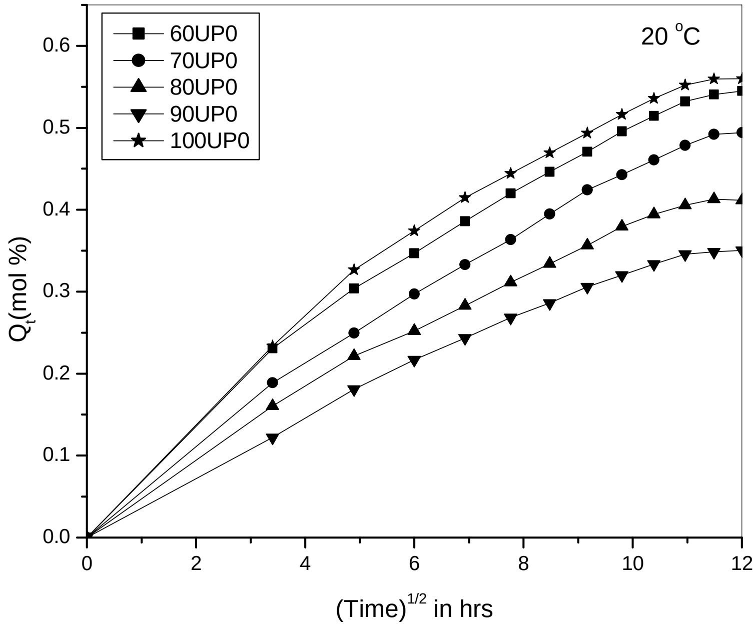


Figure 2: Sorption curve showing mole percent uptake of unsaturated polyester samples with varied acid content @ 20 °C.

For all samples the Q_t value increases with time. It is observed that on increasing the unsaturated acid content, the solvent uptake decreases and this order is well maintained for the samples 60UP0 to 90UP0. The decrease in the solvent uptake with an increase in the unsaturated contents can be attributed to the fact that with increase in unsaturated content the rate of crosslinking with styrene increases; hence crosslinking density increases, resulted in decrease in solvent uptake. The abnormal behavior is shown by the sample 100UP0, which shows the maximum increases in solvent uptake. It is assigned to fact that dilution of maleic concentration with another diacid is necessary to control crosslink density, in case of sample with 100 % unsaturated acid content, there is imbalance between diacid and glycol. This leads to decrease in the crosslinking density which is further confirmed during its calculation from the Flory-Rehner equation. In Figure 3, the neat polyester samples with varied acid content are studied at a temperature of 50±1 °C. It is observed that with an increase in temperature the solvent uptake increases for all the samples.

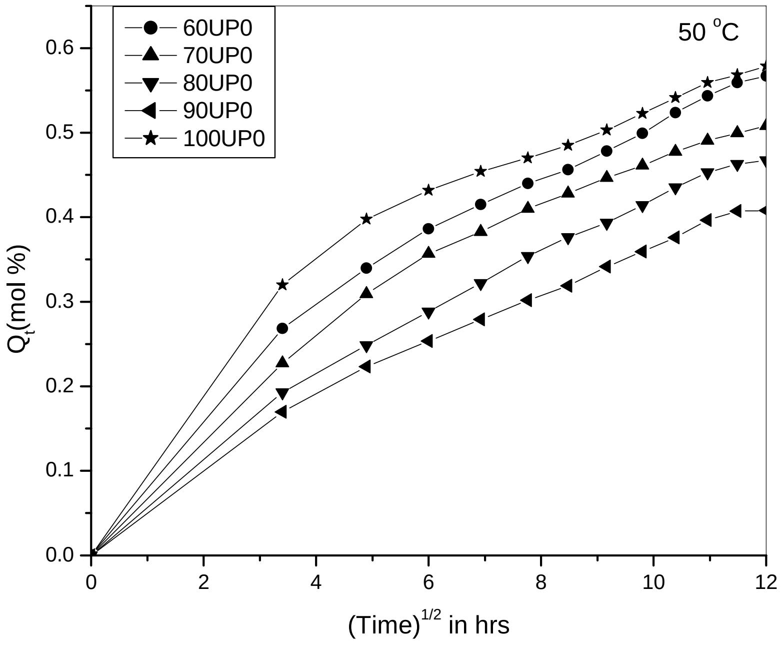


Figure 3: Sorption curve showing mole percent uptake of unsaturated polyester samples with varied acid content @ 50 °C.

The maximum value for solvent uptake is shown by 100UP0 whereas the minimum value is shown by the sample 90UP0. This is due to the fact that the polymer chain shows higher segmental mobility with an increase in temperature, hence accommodating higher amount of the solvent. Figure 4 and Figure 5 shows the sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varied acid content at fixed clay 4 wt % at 20 and 50 ^{o}C respectively. It is noticed from Figure 4 that on addition of nano-clay, the Q_t values for all the samples decreases as compared to neat unsaturated polyester samples. This indicates the enhancement in the barrier properties of the nano-clay filled polymer over the unfilled one. The increase in the barrier properties is due to the incorporation of the nano-clay. The platelet like structure with a high aspect ratio can be expected to improve the resistance towards low molecular weight solvent molecules.

On comparing the Figure 4 and Figure 5 it is justified that with an increase in the temperature the Q_t values goes on decreasing. It is due to fact 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.

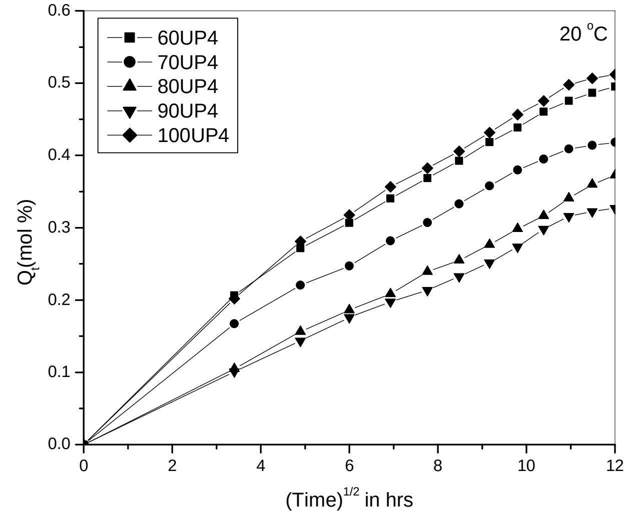


Figure 4: Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varied acid content (fixed clay 4 %) at 20 °C.

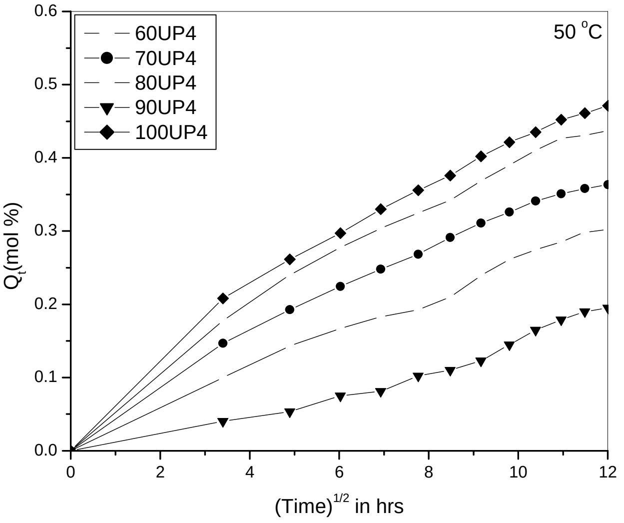
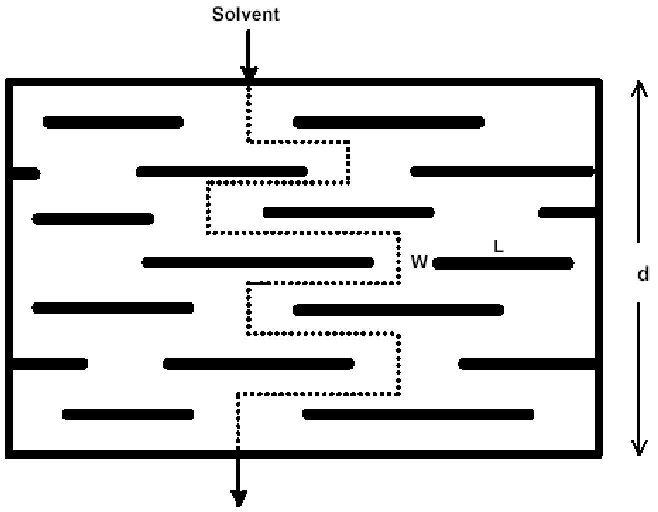


Figure 5: Sorption curve showing mole percent uptake of unsaturated polyester nanocomposite with varied acid content (fixed clay 4 %) at 50 °C

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 composite. (W is the width or thickness and L is the length of the filler platelet. d is the thickness of the polymer matrix).

Therefore, when compared to the parent polymer, a decrease in the diffusion of the solvent in the nanocomposites is observed. Figure 6 and Figure 7 shows the sorption curve showing mole percent uptake of nanocomposite samples 90UP with variation in clay percentage from 0 to 5 % at 20 and 50 °C respectively. From Figure 6 it is observed that in case of clay loading polymeric samples, the maximum and minimum swelling is observed for the samples with 5 wt % and 4 wt % clay content respectively.

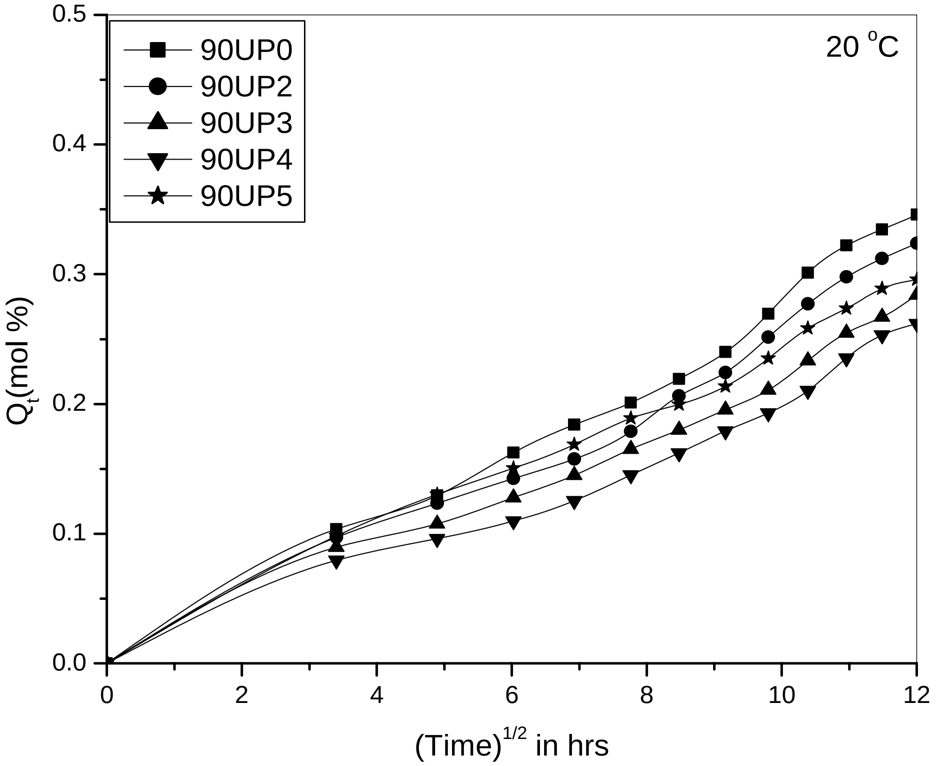


Figure 6: Sorption curve showing mole percent uptake of nanocomposite samples 90UP with variation in clay percentage from 0 to 5 % at 20 °C.

This may be due to the high nano-clay content, resulting in the accumulation of clay at the interface, hence, reducing the barrier properties of the nanocomposite.

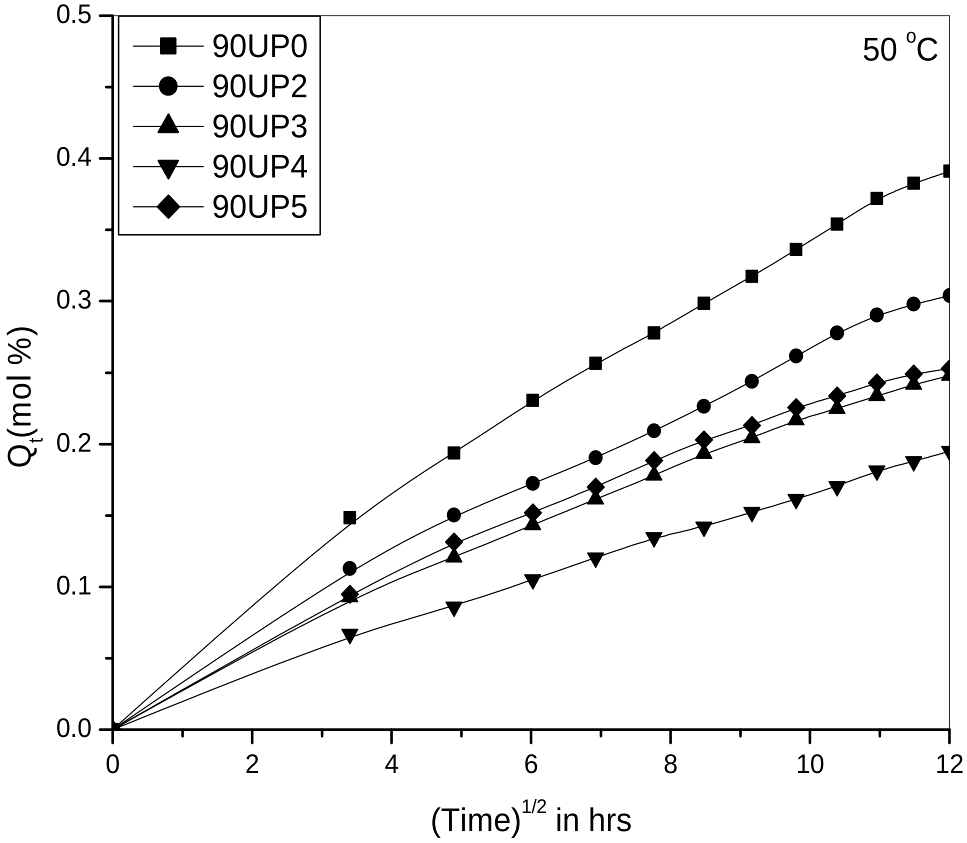


Figure 7: Sorption curve showing mole percent uptake of nanocomposite samples 90UP with variation in clay percentage from 0 to 5 % at 50 °C

This behavior is just like ordinary filler. On comparing Figure 6 and Figure 7 the Qt value decreases with rise in temperature. The value of Q_∞ for 90UP4 is observed to be .262 (mol %) at 20 °C while it is .195 (mol %) at 50 °C.

Diffusion Kinetics

In order to find out the mechanism of swelling, the diffusion data is fitted into an empirical equation (equation 3)[28] derived from equation of transport phenomena (equation 2)[27]

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

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

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 interaction between solvent and polymer and on the structure of polymer. In all the cases, the regression coefficient (r) varies between 0.96 and 0.99. The values of constant 'k' and 'n' obtained from the equation (3) and Q_∞ are represented in Tables 2 and 3. The value of 'n' gives an idea of the mechanism of sorption.[29] 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.[29] If 'n' lies between '0.5' and '1', then it is called anomalous transport.[29] For non-Fickian transport, the diffusion is more rapid than the polymer relaxation rate From Tables 2 and 3, the values of 'n' fall below '0.5', indicating the transport as non Fickian.

Table 2: The values of mole percent uptake at infinite time (Q_∞), n, k and standard deviation (SD) for different samples at 20 and 30 °C.

Temperature (°C)	**Sample ID**	**Q_∞ (mol%)**	**n**	**K**	**SD**
20	60UP0	0.515	0.268	-1.280	0.022
	70UP0	0.458	0.259	-1.158	0.020
	80UP0	0.403	0.244	-1.293	0.021
	90UP0	0.346	0.233	-1.219	0.046
	100UP0	0.545	0.176	-1.836	0.058
	60UP4	0.495	0.229	-1.870	0.071
	70UP4	0.418	0.215	-1.939	0.083
	80UP4	0.355	0.189	-1.402	0.045
	90UP4	0.262	0.163	-2.909	0.054
	100UP4	0.512	0.153	-2.469	0.034
	90UP2	0.324	0.068	-2.958	0.061
	90UP3	0.284	0.051	-2.393	0.043
	90UP5	0.296	0.041	-2.393	0.015
30	60UP0	0.523	0.253	-1.266	0.021
	70UP0	0.478	0.238	-1.167	0.023
	80UP0	0.423	0.274	-1.346	0.029
	90UP0	0.369	0.251	-1.212	0.044
	100UP0	0.553	0.378	-1.867	0.056
	60UP4	0.481	0.374	-1.848	0.069
	70UP4	0.398	0.417	-2.027	0.072
	80UP4	0.325	0.311	-1.506	0.048
	90UP4	0.240	0.437	-2.648	0.049
	100UP4	0.496	0.337	-2.648	0.049
	90UP2	0.310	0.482	-3.315	0.068
	90UP3	0.276	0.343	-2.719	0.040
	90UP5	0.266	0.377	-2.015	0.028

Table 3: The values of mole percent uptake at infinite time (Q_∞), n, k and standard deviation (SD) for different samples at 40 and 50 ^oC.

Temperature (^oC)	Sample ID	Q_∞ (mol%)	n	K	SD
40	60UP0	0.537	0.249	-1.264	0.030
	70UP0	0.498	0.242	-1.172	0.027
	80UP0	0.450	0.290	-1.410	0.031
	90UP0	0.384	0.286	-1.398	0.044
	100UP0	0.563	0.343	-1.689	0.055
	60UP4	0.461	0.389	-1.910	0.058
	70UP4	0.367	0.425	-2.092	0.056
	80UP4	0.305	0.358	-1.736	0.047
	90UP4	0.237	0.477	-2.324	0.047
	100UP4	0.474	0.446	-3.173	0.049
	90UP2	0.314	0.396	-3.378	0.075
	90UP3	0.260	0.494	-2.958	0.042
	90UP5	0.276	0.242	-2.978	0.032
50	60UP0	0.567	0.240	-1.214	0.043
	70UP0	0.508	0.185	-1.395	0.026
	80UP0	0.467	0.332	-1.632	0.038
	90UP0	0.391	0.278	-1.348	0.049
	100UP0	0.570	0.337	-1.686	0.049
	60UP4	0.447	0.429	-2.100	0.058
	70UP4	0.324	0.464	-2.264	0.054
	80UP4	0.245	0.355	-1.710	0.052
	90UP4	0.195	0.403	-1.962	0.045
	100UP4	0.424	0.298	-3.428	0.067
	90UP2	0.304	0.379	-3.799	0.105
	90UP3	0.248	0.234	-3.499	0.235
	90UP5	0.253	0.258	-1.343	0.505

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[30]

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

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[30]

$$S = \frac{\mathrm{M}_\infty}{\mathrm{M}_\mathrm{p}} \text{..............................} \ (5)$$

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[30]

$$P = D \times S \text{..............................} \ (6)$$

Values of these coefficients are reported in Tables 4 and 5. The decrease in the diffusion coefficient with an increase in MA is due to the insertion of unsaturated bond in the polymer chain. This resulted into formation of three dimensional network when cured with styrene, hence shows less affinity to water. It is observed that for unsaturated polyester samples synthesized by varied acid content, 90UP0 sample shows the lowest and the 100UP0 sample shows the highest diffusion coefficient. Except 100UP0, the value of diffusion coefficient for all the samples decreases with an increase in the acid content. It has been reported, dilution of maleic concentration with another diacid is necessary to control crosslink density otherwise phase separation would be occurred in samples that affected the crosslinking density.[31] The diffusion coefficient increases with an increase in the temperature for all virgin polyester samples. Likewise, diffusion coefficient, the sorption coefficient values increase with an increase in the temperature. The increase in sorption is quite small and almost equal to one for all samples at all temperatures. This indicates that there is very less change in the sorption properties with variation in acid contents as well as temperature. The permeability in the samples shows the same trend as that for diffusion coefficient.

For the nanocomposite samples with varied acid content at fixed organically modified nano-clay (4%), the diffusion coefficient decreases with an increase in acid content (Tables 4 and 5). It is observed that a maximum and a minimum diffusion coefficient values are shown by the samples 100UP4, and 90UP4. respectively. The sorption coefficient decreases with an increase in the acid content and increases with an increase in the temperature. The permeability in the samples is observed to show a similar trend as that for the diffusion coefficient. It is reported elsewhere[31] for natural rubber that these coefficients show an increase with a raise in the temperature. This can be explained by the dual mode model for diffusion in the polymers below glass transitions.[33] Hu and Chou worked on swelling and development of porous structure in the ionic poly(acrylonitile-acrylamide- acrylic acid) hydrogels.[34]

Table 4: Diffusion coefficient (D), Sorption coefficient (S) and permeability coefficient (P) in acetic acid medium for different samples at 20 and 30 ^{o}C.

Temperature (^{o}C)	Sample ID	D×10^{-4} (cm^{2}/sec)	S (g/g)	P×10^{-4} (cm^{2}/sec)
20	60UP0	1.573	0.135	0.212
	70UP0	1.521	0.129	0.196
	80UP0	1.470	0.127	0.186
	90UP0	1.435	0.122	0.175
	100UP0	1.582	0.143	0.226
	60UP4	1.517	0.131	0.198
	70UP4	1.478	0.124	0.183
	80UP4	1.402	0.122	0.171
	90UP4	1.380	0.117	0.161
	100UP4	1.572	0.115	0.180
	90UP2	1.421	0.115	0.163
	90UP3	1.402	0.110	0.154
	90UP5	1.432	0.123	0.176
30	60UP0	1.585	0.149	0.236
	70UP0	1.533	0.144	0.220
	80UP0	1.482	0.139	0.205
	90UP0	1.447	0.136	0.196
	100UP0	1.594	0.154	0.245
	60UP4	1.527	0.143	0.218
	70UP4	1.489	0.135	0.201
	80UP4	1.414	0.133	0.188
	90UP4	1.391	0.129	0.179
	100UP4	1.584	0.126	0.199
	90UP2	1.434	0.126	0.180
	90UP3	1.412	0.122	0.172
	90UP5	1.444	0.135	0.194

For the nanocomposite samples with varied nano-clay from 0% to 5% at fixed acid content, the diffusion coefficient decreases with an increase in the nano-clay content up to 4%. The sample 90UP0 shows maximum and 90UP4 shows minimum diffusion coefficient. With an increase in the nano- clay, the decreasing values of the diffusion coefficient are due to the incorporation of the nano-clay that increases the barrier properties. The platelet like structure with a high aspect ratio can be expected to improve the resistance towards low molecular weight solvent molecules. It is expected that a high loading of nano-clay is more effective for the solvent resistance, but the polymer with 5% filler shows high diffusion coefficient.

Table 5: Diffusion coefficient (D), Sorption coefficient (S) and permeability coefficient (P) in acetic acid medium for different samples at 40 and 50 ^{o}C.

Temperature (^{o}C)	Sample ID	D×10^{-4} (cm^2/sec)	S (g/g)	P×10^{-4} (cm^2/sec)
40	60UP0	1.596	0.160	0.255
	70UP0	1.544	0.157	0.242
	80UP0	1.495	0.153	0.228
	90UP0	1.459	0.146	0.213
	100UP0	1.607	0.167	0.268
	60UP4	1.539	0.157	0.241
	70UP4	1.499	0.146	0.218
	80UP4	1.426	0.144	0.205
	90UP4	1.403	0.140	0.196
	100UP4	1.597	0.137	0.218
	90UP2	1.445	0.139	0.200
	90UP3	1.424	0.136	0.193
	90UP5	1.457	0.148	0.215
50	60UP0	1.608	0.175	0.281
	70UP0	1.557	0.168	0.261
	80UP0	1.508	0.165	0.248
	90UP0	1.472	0.160	0.235
	100UP0	1.619	0.179	0.289
	60UP4	1.552	0.169	0.262
	70UP4	1.512	0.160	0.241
	80UP4	1.439	0.156	0.224
	90UP4	1.418	0.153	0.216
	100UP4	1.609	0.150	0.241
	90UP2	1.458	0.151	0.220
	90UP3	1.434	0.147	0.210
	90UP5	1.469	0.159	0.233

This may be due to the high nano-clay contents, resulting in the accumulation of clay at the interface. This behavior is just like ordinary filler. The higher filler contents (5 %) reduce the barrier properties of the nanocomposite. Therefore, the sample shows distortion, instead of swelling after 12 h. An increase in the temperature results in an increase in the diffusion coefficient for all these samples. The sorption coefficient for all these samples shows a decrease with an increase in GPET content up to 50% and 4% nano-clay content. This indicates that the solvent assimilation or the ability to absorb solvent decreases due to the incorporation of nano-filler. This indicates the good compatibility of the nano-clay and polymer matrix. The permeability coefficient shows similar trends as is for diffusion coefficient. A Bar diagram for virgin and nanocomposite polyester samples showing diffusion coefficient values at different temperatures is shown in Figure 8.

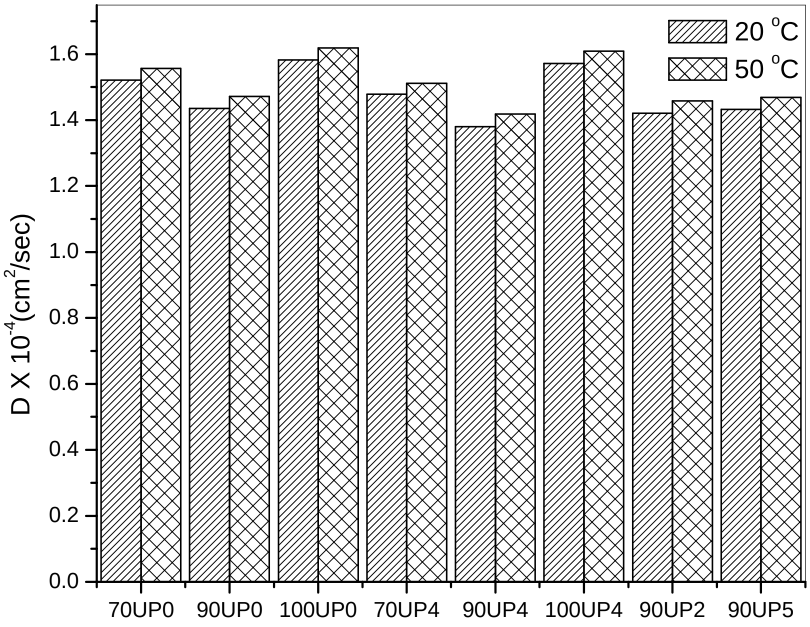


Figure 8: Bar diagram for virgin and nanocomposite polyester samples showing diffusion coefficient values at different temperatures.

It is clearly predicted that the diffusion coefficient increases with rise in temperature. The maximum value is shown for 100UP0 and minimum for the sample 90UP4.

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.[35]

$$\nu = -\frac{\ln(1-V_p)+V_p+\chi V_p^2}{V_1(V_p^{1/3}-0.5V_p)} \quad \text{.........................} \ (7)$$

where V_p is the volume fraction of the polymer in the mixture, χ is the polymer-solvent interaction parameter and V_1 is the molar volume of the solvent. V_p and χ are obtained by the following equations.[35]

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

$$\chi = \chi_H + \chi_S = \frac{V_1(\delta_p - \delta_s)^2}{RT} + 0.34 \quad \text{…...........................} \ (9)$$

Where χ_H and χ_S are the enthalpic and entropic components of χ, $\delta 1$ and $\delta 2$ 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 molecular weight between two crosslinks ($\overline{M}c$) is also calculated for all the samples by the following equation.[32]

$$\overline{M_c} = \frac{1}{2\nu} \qquad (10)$$

The value of the crosslink density is reported in Table 6. The crosslink density is in good agreement with the sorption kinetics. It is evident from the Table 6 that for virgin polyester samples the crosslink density increases with an increase in the unsaturated acid content except 100UP0. It is maximum for 90UP0 and minimum for 60UP0. It is due to higher unsaturation sites in prepolymer chain that is prone to crosslinking thus increases crosslink density.

Table 6: Volume fraction of polymer (V_p), crosslink density (ν) and molecular weight between two crosslinks ($\overline{M}_c$) for different unsaturated polyester nanocomposites.

Sample ID	$\mathbf{V_p}$	$\nu \times 10^5$ **(mol/cm^3)**	$M_c \times 10^{-5}$ **(mol/cm^3)**
60UP0	0.133	2.98	0.167
70UP0	0.163	3.12	0.160
80UP0	0.180	3.34	0.149
90UP0	0.185	3.52	0.142
100UP0	0.236	2.86	0.174
60UP4	0.241	4.02	0.124
70UP4	0.252	4.57	0.109
80UP4	0.239	4.76	0.105
90UP4	0.241	5.72	0.087
100UP4	0.231	3.70	0.135
90UP2	0.242	4.76	0.105
90UP3	0.245	5.12	0.097
90UP5	0.212	4.50	0.111

The variation in clay concentration also affects the crosslink density. With the 4 % clay loading crosslink density have maximum value for all samples. For all of the polymeric samples, the maximum value obtained by sample 90UP4, while it is minimum for the sample 100UP. The increase in the crosslink density with an increase in the unsaturated acid content and nano-filler clearly shows the increase in the barrier properties and explains the cause of increase in the sorption resistance.

Conclusion

Kinetics of swelling and sorption behavior of unsaturated polyester nanocomposite synthesized by in-situ method is studied in acetic acid medium through equilibrium swelling method at different temperatures. The values of ‘n’ in solvent transport equation are found to be below ‘0.5’, showing the non-Fickian or pseudo-Fickian transport in the polymer. For all polymeric samples Q_t value increases with time. The value of Q_t increases for virgin polyester samples, while decreases for nano filled samples with rise in temperature. The dependence of diffusion coefficient on composition and temperature has been studied for all polymeric samples. The diffusion coefficient in unsaturated polyester samples decreases with an increase in unsaturated acid content. There is sudden rise is observed in diffusion coefficient for the 100UP0 sample. The nanocomposite samples show low diffusion coefficient than corresponding pristine polymer and it decreases with an increasing in nanofiller up to 4 wt %. The diffusion coefficient, sorption coefficient and permeation coefficient increase with an increase in temperature for all the samples. For all polymeric samples the minimum D value is found to be 1.380×10^{-4} cm^2/sec and maximum be 1.573×10^{-4} for samples 90UP4 and 60UP0 respectively. The crosslink density for neat polymer with varied unsaturated acid content ranges from 2.98 to 3.52×10^5 mol/cm^3. For the nanocomposite samples it ranges from 3.70 to 5.72×10^5 mol/cm^3.

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