

Transport behavior of *n*-alkane penetrants into castor oil based polyurethane–polyester nonwoven fabric composites

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Abstract

Castor oil based polyurethane (PU)–polyester nonwoven fabric composites were fabricated by impregnating the polyester nonwoven fabric in a composition containing castor oil and diisocyanate. Composites were fabricated with two different isocyanates such as toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI). Transport behavior of *n*-alkane penetrants (pentane, hexane and heptane) into both PUs and PU–polyester nonwoven fabric composites were studied. Sorption studies were carried out at different temperatures. From the sorption results, the diffusion (*D*) and permeation (*P*) coefficients of penetrants have been calculated. Significant increase in the diffusion and permeation coefficients was observed with increase in the temperature of sorption experiments. Drastical reduction in diffusion and permeation coefficients was noticed in the composites compared to neat PUs. Attempts were made to estimate the empirical parameters like *n*, which suggests the mode of transport and *K* is a constant depends on the structural characteristics of the composite in addition to its interaction with penetrants. The temperature dependence of the transport coefficients has been used to estimate the activation energy parameter for diffusion (E_D) and permeation (E_P) processes from Arrhenius plots. Furthermore, the sorption results have been interpreted in terms of the thermodynamic parameters such as enthalpy (ΔH) and entropy (ΔS).

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1. Introduction

Unlike metals, the mechanical properties of fibre reinforced polymer composites (FRPs) have been observed to be very sensitive to the presence of common organic solvent molecules, which can easily diffuse into the polymer matrix altering the strength of the composites. In some specific applications, reinforced composites in service are subjected to the presence of various organic solvents at different temperatures and hence, this aspect of the composites has received considerable attention. Low molecular weight organic hydrocarbons released in waste landfills are known to contaminate ground water, soil, and air, posing an immediate threat to human health and hygiene [1]. In view of this, it is important to understand their interaction of polymers with organic liquids, which is of great environmental concern. As the use of polymer composites as liners, gaskets and

storage tanks [2] for hazardous liquids is increasing, it is important to understand the diffusion behavior of the composites with organic liquids. Diffusion of low molecular weight species into polymer matrix is a complex theoretical problem with diverse application. Several experimental techniques have been used to study the solvent transport properties of a polymer matrix [3–6]. Of these, simple gravimetric method has been shown by many researchers to yield reliable data [7–10].

Nonwoven fabric is one of the popularly used materials in the fabrication of composites for many applications since they possess a good blend of strength, light weight and flexibility compared to conventional materials [11]. As the nonwoven fabric alone does not have the load carrying ability [12], the use of polymeric binders is very essential for more number of various applications. Hence the authors have selected the PU as the binder for the present research work. Several researchers have reported on the binders for the fabrication of nonwoven fabric composites [13–16]. Epstein and Shishoo [17,18] reported on the fabrication of nonwoven fabric reinforced elastomers composites using PU.

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PU elastomers have a wide range of industrial applications, and they are well known for their mechanical properties. Several researchers have developed PU materials using renewable resources like castor oil [19–21]. In view of the importance of PU and its composites as a barrier material in several engineering areas, it is important to know its transport behavior in common organic solvents. Many researchers have studied the transport behavior of different common organic solvents into PU. Kendagannaswamy and Siddaramaiah [19] studied the transport behavior of *n*-alkane into castor oil-based chain extended polyurethanes (PUs). Kumar and Siddaramaiah [22] studied the sorption, desorption and diffusion of aromatic probe molecules into semi-interpenetrating polymer network (SIPN) of polyurethane/polymethyl methacrylate (PU/PMMA). Ajithkumar et al. [23] reported the anomalous behavior of sorption and diffusion of organic solvents through polyurethane and unsaturated polyester based interpenetrating polymer networks. Aminabhavi et al. have carried out extensive studies on sorption and diffusion behavior of organic probe molecules through various polymeric systems [24,25]. A detailed literature survey revealed that, the transport behavior of *n*-alkane penetrants into castor oil based polyurethane–polyester nonwoven fabric composites has not been studied yet. In the previous communication [26] authors have reported on the mechanical properties, chemical resistance and water sorption behavior of TDI and HMDI based PUs and their corresponding composites with polyester nonwoven fabric. In this research article the authors have selected to study the transport behavior of *n*-alkane penetrants into both un-reinforced PUs and reinforced PU–polyester nonwoven fabric.

2. Experimental

2.1. Materials

Needle punched polyester nonwoven fabric (400 g/m²) having density of 200 kg/m³ and burst strength of 1.8 MPa was procured from local supplier in India. The fibre used to make the fabric has 3 denier × 64 mm length. Castor oil (CO) was procured from the local market. Its average molecular weight (M_n) is 930 and hydroxyl group per molecule is 2.24. Toluene-2,4-diisocyanate (TDI), hexamethylene diisocyanate (HMDI) and dibutyl tin dilaurate (DBTL) were obtained from Sigma (USA), and were used as received. The organic solvent, methyl ethyl ketone (MEK), pentane, hexane and heptane are of AR grade, distilled before use. Some typical properties of the solvents are given in Table 1.

Table 1
Some physical properties of solvents used as penetrants at 25 °C

Penetrants	Molecular volume (cm ³ /mol)	Density (g/cm ³)	Solubility parameter (cal cm ⁻³) ^{1/2}
<i>n</i> -Pentane	115.2	0.625	7.10
<i>n</i> -Hexane	131.6	0.660	7.27
<i>n</i> -Heptane	147.5	0.683	7.24

2.2. Fabrication of composites

Castor oil (0.001 mol) was dissolved in 50 mL of MEK in a 250-mL beaker. To this, diisocyanate (0.0022 mol) was added followed by two to three drops of DBTL as a catalyst. The reactants were stirred continuously until the homogeneous solution was obtained. This mixture was poured into a stainless steel tray coated with silicone releasing agent. Polyester nonwoven fabric having the dimension of 150 mm length, 120 mm width and 2.0 mm thickness was impregnated in the reactant mixture containing castor oil and diisocyanate. The dipped fabric is squeezed in a two-roll squeezer to obtain the pickup ratio of 1:3.5 (polyester nonwoven fabric to the PU composition). The calculation of PU pickup by the fabric was made using simple gravimetric method where the MEK was considered as an evaporating medium. The maintained solid content of the impregnating composition was 50%. A portion of the PU reactant mixture was poured into the glass molds coated with silicone releasing agent to cast the neat PU membranes. The reaction mixture was allowed to polymerize for 24 h at room temperature and another 24 h at 80 °C.

3. Techniques

3.1. Sorption test

Un-reinforced PU membranes and reinforced PU–polyester nonwoven fabric composites having the thickness range of 0.204–0.249 and 0.245–0.293 cm, respectively, were cut circularly (diameter = 1.5 cm) using a sharp-edged steel die. Sorption experiments were performed at different temperatures viz., 25, 40 and 60 °C by immersing the specimens in distilled water in the metal-capped bottles maintained at the desired constant temperature (±0.5 °C) in a thermostatically controlled oven. At specified intervals of time, specimens were removed from the containers, penetrant adhered on to the surfaces were removed using soft filter paper and weighed immediately using analytical balance having ±0.1 mg accuracy. The weighing continued until the specimens attain the equilibrium values.

The percentage weight gain, Q_t of the immersed composite specimen was calculated as follows:

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

where M_i is the initial weight of the polymer specimens and M_t is the weight of the specimen at time t .

The penetration velocity (v) of solvents in each specimen was determined by weight gain method as described elsewhere [19]. The penetration velocity was calculated from slope of initial portion of the penetrant uptake curve by using the equation:

$$\text{penetration velocity } (v) = \frac{1}{2\delta A^*} \frac{dwg}{dt} \quad (2)$$

where dwg/dt denotes the slope of the percentage weight gain versus time curve, δ the density; of solvent at 25 °C. A^* is the area of the one face of the specimen and factor 2 accounts for the fact that penetration takes place thorough both sides.

The pore size of both un-reinforced PU and reinforced PU–polyester nonwoven fabric composites were determined as per IS: 6071–6086.

4. Results and discussion

Sorption of *n*-alkane penetrants such as *n*-pentane, *n*-hexane and *n*-heptane were studied for TDI and HMDI based PUs and their corresponding composites with polyester nonwoven fabric. Sorption curves are expressed as percent penetrant uptake (Q_t) versus square root of time. Typical sorption curves of TDI

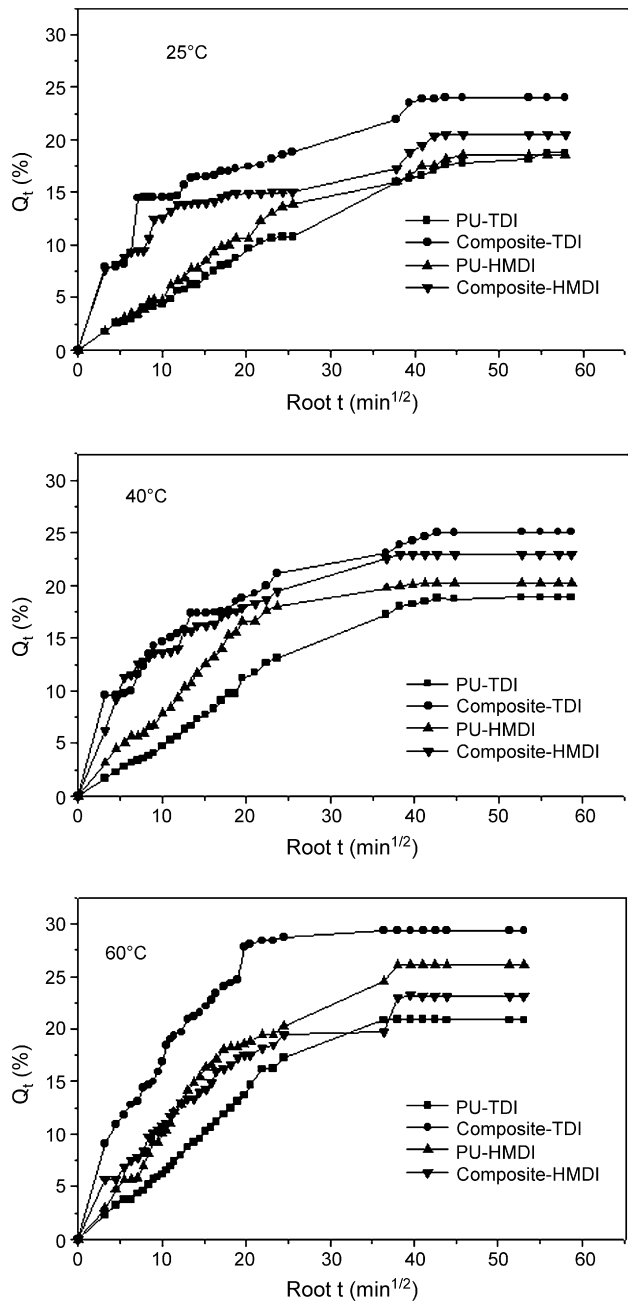


Fig. 1. Percentage mass uptake (Q_t) vs. square root of time for TDI and HMDI based PUs and PU–polyester nonwoven fabric composite with hexane penetrant at different temperatures.

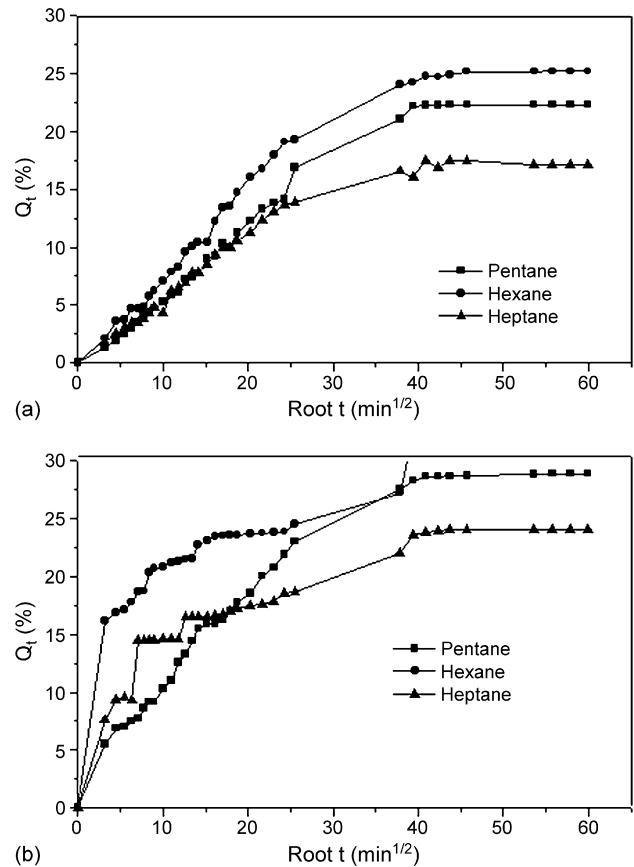


Fig. 2. Percentage mass uptake (Q_t) vs. square root of time for (a) HMDI based PU and (b) HMDI based PU–polyester nonwoven fabric composite with different alkane penetrants at 25 °C.

and HMDI based PUs and their corresponding composites in hexane penetrant at 25, 40 and 60 °C are shown in Fig. 1. The sorption curves of HMDI based PU and its composite in all penetrants is shown in Fig. 2. As shown in Fig. 1, both TDI and HMDI based PU–polyester nonwoven fabric composites showed higher mass uptake compared to their corresponding PUs. A similar behavior was observed in pentane and heptane penetrants. The penetrant mass uptake is high for reinforced PU composite specimens compared to un-reinforced PUs. This may be due to the presence of higher void content in composites compared to PUs. From the figure, it can also be observed that, the initial portion of the sorption curves are linear after which the mechanism changes to non-linear behavior. According to Southern and Thomas [27], when a polymer interacts with solvents, the surface of the polymer composite swells immediately, but the swelling will not take place in the underlying unswollen material. Thus, a two dimensional compressive stress exerts on the surface. The swelling stresses are either relaxed or dissipated by further swelling and rearrangement of the segments. Diffusion of low molecular weight probe molecules found to lead a typical phenomena of composite swelling and physical relaxation. The penetration velocity for different *n*-alkane penetrants is given in Table 2. The penetration velocity in pentane was high compared to hexane and heptane. This can be attributed to the low molecular volume of pentane [28,29]. The calculated

Table 2

Penetration velocity (v) of n -alkane penetrants for TDI and HMDI based un-reinforced and reinforced PU–polyester nonwoven fabric membranes at different temperatures

Penetrant	Temperature (°C)	Samples (penetration velocity, v ($\times 10^2$ cm/s))			
		TDI-PU	TDI-composite	HMDI-PU	HMDI-composite
n -Pentane	25	2.7	6.2	3.7	3.9
n -Hexane	25	1.3	2.4	2.4	2.5
	40	2.4	2.7	2.3	2.9
	60	2.6	3.0	2.7	3.5
n -Heptane	25	1.6	2.3	2.4	2.4
	40	1.8	2.7	2.9	2.9
	60	1.9	2.7	3.1	3.7

penetration velocity of n -alkane was high in PU–polyester nonwoven composites compared to PUs. This may be because of the presence of higher sorption incase of reinforced PU–polyester nonwoven fabric composites compared to un-reinforced PUs.

Regarding the effect of temperature on sorption, it is found that for both reinforced and un-reinforced PU specimens, the equilibrium sorption increased with increase in the temperature. This effect is shown typically in Fig. 3 for HMDI based PU and its composite in heptane. This effect follows the conventional theory that, at higher temperatures an increase in free volume occurs due to increased movement of the chain segments of the elastomers [30–31].

For Fickian behavior, the plots of Q_t versus $t^{1/2}$ should increase linearly up to about 50% sorption. Deviations from the Fickian sorption are associated with the time taken by the polymer segments to respond to swelling stresses and rearrange themselves to accommodate the solvent molecules [32]. The non-Fickian diffusion involves the tension between the two different materials (polyester fibre and PU matrix) in the composite. The non-sigmoidal behavior of sorption curves as shown in Figs. 1–3 indicates for the departure from the Fickian mode. This can be further confirmed from the analysis of sorption data.

To investigate the type of diffusion mechanism, an attempt was made to estimate the values of ‘ n ’ and ‘ K ’ by the following relation:

$$\ln \left(\frac{M_t}{M_\infty} \right) = \ln K + n \ln t \quad (3)$$

where K and n are empirical parameters, M_t and M_∞ are mass uptake values at time ‘ t ’ and at equilibrium. The magnitude of n decides the transport mode, for instance, a value of $n=0.5$ suggests the Fickian mode and for $n=1$, non-Fickian diffusion mode. The value of n ranging from 0.5 to 1 suggests the presence of anomalous transport mechanism.

In order to determine the K and n , plots of $\ln(M_t/M_\infty)$ versus $\ln t$ were plotted (Fig. 4). The calculated values for the empirical parameters n and K are given in Table 3. The average uncertainty in the estimation of n and K are around ± 0.009 and ± 0.006 , respectively. The increase of K with increase in temperature reveals that the interaction of probe molecules with the samples is high. The low value of n clearly indicates that the mechanism of molecular transport of alkane penetrants is non-Fickian mode.

The sorption values (S) are computed by the following relation:

$$S = \frac{M_\infty}{M_i} \quad (4)$$

where M_∞ and M_i represent the mass uptake values at equilibrium and initial polymer membrane weight, respectively.

The diffusion coefficient D of the penetrant molecules was calculated from the following equation:

$$D = \pi \left(\frac{h\theta}{4M_\infty} \right)^2 \quad (5)$$

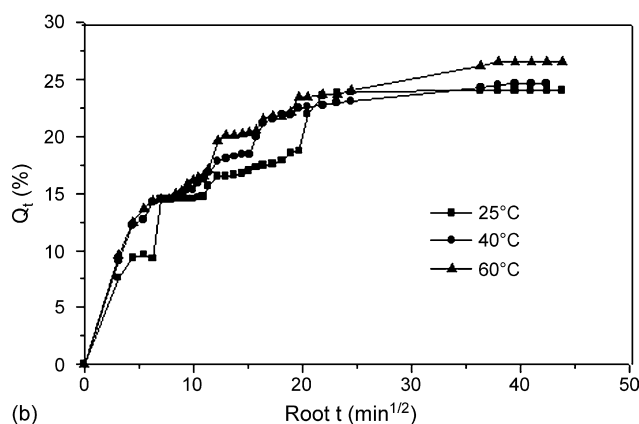
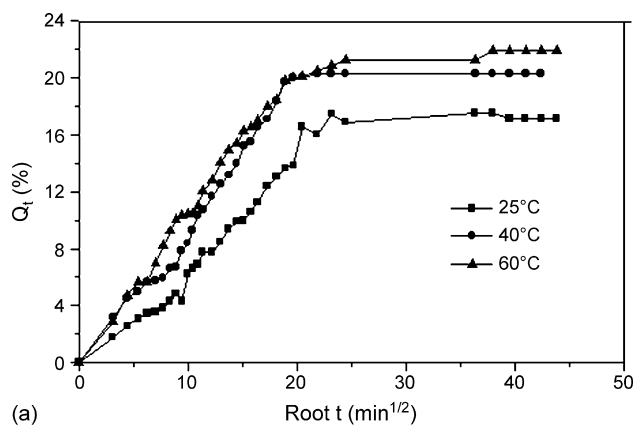


Fig. 3. Percentage mass uptake (Q_t) vs. square root of time for (a) HMDI based PU and (b) HMDI based PU–polyester nonwoven fabric composite with heptane penetrant at different temperatures.

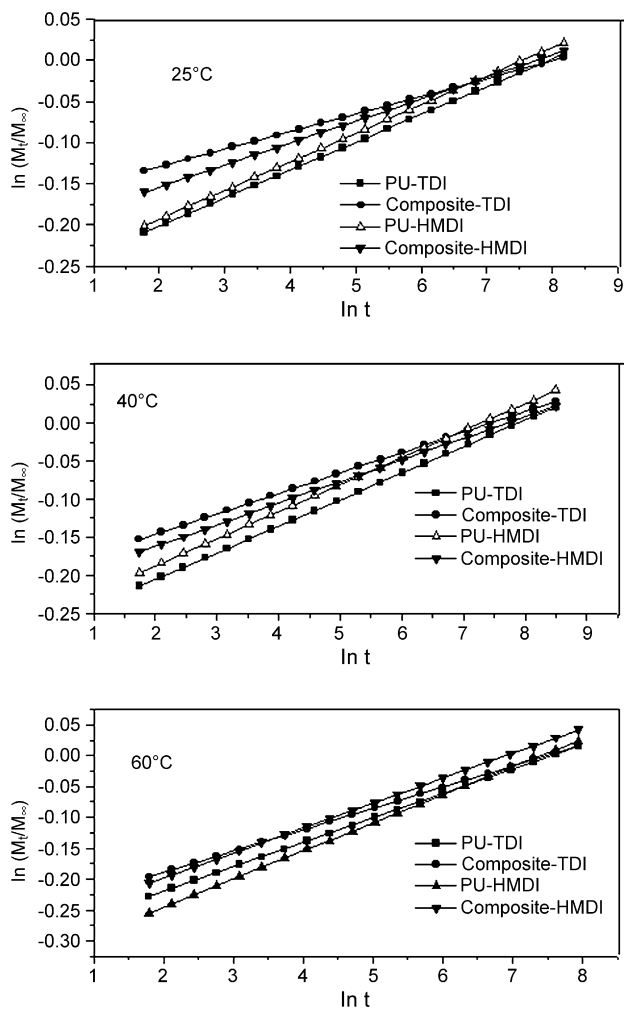


Fig. 4. The plots of $\ln M_t/M_\infty$ vs. $\ln t$ of time for TDI and HMDI based PUs and PU–polyester nonwoven fabric composite with hexane penetrants at different temperatures.

where θ is the slope of the linear portion of the sorption curves, h the initial thickness of the sample and M_∞ is the mass uptake values at equilibrium.

The transport of small molecules through polymers generally occurs through a solution diffusion mechanism, i.e., the solvent molecules are first sorbed by the polymer followed by diffusion through the polymer membrane. The net diffusion through polymer depends on the difference in the amount of probe molecules between the two successive layers. Hence, the permeability [33]:

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

where D and S are diffusion and sorption coefficients, respectively.

The calculated sorption (S), diffusion (D) and permeation (P) coefficients under working temperatures are given in Table 4. The sorption coefficients (S) of both TDI and HMDI based reinforced PU–polyester nonwoven fabric composites exhibited higher values compared to their corresponding un-reinforced PUs. Sorption values increased with increase in the temperature. The observed sorption value was relatively low in HMDI based PU–polyester nonwoven fabric composite compared to

Table 3

Values of n and K for TDI and HMDI based PUs and their corresponding composites with polyester nonwoven fabric at different temperatures

Penetrant	Temperature (°C)	Samples	n	K (g/g min)
<i>n</i> -Pentane	25	TDI-PU	0.071	0.546
		TDI-composite	0.033	0.771
		HMDI-PU	0.025	0.791
		HMDI-composite	0.044	0.712
<i>n</i> -Hexane	25	TDI-PU	0.039	0.532
		TDI-composite	0.022	0.701
		HMDI-PU	0.046	0.697
		HMDI-composite	0.022	0.781
	40	TDI-PU	0.047	0.701
		TDI-composite	0.035	0.750
		HMDI-PU	0.047	0.706
		HMDI-composite	0.0349	0.810
60	TDI-PU	0.077	0.731	
	TDI-composite	0.041	0.830	
	HMDI-PU	0.048	0.710	
	HMDI-composite	0.034	0.821	
<i>n</i> -Heptane	25	TDI-PU	0.032	0.761
		TDI-composite	0.019	0.651
		HMDI-PU	0.032	0.771
		HMDI-composite	0.026	0.801
	40	TDI-PU	0.034	0.767
		TDI-composite	0.020	0.841
		HMDI-PU	0.035	0.777
		HMDI-composite	0.026	0.817
	60	TDI-PU	0.033	0.768
		TDI-composite	0.050	0.853
		HMDI-PU	0.039	0.785
		HMDI-composite	0.030	0.834

TDI based composite. TDI and HMDI based PUs showed higher D values compared to their corresponding composites. The diffusion coefficient values (D) for TDI and HMDI based PUs and its corresponding composites follow the sequence: pentane > hexane > heptane, at all temperature. This can be attributed to the increase in molecular volume of the penetrants (Table 1). As it is well known, the diffusion process is a thermally activated process, an increase in temperature was found to increase the diffusion coefficient of the penetrant molecule. The increase in diffusion with increase in the temperature can be attributed to the development of micro cracks/voids on the surface and in the bulk of the materials [34]. In all cases, it is found that diffusivity decreases with increase in chain length of *n*-alkanes. This inverse dependence of D either on molar volume or number of carbon atoms of *n*-alkanes proves the conjecture that larger molecules in a related series of liquids occupy free volumes, leading to hindered diffusivities through polymer matrix. Kendagannaswamy and Siddaramaiah [19] noticed a similar observation in chain extended PUs. The permeation (P), which is the net effect of sorption and diffusion, followed a similar trend as D .

Diffusivities and permeation are dependent on the temperature and their values increases with temperature. The temperature dependence of transport coefficients has been used

Table 4

Diffusion (D), sorption (S) and permeation (P) coefficients of TDI and HMDI based PUs and PU–polyester nonwoven fabric composites in alkanes at different temperatures

Samples	Temperature (°C)	Pentane			Hexane			Heptane		
		D ($\times 10^6$ cm ² /s)	S ($\times 10^2$ g/g)	P ($\times 10^6$ cm ² /s)	D ($\times 10^6$ cm ² /s)	S ($\times 10^2$ g/g)	P ($\times 10^6$ cm ² /s)	D ($\times 10^6$ cm ² /s)	S ($\times 10^2$ g/g)	P ($\times 10^5$ cm ² /s)
PU-TDI	25	14.3	129	18.4	1.50	120	1.8	1.31	117	1.5
	40	–	–	–	1.90	123	2.4	1.92	120	2.3
	60	–	–	–	3.20	123	3.9	2.91	120	3.5
Composite-TDI	25	16.19	144	23.3	5.41	124	6.7	4.71	127	6.0
	40	–	–	–	11.0	124	13.6	9.70	127	11.4
	60	–	–	–	15.0	129	19.4	11.0	130	14.3
PU-HMDI	25	7.10	122	8.6	2.90	119	3.5	2.84	117	3.3
	40	–	–	–	3.90	119	4.7	3.52	119	4.2
	60	–	–	–	5.01	121	6.3	4.91	119	5.84
Composite-HMDI	25	13.0	129	16.8	3.60	120	4.3	3.20	124	3.96
	40	–	–	–	5.90	120	7.0	5.42	124	6.72
	60	–	–	–	6.50	126	8.1	6.33	127	8.03

to compute the values of activation energy for diffusion (E_D) and permeation process (E_P), which is estimated from the Arrhenius relation:

$$X = X_0 \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

where X_0 is pre-exponential factor, R the molar gas constant, T the absolute temperature, X the coefficient (D for diffusion process and P for permeation process) and E_a is the energy of activation. The Arrhenius plots of $\ln D$ and $\ln P$ versus $1/T$ are shown in Figs. 5 and 6, respectively. The calculated values of E_D and E_P are given in the Table 5. Higher E_D and E_P values were noticed for TDI and HMDI based un-reinforced PUs compared to their corresponding reinforced composites with polyester non-

woven fabric. This can be attributed to high degree of cohesive energy density in PUs compared to its composites. As the composites are heterogeneous (PUs are homogeneous), the interface between the PU and nonwoven fabric increases the sorption and hence the lower activation energy is sufficient for the diffusion process in case of composites. The E_D and E_P values of HMDI

Table 5

Values of activation energy for diffusion (E_D , kJ/mol), permeation (E_P , kJ/mol), enthalpy of sorption (ΔH , kJ/mol) and entropy of sorption (ΔS , J/mol) for TDI and HMDI based PUs and their corresponding composites with polyester nonwoven fabric

Samples	Parameters	Penetrants	
		<i>n</i> -Hexane	<i>n</i> -Heptane
PU-TDI	E_D	23.10	18.21
	E_P	24.10	19.02
	ΔH	0.91	0.90
	$-\Delta S$	78.50	79.3
Composite-TDI	E_D	10.92	13.72
	E_P	13.09	15.92
	ΔH	2.18	1.33
	$-\Delta S$	76.8	75.9
PU-HMDI	E_D	16.92	14.72
	E_P	18.11	16.10
	ΔH	1.82	1.33
	$-\Delta S$	75.40	77.70
Composite-HMDI	E_D	11.21	14.76
	E_P	13.12	16.01
	ΔH	1.30	1.30
	$-\Delta S$	76.90	77.30

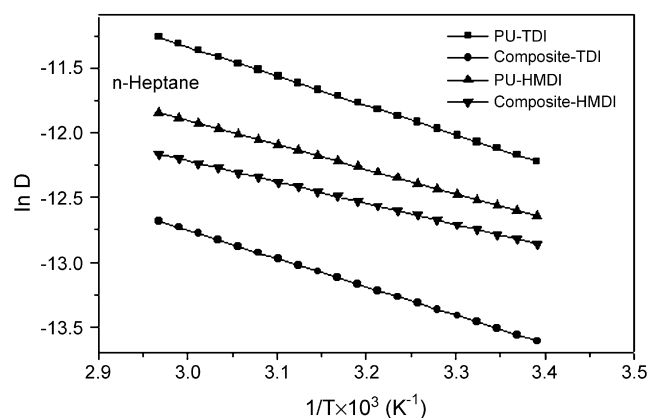
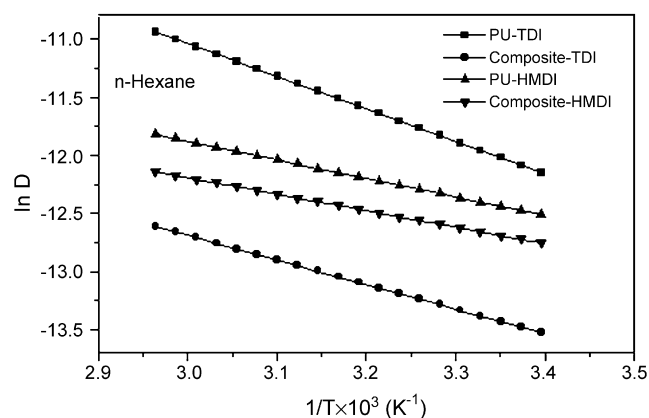


Fig. 5. The plot of $\ln D$ vs. $1/T$ for TDI and HMDI based un-reinforced PUs and their corresponding polyester nonwoven fabric reinforced composites.

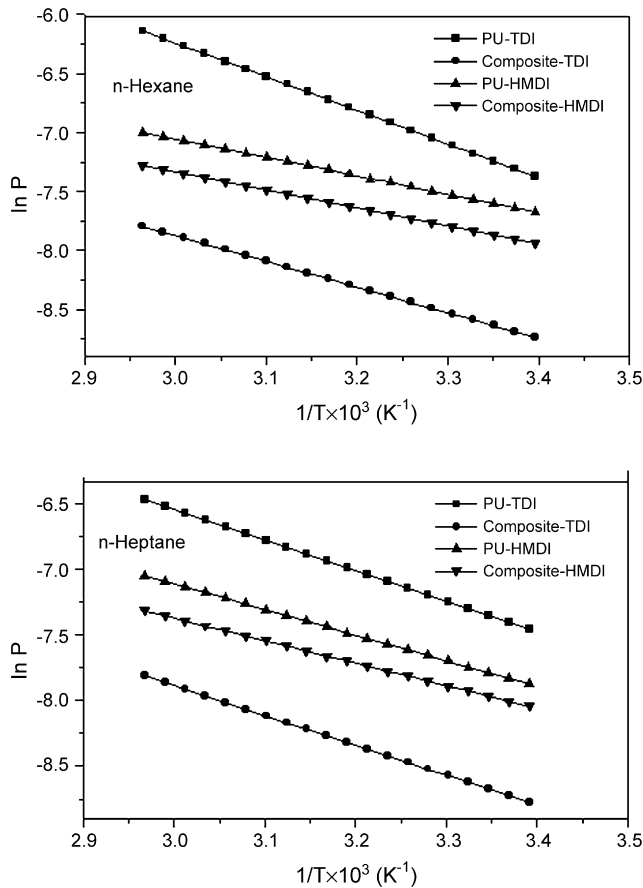


Fig. 6. The plot of $\ln P$ vs. $1/T$ for TDI and HMDI based PUs and its corresponding composites with polyester nonwoven fabric.

based composite is high compared to TDI based composite. This can be attributed to strong interfacial bonding of HMDI based PU with polyester nonwoven fabric [26]. As a result of strong interfacial bonding, the obtained void content was relatively low in HMDI based composite (16%) compared to TDI based composite (18%) [26] and this may be the reason for slightly higher activation energy in HMDI based composite. The effect of pore size on E_D and E_P values are shown in Fig. 7. From the figure, it

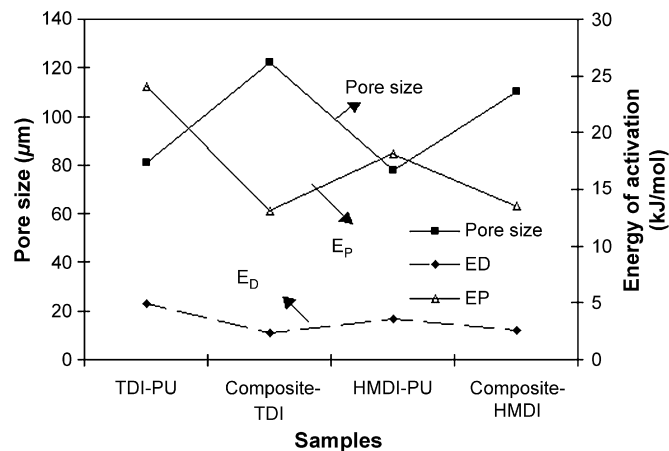


Fig. 7. Effect of pore size on the activation energy of un-reinforced PU and reinforced PU–polyester nonwoven fabric composites.

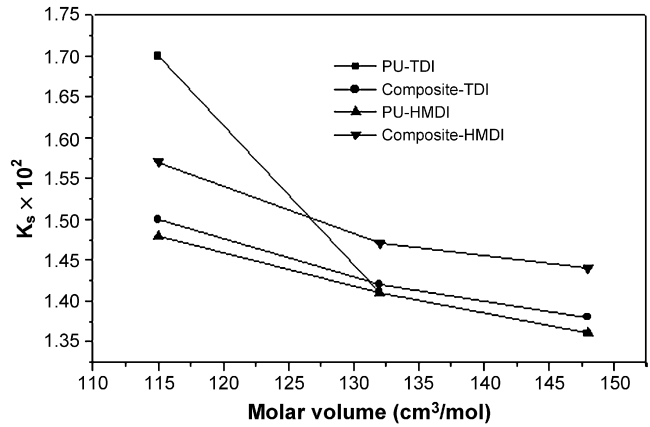


Fig. 8. Variation of K_S with molar volume for TDI and HMDI based PUs and their corresponding composites with polyester nonwoven fabric.

can be observed that HMDI based composite has low pore size and high E_D and E_P values compared to TDI based composite. This may be due to the fact that, the composites with lower pore size require relatively high energy for the process of diffusion and permeation. It is also observed that $E_P > E_D$ for both reinforced and un-reinforced PU specimens in all penetrants. This can also be explained on the fact that, heat of sorption is a composite parameter, which involves contribution from Henry's law mode, with the endothermic reaction contributions to Langmuir's (hole filling) type sorption giving exothermic heats of sorption.

Attempts have been made to calculate the equilibrium sorption constants, K_S from consideration on the equilibrium process occurring in the liquid phase at constant temperature and pressure.

$$K_S = \frac{\text{number of moles of penetrant sorbed}}{\text{unit mass of the polymer}} \quad (8)$$

The variation in K_S and D values with molar volume of *n*-alkane penetrants are shown in Figs. 8 and 9. A systematic decrease in K_S and D values with increase in molecular volume of penetrants suggests an inverse dependence of K_S or D on molecular volume of probe molecules. This may be more logical as larger molecules tend to occupy more free volume in the amorphous regions of PU chains than smaller molecules. Kenda-

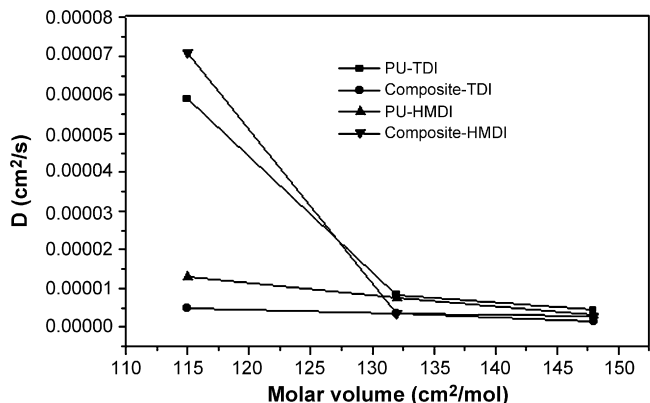


Fig. 9. Dependence of diffusivity (D) on molar volume of penetrants.

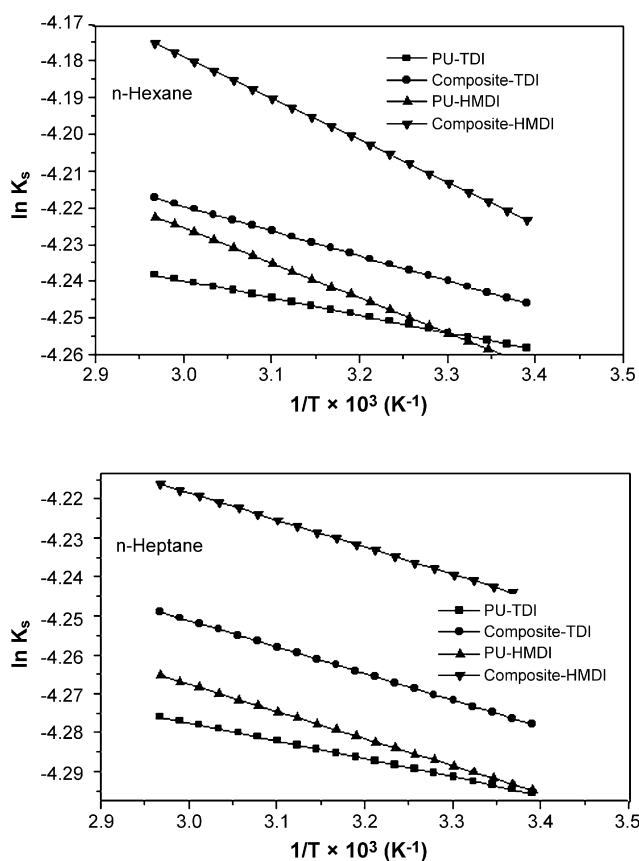


Fig. 10. The plot of $\ln K_S$ vs. $1/T$ for TDI and HMDI based PUs and its corresponding composites with polyester nonwoven fabric.

gannaswamy and Siddaramaiah [35] made a similar observation for diol chain extended PU membranes in chlorinated aliphatic hydrocarbon penetrants.

The temperature dependent equilibrium sorption constant (K_S) values can be fitted to the vant Hoff's relation to estimate the enthalpy (i.e., heat of sorption) ΔH and standard entropy, ΔS of the sorption process:

$$\ln K_S = \left[\left(\frac{\Delta S}{2.303R} \right) - \left(\frac{\Delta H}{2.303R} \right) \left(\frac{1}{T} \right) \right] \quad (9)$$

ΔH and ΔS were calculated from the slope and intercepts, respectively, by the vant Hoff's plot (Fig. 10). The estimated ΔH and ΔS values are given in the Table 5. Low values of ΔH for neat PU membranes compared to composites with polyester nonwoven fabric suggests that there exists a mild interaction of the penetrant with the polymer matrix giving a high endothermic heat of sorption. For all liquids, the values of ΔH were positive suggesting that the sorption is an endothermic process and it is dominated by Henry's law mode, i.e., sorption proceeds through the creation of new sites or pores in the polymer. It is also noted that the HMDI based composite has low ΔH value compared to TDI based composite. Since $P = DS$, one may also obtain ΔH from the difference [36]:

$$\Delta H = E_P - E_D \quad (10)$$

It is interesting to note that the ΔH estimated from Eqs. (8) and (9) are almost same. The calculated ΔS values are negative for all the systems. This suggests that the solvent molecules are retained in the sorbed state.

5. Conclusions

The diffusion coefficient values of *n*-alkane penetrants into reinforced TDI and HMDI based PU–polyester nonwoven fabric composites are higher compared to un-reinforced PUs. The diffusion (D) and permeation (P) coefficients obtained were found to decrease with increase in molar volume of the penetrants. The D and P values of HMDI based composite is relatively low compared to TDI based composite. The increase in temperature has increased the D , P and S values. The lower value of ' n ', which is less than 0.5, clearly revealed that the mechanism of transport of *n*-alkanes into both reinforced and un-reinforced PUs deviates from the Fickian mode. The increased K -values with increase in the temperature shows the high interaction of alkane penetrants with the PUs and their composites. E_D and E_P values found to be high for TDI and HMDI based PUs compared to their corresponding polyester nonwoven fabric composites. K_S and D values decreased with increase in molar volume of penetrant suggest an inverse dependence of K_S or D on molar volume of probe molecules. The specimens having lower pore size and void content showed higher activation energy. For all liquids, the values of ΔH were positive suggesting that sorption is an endothermic process and it is dominated by Henry's law mode. The negative values of ΔS suggest that the structure of alkane penetrant molecules is retained even in the sorbed state.

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