Chapter 5

Effect of chain length and crosslink density on polyurethanes

5.1 PREVIEW:

In this chapter we studied sorption and diffusion behavior of some polyurethane systems by swelling method. The effect of chain length of polyethylene glycol and cross link density on sorption and diffusion of solvent through polyurethane were studied. The molecular weight between two crosslink points was calculated using well known Flory Rehner equations and hence the number of chains per unit volume as well as degree of crosslinking in all polyurethane in the study were determined. Also the stress/strain properties of some of the polyurethanes were studied by tensile strength measurements.

5.2 INTRODUCTION

The sorption and diffusion of gases and organic solvents in polymer has been a topic of great relevance, both from the theoretical and technological point of view [1-4]. When a crosslinked polymer is placed in contact with a suitable solvent, imbibition of the solvent takes place with consequent swelling of the specimen. This phenomenon of expansion of three-dimensional network continue until equilibrium swelling is achieved at which the rate of imbibition of solvent equals the rate of expulsion. The sorption behavior gives an idea about the permeability and diffusion coefficient of penetrant through polymer networks, which are used in various applications such as membranes, paints, gels, ion exchangers etc [5-8]. Polyurethane have an important application such as barrier materials in engineering works [9]. Therefore, it is necessary to study interaction with various commonly used organic solvents. A knowledge of the mechanism of transport of solvents into the PU matrix can also be used to established structure- property relationship under service condition [10]. Often the diffusion of liquids through rubbery polymer is described by Fick's law of diffusion. However in some instances, deviation from Fick's law has been observed. The sorption behavior of rubber like polymer is controlled by polymer structure, crosslink density, type of solvents and temperature [11].

Several authors have studied the diffusion and sorption properties of polyurethanes in different solvents. Schneider et. al [12-14] have investigated the effect of structural variation on transport phenomena.

Aminabhavi et. al. [15] as well as S. Devi et. al. [16] have studied transport of organic solvents through commercially available PU membranes and polyether based polyurethanes respectively.

The effect of crosslink density and different weight composition of PU and UPE (unsaturated polyester) used in IPNs were studied by Ajith et. al. [17,18] and the effect of chain length of polyethylene glycol on PU, were studied by Bharadwaj et. al [19].

5.3 SWELLING STUDY:

Physical properties of cross-linked polymers are largely influenced by Mc, the average chain length between two cross links and hence the crosslink density. The most widely used method to determine Mc of castor oil based polyurethanes by swelling method. When a cross linked polymer is placed in contact with a suitable solvent, imbibitions of the solvent takes place with consequent swelling of specimen. As a result, the polymeric network gets extended until equilibrium swelling is achieved at which the, rate of imbitition of solvent equals the rates of expulsion. The equilibrium swelling is the key parameter to determine Mc.

5.3.1 Experimental:

The equilibrium swelling studies of polyurethane synthesized by reacting (i) novel polyol (EpxR) (ii) PEG 200 or PEG 400 or PEG 600 and (iii) 50 :50 mixture of novel polyol (EpxR) and each of polyethylene glycols (PEG 200, PEG 400, PEG 600) with R 60 isocyanate at different NCO/OH ratios viz. 1, 1.3 and 1.7 was carried out in different solvents at 30 ± 1 ^{0}C in order to calculate their solubility parameter.

Different Polyurethane systems employed in the study are as follow.

EpxR : PUR 60 (NCO/OH = 1, 1.3 and 1.7)
PEG 200: PUR 60 (NCO/OH = 1, 1.3 and 1.7)
PEG 400: PUR 60 (NCO/OH = 1, 1.3 and 1.7)
PEG 600: PUR 60 (NCO/OH = 1, 1.3 and 1.7)

(EpxR + PEG 200, 50+50 w/w%) : PUR 60 (NCO/OH = 1, 1.3 and 1.7)
(EpxR + PEG 400, 50+50 w/w%) : PUR 60 (NCO/OH = 1, 1.3 and 1.7)
(EpxR + PEG 600, 50+50 w/w%) : PUR 60 (NCO/OH = 1, 1.3 and 1.7)

For the swelling studies, circular samples of diameter ~1.5 cm cut and the definite thickness were measured using a micrometer screw. The samples after taking the initial weights were soaked in various solvents having different solubility parameter [δ (cal/cm^3)^{½}] value i.e. cyclohexane (8.2), xylene (8.8), ethyl acetate (9.1),dioxane(9.8), n-butanol (11.4), ethanol (12.7) and Methanol (14.5).

Swelling was carried out in various solvents until an equilibrium swelling was achieved in each case. The samples were blot dried and immediately weighted. This was repeated for three specimens for each individual PU systems in order to ensure the reproducibility of the results. The equilibrium swelling was determined from the initial weight and the equilibrium swollen weight. Density measurements of the samples were carried out by floatation method [20].

5.3.2 Results and Discussion:

The equilibrium degree of swelling (Q), which is the reciprocal of the volume fractions of polymer in swollen state (V_p), was calculated using swelling data of samples in various solvents using the following relations.

$$Q = \frac{1}{V_p} \qquad \text{------------------------ (i)}$$

Where Vp is calculated by following equations,

$$V_p = \frac{W_p / d_p}{W_p / d_p + W_s / d_s} \qquad \text{-------------------------------------- (ii)}$$

where,

w_p = dry wt. of polymer

w_s = wt. of solvent taken up at equilibrium

d_p = density of polymer

d_s = density of solvent

In order to determine the solubility parameter of PUs, Q was plotted against solubility parameter (δ) of all solvents studied. From the representative plots (Fig. 1 to 7), it was found that dioxane [$\delta = 9.8$ $(cal/cm^3)^{1/2}$] gave maximum value of Q for all the systems studied and hence was used for further sorption studies.

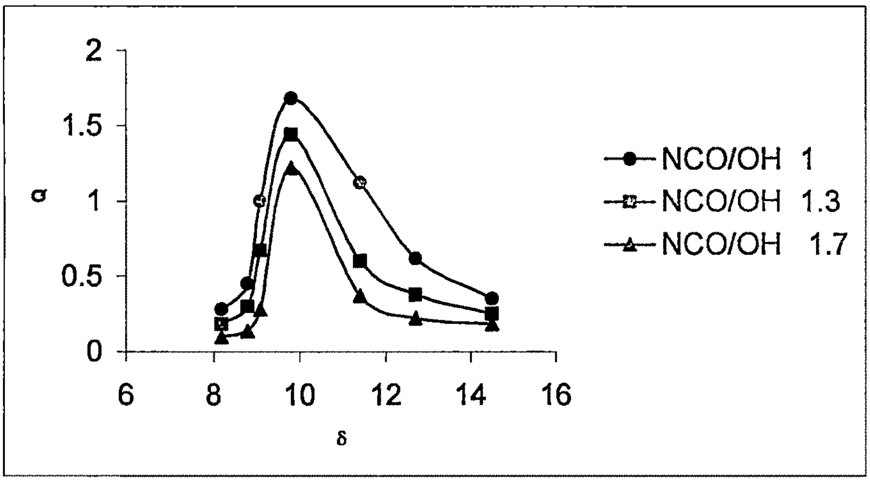

Fig 1: Plot of degree of swelling (Q) vs solubility parameter (δ) for PU system, EpxR : PUR 60 (NCO/OH = 1, 1.3 and 1.7)

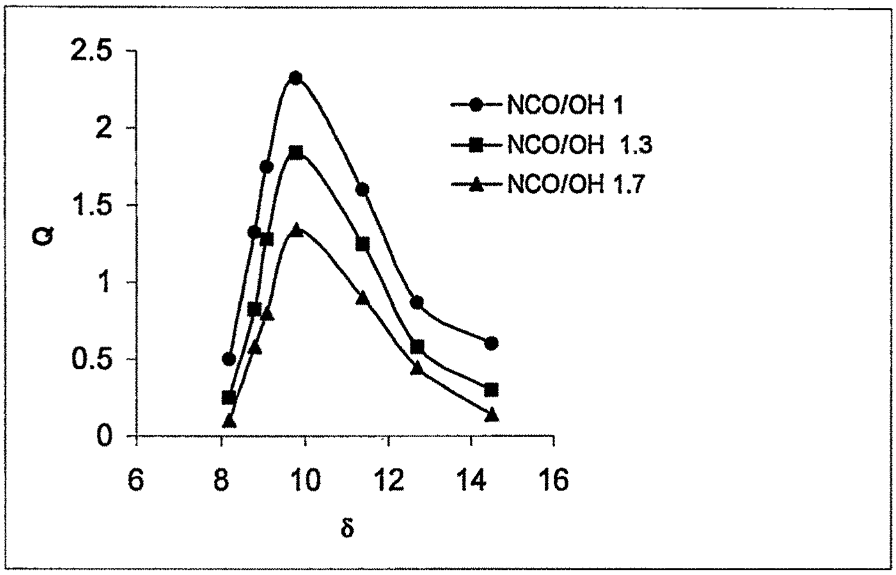

Fig 2: Plot of degree of swelling (Q) vs solubility parameter (δ) for PU system, PEG 200 : PUR 60 (NCO/OH = 1, 1.3 and 1.7)

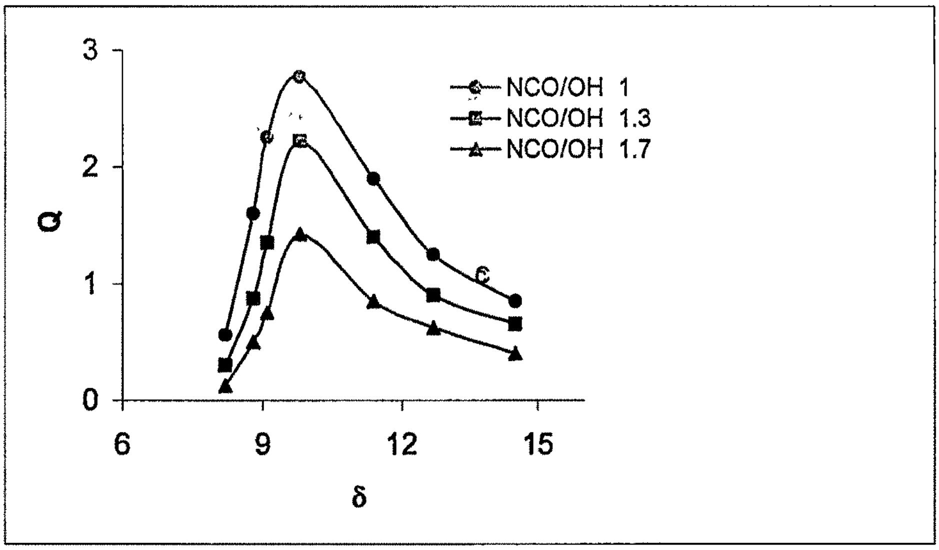

Fig 3: Plot of degree of swelling (Q) vs solubility parameter (δ) for PU system, PEG 400 : PUR 60 (NCO/OH = 1, 1.3 and 1.7)

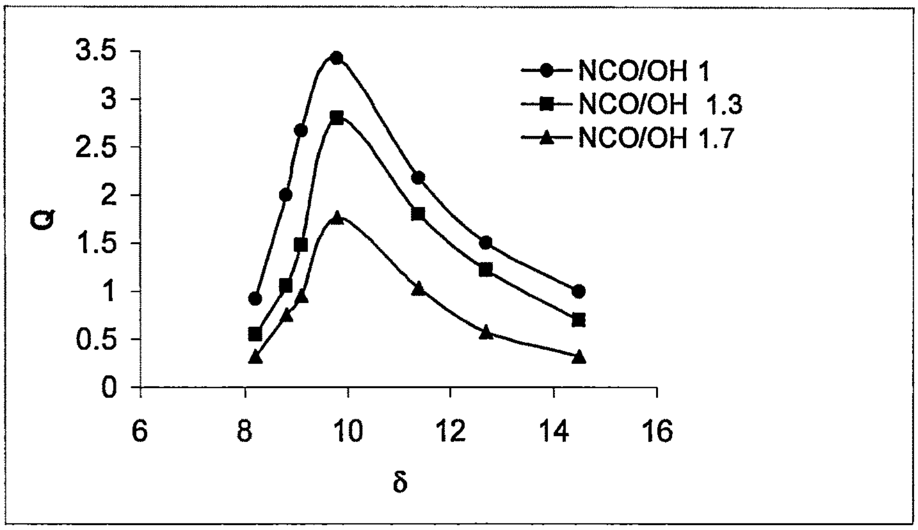

Fig 4: Plot of degree of swelling (Q) vs solubility parameter (δ) for PU system, PEG 600 : PUR 60 (NCO/OH = 1, 1.3 and 1.7)

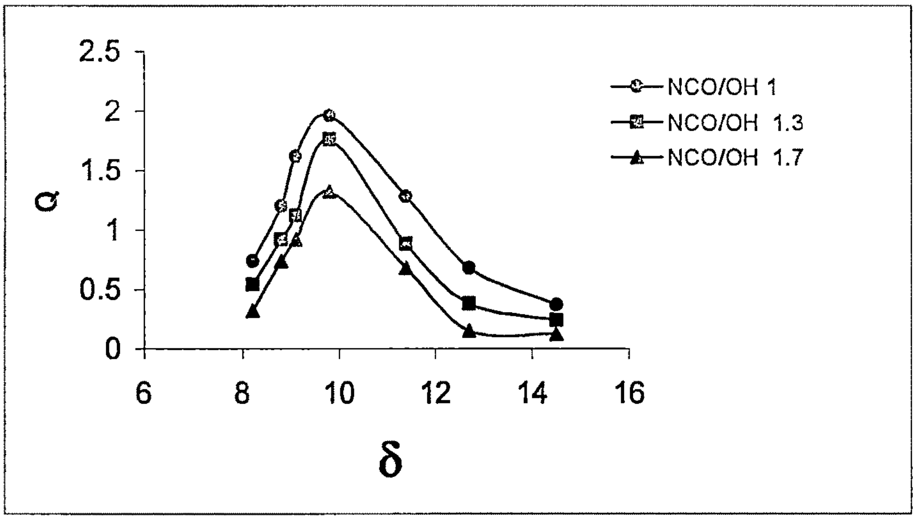

Fig 5: Plot of degree of swelling (Q) vs solubility parameter (δ) for PU system, (EpxR + PEG 200, 50+50 w/w%) : PUR 60 (NCO/OH = 1, 1.3 and 1.7)

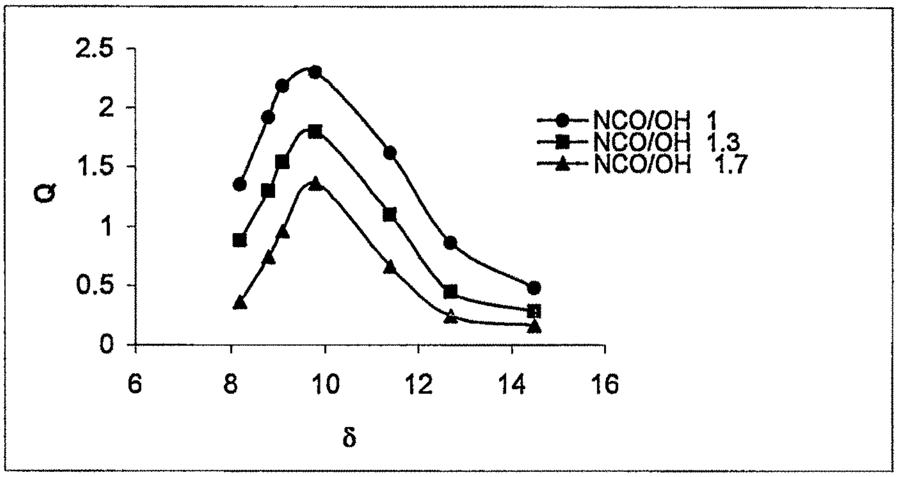

Fig 6: Plot of degree of swelling (Q) vs solubility parameter (δ) for PU system, (EpxR + PEG 400, 50+50 w/w%) : PUR 60 (NCO/OH = 1, 1.3 and 1.7).

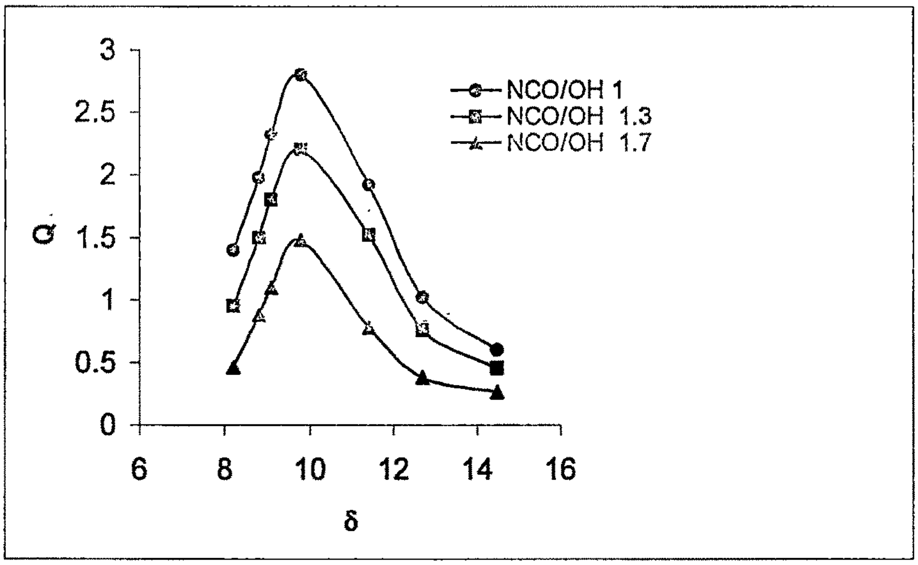

Fig 7: Plot of degree of swelling (Q) vs solubility parameter (δ) for PU system, (EpxR + PEG 600, 50+50 w/w%) : PUR 60 (NCO/OH = 1, 1.3 and 1.7)

The average molecular weight between two crosslink points (Mc), which is a direct measure of crosslink density, was determined from the well known Flory Rehner equation [21-23].

$$M_c = -\frac{\rho V_1 (V_p)^{1/3}}{\ln(1-V_p)+V_p+\chi_{12}V_p^{\,2}} \quad \text{-- (iii)}$$

V_1 = molar volume of solvent

ρ = Density of network

χ_{12} = polymer -solvent interaction parameter which was calculated using the equation [24].

$$\chi_{12} = \mathrm{B} + \frac{V_1(\delta_p-\delta_s)^2}{RT} \quad \text{---------------------------------- (iv)}$$

Where,

δ_p = solubility parameter of polymer

δ_s = solubility parameter of solvent

R = gas constant

T = absolute temperature

B = Lattice constant which is generally taken as 0.34 for good solvent.

The degree of crosslinking (v) and number of chains per unit volume (N) were also calculated using the following relations [11,25].

$$\nu = \frac{1}{2M_c} \qquad N = \frac{\rho}{M_c} \quad \text{------------------------ (v and vi)}$$

The values of V_p, N and v for all the system are given in Table 1. From the table, it can be inferred that the present system has high crosslink density and becomes more flexible when polyethylene glycol molecules are introduced. At a particular ratio i.e NCO/OH 1, V_p increases as EpxR content increases in the polyurethane system. As chain length of PEG increases, V_p decreases. Mc also increases with increase in PEG moieties in PU systems.

Swelling of PEG 600 with PUR 60 having NCO/OH ratio 1 gives maximum value. While in case of EpxR polyol with PUR 60 having same ratio gives minimum value. This means that EpxR - PUR 60 polymer is highly crosslinked. Thus Mc value of PEG 600 with PUR 60 and EpxR with PUR 60 are maximum and minimum respectively. The Mc values of rest of the system fall in between these extremes. The effect of crosslink density on V_p and Mc follow same trend, i.e. V_p also increases with increasing NCO/OH ratio. However, in case of higher NCO/OH ratio, number of crosslink points increase, suggesting that distance between two crosslink points decreases and ultimately more rigid structure is formed. As NCO/OH ratio increases in the PU system than more and more compact structure is formed and distance between crosslink points decreases, so Mc decreases.

In case of PU obtained from EpxR polyol and PUR 60, more rigid structure is formed compared to others, because of more hydroxyl groups in polyol which reacts with more NCO groups of PUR 60, leading to formation of more number of crosslink points hence lower value of Mc. If we mix EpxR polyol with polyethylene glycol, the hydroxyl groups of PEG also react with free NCO of PUR 60, so the formation of PU structure having flexible chain length takes place and distance between two crosslink point increases, thus Mc increases. The values of Mc increase from PEG 200 to PEG 600 with respective PU network.

Table 1: Values of volume fraction of polymer (Vp) , number of chains per unit volume (N) and degree of crosslinking (ν).

Prepolymer	NCO/ OH	Vp			[$N \times 10^3$ (mol/cm^3)]			[$\nu \times 10^3$ (mol/g)]		
		PEG 200 : Epx R polyol (w/w %)			PEG 200 : Epx R polyol (w/w %)			PEG 200 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	0.3311	0.3893	0.4229	0.572	0.842	1.034	0.282	0.435	0.540
	1.3	0.3822	0.4077	0.4594	0.804	0.943	1.278	0.394	0.486	0.647
	1.7	0.4365	0.4739	0.4803	1.120	1.384	1.439	0.495	0.750	0.723
		PEG 400 : Epx R polyol (w/w %)			PEG 400 : Epx R polyol (w/w %)			PEG 400 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	0.2831	0.3495	0.4229	0.472	0.650	1.034	0.236	0.329	0.540
	1.3	0.2983	0.3973	0.4594	0.631	0.855	1.278	0.285	0.447	0.647
	1.7	0.3043	0.4724	0.4803	0.719	1.376	1.439	0.321	0.692	0.723
		PEG 600 : Epx R polyol (w/w %)			PEG 600 : Epx R polyol (w/w %)			PEG 600 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	0.2608	0.3011	0.4229	0.336	0.462	1.034	0.167	0.230	0.540
	1.3	0.2821	0.3462	0.4594	0.399	0.636	1.278	0.181	0.306	0.647
	1.7	0.3756	0.4158	0.4803	0.576	0.991	1.439	0.252	0.431	0.723

5.4 TRANSPORT PROPERTIES:

Polymers used for transport properties display their ability to resist the passage of penetrants like gases, vapors and organic liquids. The transports of penetrant molecules through polymer is of great importance in many areas of technology like membranes, barrier plastics, foams and many other applications requiring protective packaging and shelf life extension of food and beverages.

Transport properties of various engineering polymers like polyurethanes, crosslinked polystyrene, natural rubber and various synthetic rubbers have been extensively studied by using organic solvents of various polarity and interacting groups and also by using aqueous salt solutions of acids by many researchers [11,26-29].

However transport properties of castor oil based PUs excepts some IPNs [30,31] are rarely found in literature, even though they are widely used in many applications such as membranes, GPC, controlled release agents and enzyme immobilizations. The transport phenomenon of penetrant in PU systems differ from other crosslinked polymers as they consists of two components , one rubbery or soft segments from polyol and other is glassy or hard segments from isocyanates groups . The behavior of rubbery polymers towards solvents would be different from glassy polymer as there is a difference in their free volume and molecular mobility [28].

5.4.1Experimental:

In the kinetic experiments, the so called pat and weight technique was used for liquid sorption [32]. Circular samples (diameter of ~1.5 mm) of definite thickness after their recording dry weight were placed in dioxane in a standard glass bottle which was maintained at constant temperature of 30 ±1 ^{0}C. Specimens were taken out at regular intervals of time, solvent adhering to the surface was removed with filter paper and a weighed immediately and placed into the solvent. This procedure was continued till equilibrium swelling was achieved. This was repeated for at least three specimens from each PU system, in order to ensure the reproducibility of results. The time taken for wiping out the solvents from sample surface and weighing was kept minimum in order to minimize the error due to solvent evaporation.

5.4.2 Result and Discussion:

The sorption of penetrant species into polymer matrix is quantified in terms of mole percent uptake (Q_t), which was calculated at each time interval using the equation [11]

$$Q_t = \frac{m_e / m_r}{m_i} \times 100 \text{ -- (vii)}$$

where,

m_e = mass of solvent taken up at equilibrium

m_r = relative molecular mass of solvent

m_i = dry mass of sample.

At equilibrium swelling, Q_t was considered to be Q_∞, mole percent uptake at infinite time. The results are tabulated in Table 2. Fig. 8 to 14 shows the sorption curve of the PU systems having different compositions and crosslink densities. The curves were obtained by plotting Q_t against $(T)^{1/2}$. It can be inferred that PU system made from EpxR with PUR 60 having NCO/OH ratio1.7 gives minimum value of Q_t and PU made from PEG 600 with PUR 60 having NCO/OH ratio 1 gives maximum value of Q_t at a time of equilibrium.

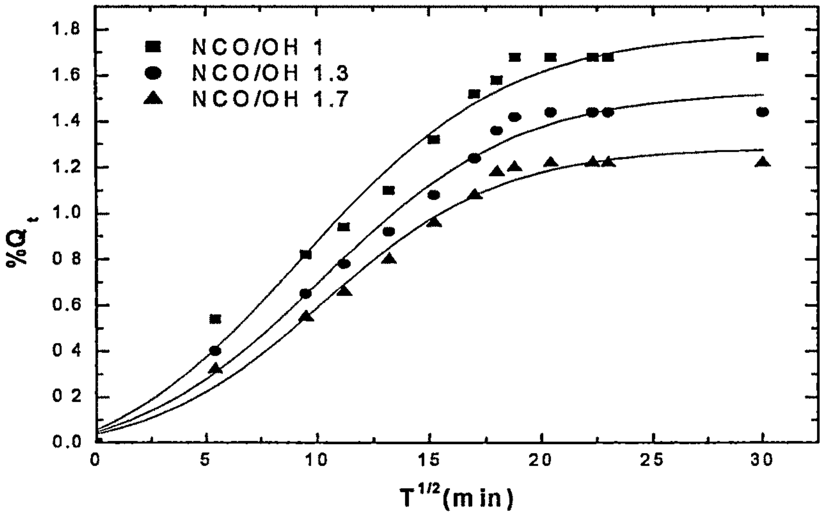

Fig 8: Sorption curves showing the mole percent uptake of PU system EpxR : PUR 60 (NCO/OH = 1, 1.3 and 1.7)

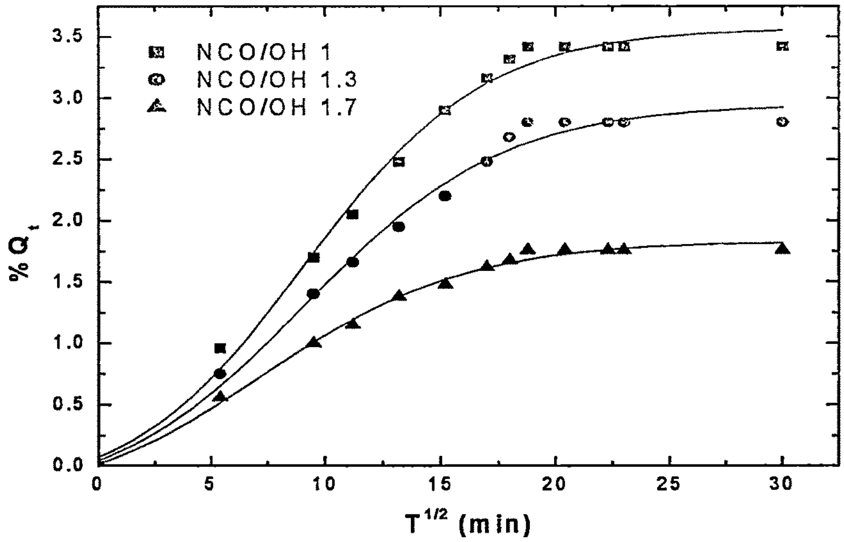

Fig 9: Sorption curve showing the mole percent uptake of PU system PEG 200: PUR 60 (NCO/OH = 1, 1.3 and 1.7)

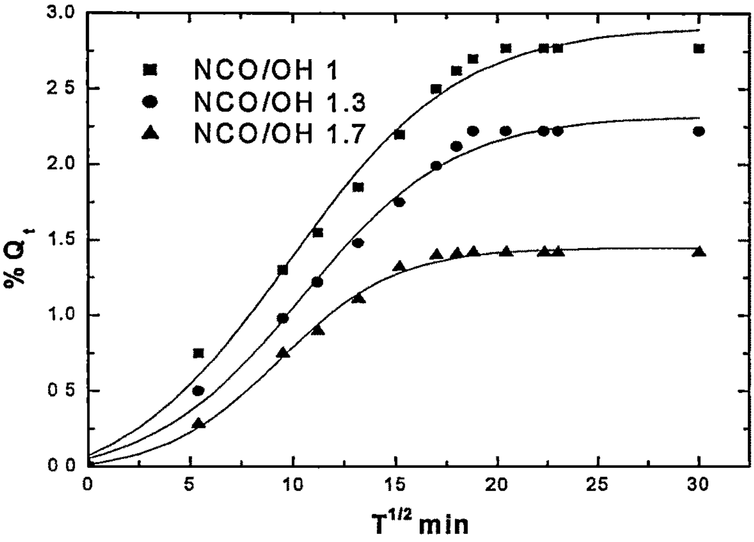

Fig 10: Sorption curve showing the mole percent uptake of PU system PEG 400: PUR 60 (NCO/OH = 1, 1.3 and 1.7)

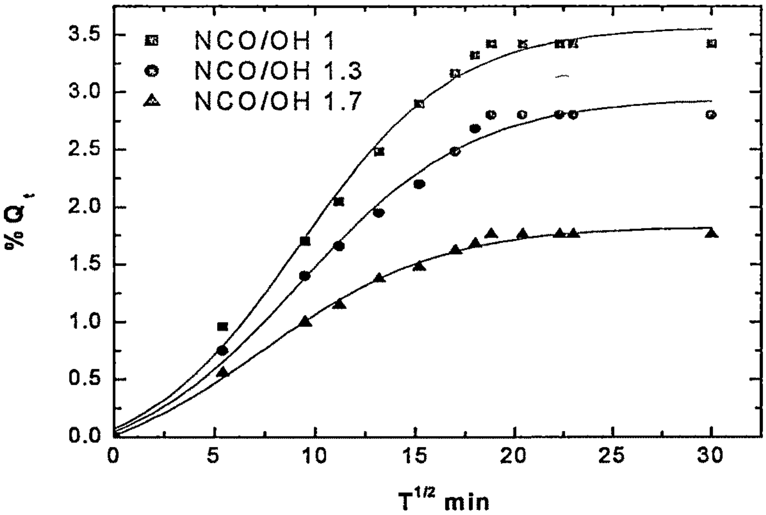

Fig 11: Sorption curve showing the mole percent uptake of PU system PEG 600: PUR 60 (NCO/OH = 1, 1.3 and 1.7)

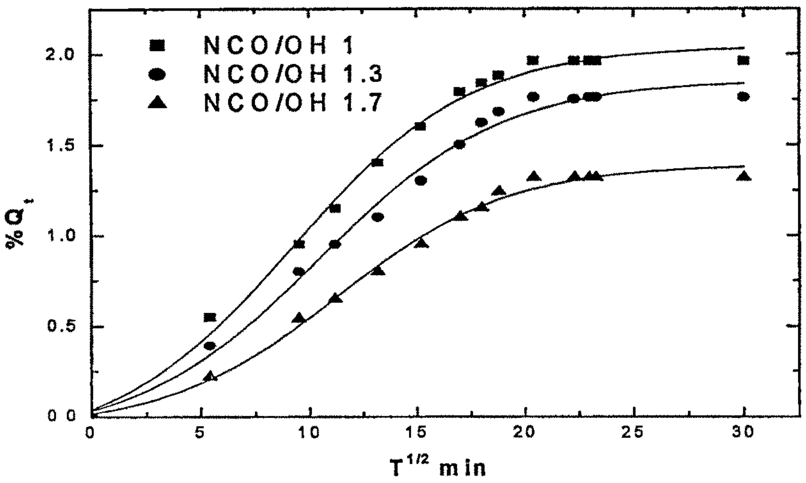

Fig 12: Sorption curve showing the mole percent uptake of PU system (EpxR + PEG 200, 50+50 w/w%) : PUR 60 (NCO/OH =1, 1.3,1.7)

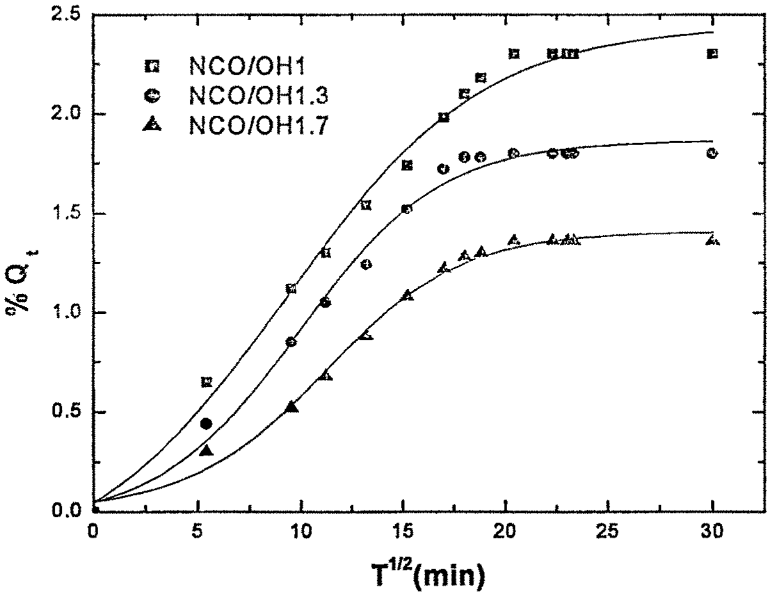

Fig 13: Sorption curve showing the mole percent uptake of PU system (EpxR + PEG 400, 50+50 w/w%) : PUR 60 (NCO/OH = 1, 1.3, 1.7)

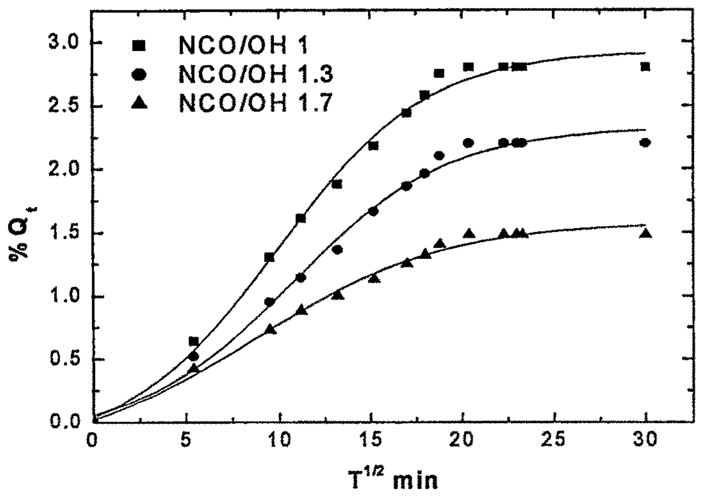

Fig 14 : Sorption curve showing the mole percent uptake of PU system (EpxR + PEG 600, 50+50 w/w%) : PUR 60 (NCO/OH = 1,1.3, 1.7)

The solvent uptake capacity decreases with decrease in chain length of polyethylene glycol. Solvent uptake capacity of the polymer also decreases as NCO/OH ratio in the polymer increases at a give time. The data show that Q_t value of system {(PEG + EpxR), 50:50 % w/w} with PUR 60 was found to be intermediate between 100% PEG with PUR 60 and 100% EpxR with PUR 60 for all systems i.e. NCO/OH ratios being 1,1.3 and 1.7 (PEG with PUR 60) of different PEGs. The values of Q_∞ also follow the same trend.

The observation can be explained on the basis of crosslink density (NCO/OH ratio) and composition of PEGs with EpxR polyol. As NCO/OH ratio increases, corsslink density increases and the chains become more rigid and dense and thus the ability of polymer chains to accommodate solvent molecules decreases. At lower NCO/OH ratio, the chains will have maximum flexibility and less crosslink points hence the sorption capacity will be maximum. With further increase in the NCO/OH ratio to 1.3 and 1.7, flexibility of chains gradually decreases. In case of systems made from PEG 600, the chains are of maximum length (*cf.* PEG 400 and PEG 200) and have maximum flexibility. Here the sorption capacity of solvent will be maximum. Flexibility of chains gradually decreases from PEG 600 to 400 to 200, resulting in less sorption and hence low value of Q_t and Q_∞. From Table 2, it is clear that PUs made from reaction of PEG 600 with PUR 60 (NCO/OH = 1) has more solvent uptake capacity. Results show that PU obtained by reacting EpxR with PUR 60 (NCO/OH = 1) show less solvent uptake capacity. This is due to presence of more number of hydroxyl group in EpxR, so it produces more crosslinked polymer network with PUR 60. Here as NCO/OH ratio increases, the number of crosslink points increase so solvent uptake capacity decreases i.e the solvent molecule cannot diffuse in polymer network. The value of N and V_P shown in Table 1, also support the above.

Table 2: Values of mole percent uptake at infinite time (Q_∞), n and k value for all sample studied.

Prepolymer	NCO/ OH	Q_∞(mole %)			[n]			[k × 10^2]		
		PEG 200 : Epx R polyol (w/w %)			PEG 200 : Epx R polyol (w/w %)			PEG 200 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	2.32	1.96	1.68	0.55	0.50	0.48	3.7	5.2	6.3
	1.3	1.84	1.76	1.44	0.59	0.57	0.52	3.1	3.2	4.9
	1.7	1.34	1.32	1.28	0.55	0.71	0.54	5.5	1.4	4.3
		PEG 400 : Epx R polyol (w/w %)			PEG 400 : Epx R polyol (w/w %)			PEG 400 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	2.77	2.30	1.68	0.53	0.49	0.48	4.3	5.6	6.3
	1.3	2.22	1.80	1.44	0.60	0.56	0.52	2.9	3.8	4.9
	1.7	1.42	1.36	1.28	0.57	0.61	0.54	3.9	2.5	4.3
		PEG 600 : Epx R polyol (w/w %)			PEG 600 : Epx R polyol (w/w %)			PEG 600 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	3.42	2.80	1.68	0.52	0.51	0.48	4.7	3.5	6.3
	1.3	2.80	2.20	1.44	0.53	0.56	0.52	4.6	3.5	4.9
	1.7	1.76	1.48	1.28	0.48	0.57	0.54	7.0	5.7	4.3

To understand the mechanism of sorption; the values of Q_t and Q_∞ were substituted in the equation for transport phenomena [33,34]

$$Q_t / Q_\infty = k\, t^n \text{ ---------------------------- (viii)}$$

$$\log Q_t + \log Q_\infty = \log k + n \log t \text{ ----------------------------(ix)}$$

Where Q_t is the mole percent uptake at time t and Q_∞ is the equilibrium mole percent. k is constant, which depends on the structural characteristics of the polymer and its interaction with solvent. The value of n determines the mode of transport. When n=1/2, in equations (viii) diffusion obeys Fick's law, which occurs when segmental mobility of polymeric chain is faster than the rate of diffusion of penetrant molecules. When n =1 the diffusion is said to be non-Fickian, which means that diffusion rate of penetrant molecules is much faster than polymer chain relaxation time. In the present systems, the values of k and n were obtained from the linear plot of log Q_t/Q_∞ vs. log t (correlation coefficient > 0.99) and the values are presented in Table 3. In all the cases, the magnitude of n varies from 0.48 to 0.71. This suggests that diffusion process of solvent through polymer deviates slightly from the normal Fickian behavior but not completely non-Fickian . Earlier also the 'n' values were found to be higher than 0.5 and the systems were thought to be non-Fickian in nature [17,18]. However we believe that in the present systems the behavior is not much different from Fickian one.

The transport of penetrant molecules through polymers is also quantified by other terms such as diffusion coefficient (D) and sorption coefficient (S). The diffusion coefficient which is a measure of the ability of the penetrant molecule to move among the polymer segment and the sorption coefficient gives an idea about the equilibrium sorption, were calculated from the following equations [4,35]

$$D=\pi(h\theta/4Q_\infty)^2 \text{ ---------------------------- (x)}$$

$$S = \frac{m_\infty}{m_p} \qquad \text{------------------------------(xi)}$$

Where h is the thickness of the sample and θ is the slope of the sorption curve (Fig 8 to 14). m_∞ and m_p are the mass of the solvent taken up at equilibrium and initial mass of the sample respectively. The transport of penetrant molecules through polymers is also quantified by another term permeability coefficient (P), which gives the combined effect of both D and S, and was calculated using the equation.

$$P = D \times S \qquad \text{------------------------------ (xii)}$$

The permeability (P) of small molecules in polymers usually occur through the following steps (i) sorption of penetrating species onto polymer network, (ii) diffusion of penetrating species through polymer network (iii) desorption of penetrating species through polymer wall. The values of D, S and P for all the systems are summarized in Table 3.

For a given NCO/OH ratio, diffusion coefficient increases and sorption coefficient decreases with increase in the amount of EpxR. By increasing EpxR content more crosslinked structure of PU is developed. This signifies less affinity of solvent molecule to PU network derived from EpxR with PUR 60, as can also be seen for their Q_∞ value. PU network made from polyethylene glycol and PUR 60 at a given NCO/OH ratio show high sorption of solvent (dioxane) compared to PU made from EpxR polyol and PUR 60. This is because EpxR polyol has more hydroxyl groups which react with more NCO groups in PUR 60 to form a highly crosslinked polymer network. These polymer networks have less affinity to solvent molecule.

The value of D is higher in PU systems synthesized by using PEG 200 compared to PEG 400 and PEG 600. In these cases, PEG 200 to PEG 600, chain length of ethylene oxide increases, so that more and more flexible polymer network is formed which can easily accommodate solvent molecule. PEG blended with EpxR polyol reacts with PUR 60 at NCO/OH ratio 1 leads to formation of PU network containing more no of urethane linkages due to presence of more hydroxyl groups in EpxR polyol. Presence of PEG confers more flexible to the resultant polyurethane due to enhanced salvation by dioxane (solvent). It is also observed that when NCO/OH ratio is 1, network structure is more flexible and mainly forms urethane linkages, which may have specific interaction with solvent molecules. However as the NCO/OH ratio increases, more no of allophanate linkage will be found [36] along with the urethane linkages. Hence there will be less interaction with solvent molecules and a reduction of the sorption coefficient values. Permeability coefficients of systems having PU network derived from PEG and PUR 60, indicate that P increases with increase in chain length of ethylene oxide and in other cases permeability coefficient did not show any regularity in behavior with either in composition or the NCO/OH ratio in all the system studied.

The data of D, Mc and Vp were also used to established a relationship proposed by de Gennes [37] for swollen polymer network, which is as shown below.

$$D \sim Vp^{\beta} \qquad \text{(xiii)}$$

$$D \sim Mc^{\gamma} \qquad \text{(xiv)}$$

Where β=3/4 and 1 for a good and theta solvent respectively and γ =3/5. Straight line plots as shown in Fig. 15, for PU systems having NCO/OH ratio 1 represent the power laws. The exponent value of β for all the systems are approximately near to 1. However in dioxane all PU systems show high swelling, but the value of β which is near to 1 indicates that dioxane is not good solvent for these systems. The value of γ were found to be in range from 0.21-0.50 which are rather small than the theoretical prediction .

Incidentally, Oikawa and Murakami [38] have investigated poly(dimethyl siloxane) gels in benzene by means of dynamic light scattering technique and obtained $\gamma = 0.29$. Chee [39] also observed low values of γ for the poly(ethyl methacrylate) crosslinked system.

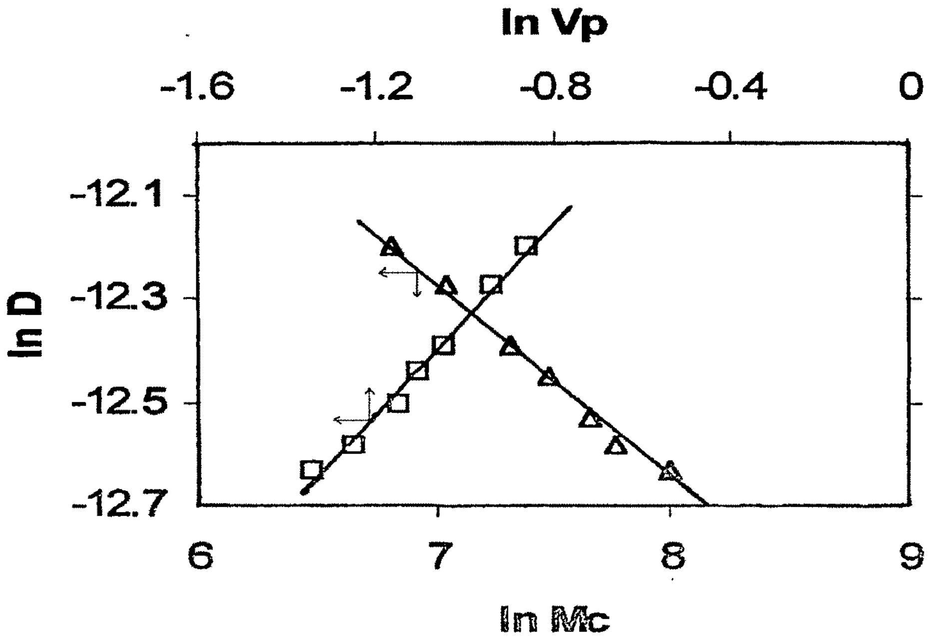

Fig 15 : log-log plot of diffusion coefficient (D) against Mc (Δ) and Vp (□) for PU systems having NCO/OH =1.

Table 3: Values of diffusion coefficient (D), sorption coeffcient (S), and permeability coeffcient (P) for various samples in dioxane.

Prepolymer	NCO/ OH	[D×10^{6} (cm^2/s)]			[S (g/g)]			[P× 10^{6} (cm^2/s)]		
		PEG 200 : Epx R polyol (w/w %)			PEG 200 : Epx R polyol (w/w %)			PEG 200 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	4.08	4.69	5.03	2.041	1.724	1.474	8.32	8.08	7.41
	1.3	4.32	4.99	5.28	1.619	1.548	1.267	6.99	7.72	6.68
	1.7	4.68	5.09	6.14	1.178	1.160	1.126	5.51	5.92	6.91
		PEG 400 : Epx R polyol (w/w %)			PEG 400 : Epx R polyol (w/w %)			PEG 400 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	3.61	4.15	5.03	2.422	2.023	1.474	8.74	8.39	7.41
	1.3	4.02	4.25	5.28	2.037	1.5839	1.267	8.18	6.73	6.68
	1.7	4.58	4.72	6.14	1.248	1.196	1.126	5.71	5.64	6.91
		PEG 600 : Epx R polyol (w/w %)			PEG 600 : Epx R polyol (w/w %)			PEG 600 : Epx R polyol (w/w %)		
		100:00	50:50	00:100	100:00	50:50	00:100	100:00	50:50	00:100
PUR 60	1	3.27	3.44	5.03	3.009	2.463	1.474	9.83	8.47	7.41
	1.3	3.74	3.78	5.28	2.463	1.935	1.267	9.21	7.31	6.68
	1.7	4.18	4.62	6.14	1.548	1.302	1.126	6.47	6.01	6.91

5.5 MECHANICAL PROPERTY:

Stress/Strain properties of some of the polyurethane systems were measured using a standard Instron machine (UTM 4467) according to ASTM D 638 procedure. The crosshead speed used was 10 mm/min at

25 ^{0}C and 50 ±1 % relative humidity. At least five specimens were tested for each sample. The specimens, which do not break between predetermined gauge (50.0 mm.) marks or those breaking at some obvious fortuitous flaw were discarded.

5.5.1 Result and Discussion:

Effect of chain length and cross-link density on the tensile strength and % elongations at breaks of some PU systems were studied. The tensile properties in terms of tensile strength and % elongation evaluated from stress- strain curves are tabulated in Table 4.

5.5.1 (1) Effect of Polyol :

EpxR polyol containing five-hydroxyl functional groups reacts with PUR 60 forming a polyfunctional network of Polyurethane. Network formation reduces flexibility of the polymer, on the other hand PEG polyol formed a linear polymeric chain with PUR 60. Thus EpxR based PUs showed a higher tensile strength and lower elongations compared to PEG based PUs.

Polyethylene glycol (PEG) based PU formed a linear polymer chain with PUR 60. The data show (Table 4) a gradual increase in all mechanical properties studied with decrease in molecular weight of polyol incorporated with the PUR 60. The ratio of NCO/OH when maintained same in all PU samples the higher molecular weight polyol (PEG 600) which is linear in nature causes formation of weak polymer network as a result of (i) direct decrease in crosslink density and (ii) indirectly not allowing uniform distribution of load through out the network because of its longer chain length. In otherwords when the load is applied to the network, polyol PEG 600 because of its high flexibility throw away the load to the rigid part (castor oil and TDI) of the network and create stress concentration at that region. Ultimately, the rupture takes place at low values of load and elongation. Thus, the lack of concert between the rigid and flexible regions in sharing the load applied, resulted into the decrease in tensile strength and elongation.

When polyol PEG 200 is used, the shorter length of flexible chain contributes to bear load along with PUR 60 part coordinately this leads to an increase in tensile properties of PU 200 system.

5.5.1 (2) Effect of NCO /OH ratio:

Three different NCO/OH ratios were selected to obtain different sets of PUs. Since the NCO/OH ratio is more then one the polyurethane formed would have more NCO end groups. These free NCO groups react further with the urethane linkage. Thereby, affecting mechanical properties of the resulting polyurethanes formed. Consequently, the increase in NCO/OH ratio increases the intermolecular attraction between two hard segments of isocyanate i.e. between -NH and $-C=O$, groups due to hydrogen bonding which in turn increases the tensile strength and also decreases the elongations [40].In polyurethane systems formed by reacting EpxR with PUR 60, as the NCO/OH ratio was increased, the tensile strength also increased from 9.42 to 30.28 MPa (Table 4).In contrast, the % elongation at break was found to decrease from 16 to 4 %.

Systems	Tensile Strength M.Pa.	% Elongations at break
EpxR : PUR 60 (NCO/OH 1)	9.42	16
EpxR : PUR 60 (NCO/OH 1.3)	16.7	12
EpxR : PUR 60 (NCO/OH 1.7)	30.28	4
PEG 200 : PUR 60 (NCO/OH 1.3)	5.3	248
PEG 400 : PUR 60 (NCO/OH 1.3)	3.5	127
PEG 600 : PUR 60 (NCO/OH 1.3)	1.0	48
{PEG 200 + EpxR, (50+ 50 %w/w)}: PUR 60 (NCO/OH 1.3)	12.2	100
{PEG 400 + EpxR, (50+ 50 %w/w)}: PUR 60 (NCO/OH 1.3)	8.6	68
{PEG 600 + EpxR, (50+ 50 %w/w)}: PUR 60 (NCO/OH 1.3)	6.2	48

Table 4 : Tensile strength and % elongations at break of Polyurethane systems.

5.5.1 (3) Effect of Mixture of polyols:

Compared to the tensile strength obtained for the polyurethanes formed by reacting either PEG or EpxR alone with PUR 60, the polyurethanes synthesized from mixture of PEG and EpxR showed increase in tensile strength as given in Table 4, and simultaneous the % elongations decreased. The above observation suggested that the crosslink density and uniform distribution of the load throughout the network was related to the tensile strength.

5.6 CONCLUSIONS

The sorption of solvent under swelling study is inversely proportional to crosslinking density and directly proportional to the chain length of PEGs in the series of Polyurethane systems synthesized by us. Diffusion process from the sorption kinetic study was found to be not much different from the normal Fickian behavior. The value of diffusion coefficient (D) and sorption coefficient (S) is found to be directly related to the function of flexibility and rigidity of Polyurethane networks and the results clearly indicates that the novel polyol (EpxR) based on epoxy resin increases the rigidity and PEGs increases the flexibility. Therefore we can tailor PU systems by varying combinations of EpxR and PEGs having different NCO/OH ratio, which plays important role in controlling sorption and diffusion of solvents in PU networks.

Polyurethane elastomers containing PEG-200 with PUR 60 having NCO/OH ratio 1.3 and EpxR with PUR 60 having NCO/OH ratio 1.7 showed the best mechanical properties.

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