## Effect of Chain Length of Polyethylene Glycol and Crosslink Density (NCO/OH) on Properties of Castor Oil Based Polyurethane Elastomers

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*The equilibrium swelling study of polyurethanes (PU) was carried out in various solvents in order to calculate their solubility parameter. The kinetics of swelling and sorption have also been studied in 1,4-dioxane at 30°C. The PU was synthesized by reacting a novel polyol (castor oil derivative and epoxy based resin, EpxR) and one of the polyethylene glycols (PEG 200, PEG 400, PEG 600) with different weight compositions, with a toluene diisocyanate (TDI) adduct (derived from toluene diisocyanate and R60 polyol). Different NCO/OH ratio viz. 1, 1.3 and 1.7 were employed in the study. The results were found to vary with the weight composition of polyol components, as well as the crosslink density of the samples. The sorption behavior is also found to vary with the molecular weight of polyethylene glycol employed in the preparations of the polyurethanes. Kinetic studies of swelling revealed that the sorption is anomalous in nature. The diffusion coefficient (D) increased with an increase in the NCO/OH ratio and decreased with an increase in chain length of polyethylene glycol. The sorption coefficient (S) decreased with an increase in crosslink density (NCO/OH) and increased with increasing polyethylene glycol (i.e., PEG 200, PEG 400, and PEG 600) moieties in the polyurethanes. The molecular weight between two crosslink points was calculated using the Flory Rehner equation (24), and hence, the number of chains per unit volume (N) and degree of crosslinking (v) in all the samples were determined.*

**Keywords**   castor oil, polyurethane, diffusion coefficient, sorption coefficient

## Introduction

The sorption and diffusion of gases and organic solvents in polymers has been a topic of great relevance, both from the theoretical and technological points of view (1–4). When a crosslinked polymer is placed in contact with a suitable solvent, imbibitions of the

solvent takes place with consequent swelling of the specimen. This phenomenon of expansion of three-dimensional network continues until equilibrium swelling is achieved, at which time the rate of imbibitions 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 has an important application as barrier materials in engineering works (9). Therefore, it is necessary to study interaction of PU with various commonly used organic solvents. A knowledge of the mechanism of transport of solvents into the PU matrix can also be used to establish structure- property relationship under service conditions (10). Often, the diffusion of liquids through a rubber-like polymer is described by Fick's law of diffusion (11). However, in some instances, deviation from Fick's law has been observed. The sorption behavior of a rubber-like polymer is controlled by polymer structure, crosslink density, type of solvents and temperature (12). Several authors have studied the diffusion and sorption properties of polyurethanes in different solvents. Kwan et al. (13) and Dixon-Garrett et al. (14) have investigated the effect of structural variation on transport phenomena. Aminabhavi and coworkers (15), as well as Devi and coworkers (16), have studied the 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 and the effect of chain length of polyethylene glycol on PU, were studied earlier by some of us (17–19). In continuation of our interest in this field, we have directed our study to the transport (diffusion and sorption) of some solvents through polyurethane elastomers synthesized in our laboratory from various polyols (EpxR and/or polyethylene glycol) and an isocyanate adduct (PUR 60) in various proportions, having different crosslink densities (NCO/OH viz. 1, 1.3 and 1.7). The data obtained from the swelling experiments were used to calculate diffusion (D), sorption coefficients (S) and permeability (P).

## Experimental

### Materials

Ricinoleic acid (Jayant Oil Mills, Vadodara, India) was used after drying in an oven at 100°C for 2 h. Epoxy resin (DGEBA, mol. wt. 392, Atul Industries, Valsad, India) were used as received. Triethylamine (Merck, USA) was used without purification and 1,4-dioxane (Qualigens, India) was distilled before use. Polyethylene glycol (PEG) of molecular weight 200, 400 and 600 (Sisco Chem. Industries, Vadodara, India) used in the study was dried over anhydrous $Na_2SO_4$. The castor oil based polyol designated R 60, having hydroxyl value 255, and five free hydroxyl groups per mole, was obtained from H. K. Agencies, Ahmedabad, India. Toluene diisocyanate (TDI) (Merck USA) was used without any treatment Toluene (Qualigens, India) was used after distillation. All the solvents used in the swelling study were of analytical grade and were further purified by distillation and dried over molecular sieves (4 Å).

### Novel Polyol Synthesis (EpxR)

In a three-necked flask equipped with stirrer, nitrogen inlet and condenser the reactant, ricinoleic acid (0.2 mole) and epoxy resin (0.1 mole) were charged along with

CH₂—CH—CH₂—O—⟨benzene⟩—C(CH₃)₂—⟨benzene⟩—O—CH₂—CH—CH₂

DIGLYCIDYL ETHER OF BIS PHENOL A

$+$

2 CH₃—(CH₂)₅—CH—CH₂—CH=CH—(CH₂)₇—COOH
                    |
                    OH

RICINOLEIC ACID

Dioxane          N2 atm
Reflux Temperature   Tri ethyl amine
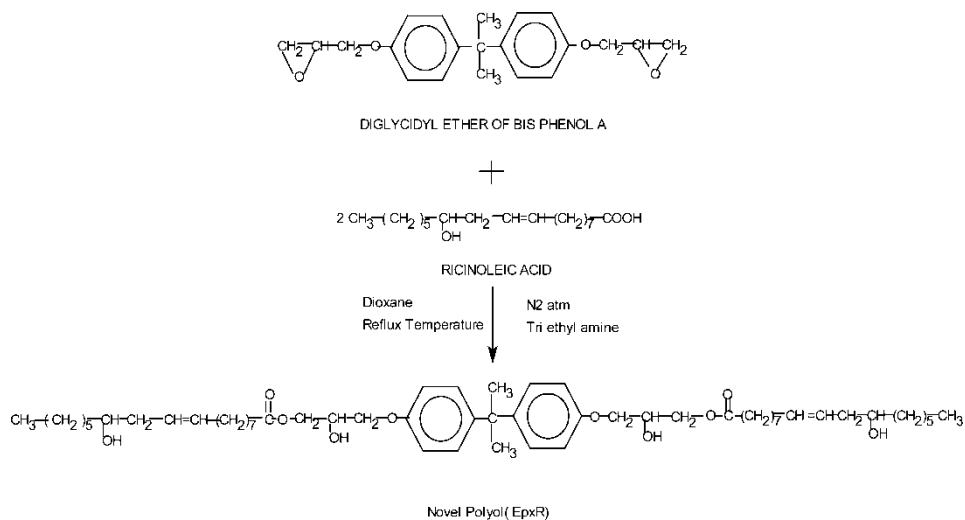
Novel Polyol (EpxR)

**Scheme 1.** Synthesis of Novel polyol (EpxR).

0.005 mole of triethylamine as catalyst in 100 ml of dioxane. The reaction mixture was heated to reflux temperature and the reaction was continued for 2 h. After completion of the reaction, monitored by zero epoxy equivalent and zero acid value of the reaction mixture, the dioxane was distilled out and the viscous liquid was collected. The reaction is presented in Scheme 1. The polyol thus obtained, designated as EpxR, was characterized by determining its viscosity, hydroxyl value, acid value and percentage of non-volatile matter. The results are shown in Table 1.

### Preparation of R-60 Isocyanate adduct (PUR 60)

Dried R-60 resin (1.0 mol) placed in a three-necked round bottom flask, equipped with a nitrogen inlet tube, mechanical stirrer and condenser, was kept in a thermostated water bath at 30°C. TDI (5.0 mole) in 500 ml. of toluene was added dropwise using a dropping funnel with continuous stirring over a period of 5 h. After completion of the reaction, the viscous liquid was collected in an airtight bottle. Physical properties of PUR 60 are shown in Table 2.

**Table 1**
Physical properties of Novel polyol (EpxR)

| Polyol | Hydroxyl value | Acid value (mg/KOH) | Hydroxyl equivalent weight | Viscosity 30°C brookfield viscometer (c$P$ at 5 rpm) | Percent non volatile matter (%NVM) |
|--------|----------------|---------------------|----------------------------|-------------------------------------------------------|------------------------------------|
| EpxR   | 231            | 2.3                 | 243                        | 13320                                                 | 99.20                              |

**Table 2**
Physical properties of PUR 60

| Isocyanate adduct | Percent free NCO content | Isocyanate equivalent weight | Specific gravity 30°C | Viscosity at 30°C by FC-B IV (secs). |
|---|---|---|---|---|
| PUR 60 | 9.9 | 425 | 1.35 | 325 |

### Preparation of Castable PU Elastomers

Different PU resin sheets were prepared by a solution casting method. For this purpose, the required quantity of PUR 60 and either polyol or mixture of polyols were mixed and poured into a leveled glass plate cavity, which was subsequently placed in a vacuum desiccator. The crosslinking reaction was accomplished on the glass plate along with evaporation of the solvent at room temperature under vacuum. The different weight compositions of PEG and EpxR used were 100:00, 50:50, and 0:100. The amount of PUR 60 adduct used was such that the NCO/OH ratios obtained were 1, 1.3 and 1.7. It may be noted that prior to pouring a reaction mixture in the leveled glass plate, the mixtures were stirred and degassed under reduced pressure (2–5 mm of Hg). The sheet thickness was maintained roughly at 1 mm and was removed after overnight in the cavity.

### Swelling Experiments

The solubility parameter of the PU systems, having different crosslink densities, different compositions of EpxR polyol and different polyethylene glycol content were determined at 30°C by an equilibrium swelling method. The swelling study was carried out in various solvents with their solubility parameter ($\delta$) ranging from 7.4 to 14.5 $(cal/cm^3)^{1/2}$, where equilibration was reached. The equilibrium degree of swelling (Q) was plotted against $\delta$ in various solvents. From the plots (Figures 1, 2, and 3) it is evident that dioxane [$\delta = 9.8$ $(cal/cm^3)^{1/2}$] shows a maximum value of Q for all samples studied and hence, was used for further sorption kinetic study.
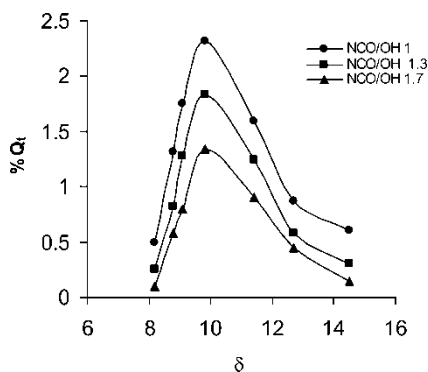


**Figure 1.** The plots of volume equilibrium degree of swelling %$Q_t$ vs. solubility parameter ($\delta$) for the system based on PEG 200: PUR 60 (NCO/OH ratio 1, 1.3 and 1.7).
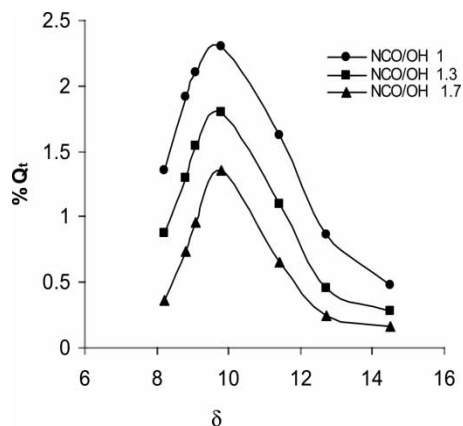
**Figure 2.** The plots of volume equilibrium degree of swelling $\%Q_t$ vs. solubility parameter ($\delta$) for the system based on PEG 400 + EpxR {50:50 w/w%}: PUR 60 (NCO/OH ratio 1, 1.3 and 1.7).

In the kinetic experiments, the so-called pat and weight technique was used for liquid sorption (20). Circular samples ($\sim$15 mm diameter) and definite thickness ($\sim$1.5 mm), after their recording dry weight, were placed in 1,4-dioxane in a standard glass bottle which was maintained at a constant temperature of $30 \pm 1°C$. Specimens were taken out at regular time intervals, with solvent adhering to the surface removed with filter paper, weighed immediately and placed into the solvent again. 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 reproducibility of results. The time taken for wiping out the solvents from the sample surface and weighing was kept minimum in order to minimize the error due to solvent evaporation.
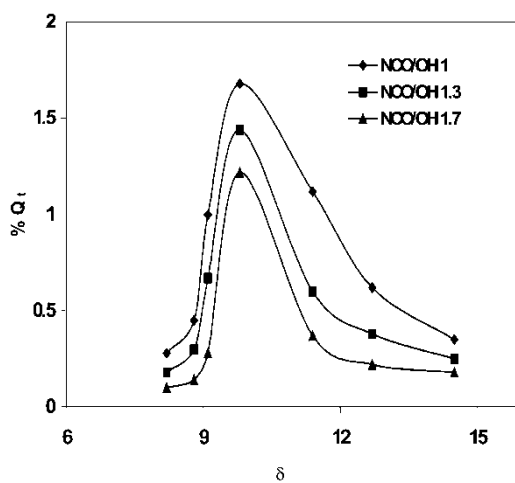


**Figure 3.** The plots of volume equilibrium degree of swelling $\%Q_t$ vs. solubility parameter ($\delta$) for the system based on EpxR: PUR 60 (NCO/OH ratio 1, 1.3 and 1.7).

## Results 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 a known equation (1) (12).

$$Q_t = [n_i/m_i] \times 100 \tag{1}$$

where, $n_i$ = moles of the solvent taken up at time t. $m_i$ = dry mass of sample.

At equilibrium swelling, $Q_t$ was considered to be $Q_\infty$, mole percent uptake at infinite time. The results are tabulated in Table 3. Figures 4, 5, and 6 show the sorption curves 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 the PU system made from EpxR with PUR 60 having NCO/OH ratio 1.7 gives a minimum value of $Q_t$ and PU made from PEG 600 with PUR 60 having NCO/OH ratio 1 gives a maximum value of $Q_t$ at the time of equilibrium. The solvent uptake capacity decreases with a decrease in the chain length of polyethylene glycol. Solvent uptake capacity of the polymers also decreases as NCO/OH ratio in the polymer increases at a given time. The data shows 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., the NCO/OH ratios being 1, 1.3, and 1.7 (PEG with PUR 60) of different PEGs. The values of $Q_\infty$ also follow the same trend.

The whole phenomena can be explained on the basis of crosslink density (NCO/OH ratio) and composition of PEGs with EpxR polyol. As the NCO/OH ratio increases, crosslink density increases and the chains become more rigid and dense and thus, the ability of polymer chains to accommodate a solvent molecule decreases. To understand the mechanism of sorption; the values of $Q_t$ and Q were substituted in the equation 2 for transport phenomena (21):

$$Q_t/Q_\infty = kt^n \tag{2}$$

where $Q_t$ is the mole percent uptake at time t and $Q_\infty$ is the equilibrium mole percent. The k constant depends on the structural characteristics of the polymer and its interaction with a solvent. The value of n determines the mode of transport. When n = 1/2, in equation (2), the 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 $Q_t/Q_\alpha$ vs. log t (correlation coefficient >0.97) with the values presented in Table 3. It was observed that the magnitude of n varied from 0.48 to a maximum 0.71, suggesting that diffusion of the solvent through the polymer was slightly deviated from the normal Fickian behavior, which may be treated as anomalous in nature. Earlier (17, 18), the n value were found to be higher than 0.5. 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

**Table 3**
Values of mole percent uptake at infinite time ($Q_\infty$), n and k value for all samples studied

| Prepolymer | NCO/ OH | $Q_\infty$(mol%) | | | [n] | | | [k × 10²] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 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 |
| PUR 60 | | 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 |
| | 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 |
| PUR 60 | | 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 |
| | 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 |
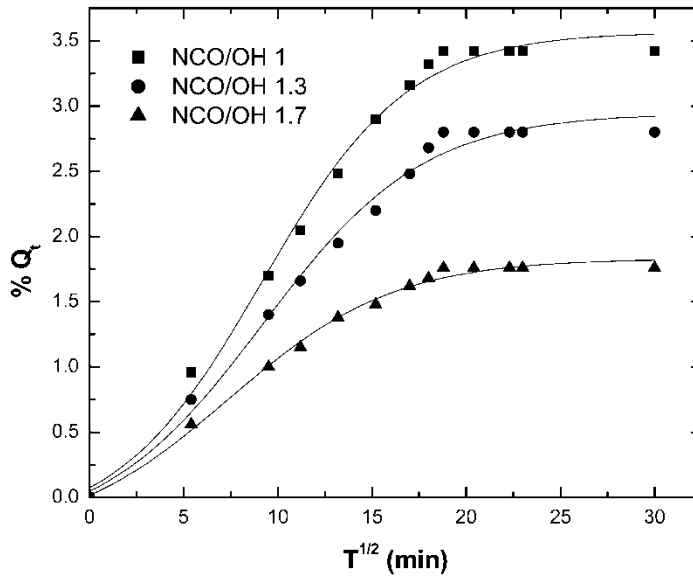
**Figure 4.** The sorption curve showing the mole percent uptake of PU network %$Q_t$, vs. (time)$^{1/2}$ system PEG 600: PUR60 NCO/OH 1, 1.3, 1.7.

calculated from the following equations (3) and (4), respectively (4, 22):

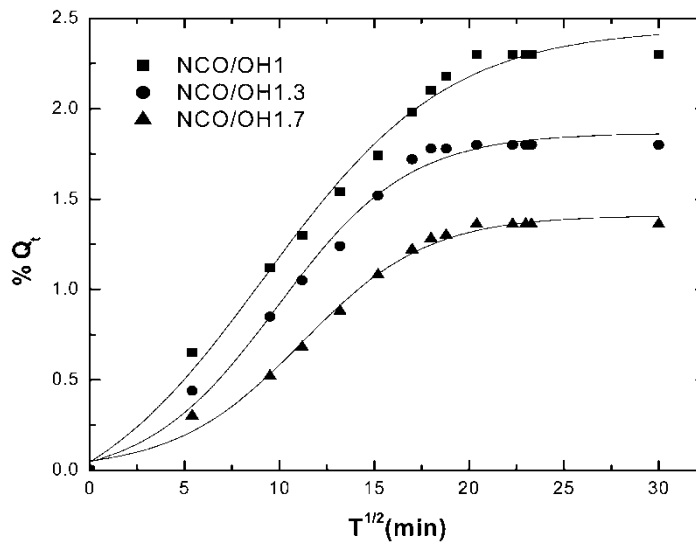$$D = \pi(h\theta/4Q_\infty)^2 \tag{3}$$

$$S = \frac{m_\infty}{m_p} \tag{4}$$



**Figure 5.** The sorption curve showing the mole percent uptake of PU network %$Q_t$, vs. (time)$^{1/2}$ system PEG 400 + Epx R(50:50% w/w): PUR 60 NCO/OH 1,1.3,1.7.
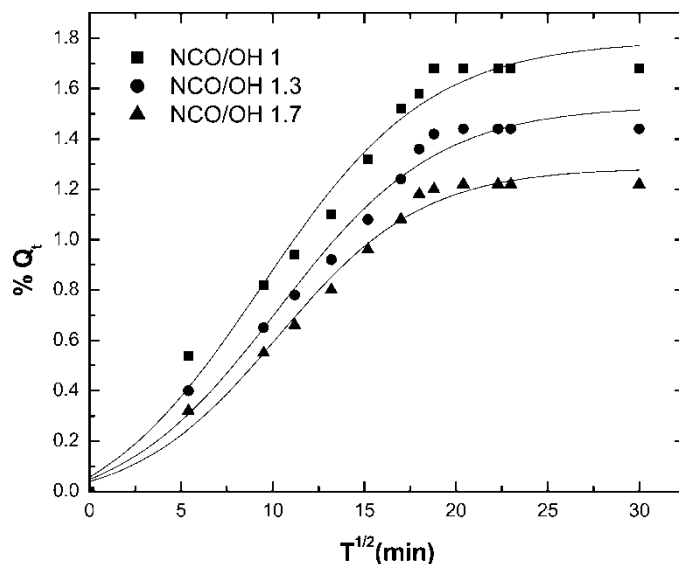
**Figure 6.** The sorption curve showing the mole percent uptake of PU network %$Q_t$, vs. $(time)^{1/2}$ system EpxR: PUR 60 NCO/OH 1, 1.3, and 1.7.

where h is the thickness of the sample and $\theta$ is the slope of the sorption curves (Figures 4, 5, and 6). Variables $m_\infty$ and $m_p$ are the mass of the solvent taken up at equilibrium and initial mass of the sample, respectively. The permeability coefficient, P, which gives the combined effect of both D and S was calculated using equation (5).

$$P = D \times S \qquad (5)$$

The values of D, S and P for all the systems are summarized in Table 4. For a given NCO/OH ratio, the diffusion coefficient increases and sorption coefficient decreases with an increase in the amount of EpxR. By increasing the EpxR content, more crosslinks develop in the PU structure. This signifies less affinity of solvent molecule for the PU network derived from EpxR with PUR60, as also seen bt the $Q_\infty$ value. The value of D is higher for PU systems synthesized 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 an increasingly more flexible polymer network is formed which can easily accommodate solvent molecules. While PEG blended with EpxR polyol reacts with PUR 60 at a given ratio of NCO/OH = 1 leads to formation of a PU network containing a greater number of urethane linkages, due to the presence of more hydroxyl groups in EpxR polyol. The resultant PU has more flexibility due to the presence of PEG and thus, it is more susceptible to attack 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 allophanate linkage will be found (23) along with the urethanes linkages having less interaction with solvent molecules, reducing the sorption coefficient values. Permeability coefficients of systems having PU network derived from PEG and PUR 60, indicate that P increases with an increase in chain length of ethylene oxide and in other cases, permeability coefficient did not show any regularity in behavior either in composition or the NCO/OH ratio in all systems studied.

**Table 4**

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

| Prepolymer | NCO/OH | [D × 10⁶ (cm²/s)] | | | [S (g/g)] | | | [P × 10⁶ (cm²/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 |
| PUR 60 | | 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 |
| | 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 |
| PUR 60 | | 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 |
| | 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 |

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 (6) (24):

$$M_c = -\frac{dV_1(V_p)^{1/3}}{\ln(1 - V_p) + V_p + \chi_{12}V_p^2} \tag{6}$$

where $V_p$ is the volume fraction of the polymer in swollen state and was calculated using the equation (7):

$$V_p = \frac{W_P/d_p}{W_P/d_P + W_S/d_S} \tag{7}$$

$w_p$ = dry wt. of polymer, $w_s$ = wt. of solvent taken up at equilibrium, $d_p$ = density of polymer, $d_s$ = density of solvent, $V_1$ = molar volume of solvent, $d$ = Density of network.

$\chi_{12}$ = polymer-solvent interaction parameter which was calculated using the equation (8) (25):

$$\chi_{12} = B + \frac{V_1(\delta_p - \delta_s)^2}{RT} \tag{8}$$

where, $\delta_p$ = solubility parameter of polymer, $\delta_s$ = 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 ($\nu$) and number of chains per unit volume (N) were also calculated using the following relations (9) and (10), respectively (12, 26):

$$\nu = \frac{1}{2M_c} \tag{9}$$

$$N = \frac{d}{M_c} \tag{10}$$

The values of $V_p$, N and $\nu$ for all the systems are given in Table 5. From Table 5, 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 the chain length of PEG increases, $V_p$ decreases. Mc also increases with increases in PEG moieties in PU systems.

Swelling of PEG 600 with PUR 60 having NCO/OH ratio 1 gives maximum value (3.42 mol%). While, in the case of EpxR polyol with PUR 60 having same ratio gives minimum value (1.28 mol%). 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 the rest of the system fall in between these extremes. The effect of crosslink density on $V_p$ and Mc follow the same trend, i.e., $V_p$ also increases with increasing the NCO/OH ratio. However, in the case of a higher NCO/OH ratio, an increase in the number of crosslink points, suggesting that distance between two crosslink points decreases and ultimately a more rigid structure is formed. As NCO/OH ratio increases in the PU system, an increasingly

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**Table 5**
Values of volume fraction of polymer (Vp), number of chains per unit volume (N) and degree of crosslinking ($\nu$)

| 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 |
| PUR 60 | | 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 |
| | 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 |
| PUR 60 | | 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 |
| | 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 |

more compact structure is formed and distance between crosslink points decreases, therefore, Mc decreases.

In the case of PU obtained from EpxR polyol and PUR 60, a more rigid structure is formed compared to the others, because of more hydroxyl groups in the polyol which reacts with more NCO groups of PUR 60, leading to formation of more crosslink points and a 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 the distance between two crosslink points increases, thus Mc increases. The values of Mc increase from PEG 200 to PEG 600 with a respective PU network. The above data were also used to establish a relationship presented by de Gennes (27) for a swollen polymer network, which is as shown below,

$$D \sim V_p^\beta \quad \text{and} \quad D \sim M_c^{-\gamma}$$

where $\beta = 3/4$ and 1 for a good and theta solvent, respectively and $\gamma = 3/5$.

Straight-line plots as shown in Figure 7, for PU systems having NCO/OH ratio 1 represent the power laws. The exponent value of $\beta$ for all the systems are approximately 1. However, in dioxane, all PU systems show high swelling, but the value of $\beta$, which is close to 1, indicates that dioxane is not a good solvent for these systems. The value of $\gamma$ were found to be in the range from 0.21–0.50, which are rather low for the theoretical prediction.

Incidentally, Oikawa and Murakami (28) have investigated poly(dimethyl siloxane) gels in benzene by means of dynamic light scattering technique and obtained $\gamma = 0.29$. Chee (29) also observed low values of $\gamma$ for the poly(ethyl methacrylate) crosslinked system.

## 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
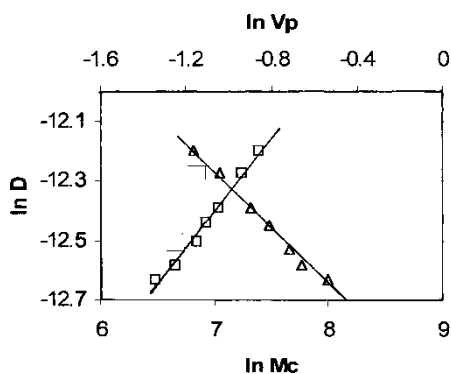


**Figure 7.** The log-log plot of diffusion coefficient (D) against $M_c$ ($\triangle$) and $V_p$ ($\square$) for polyurethanes based on systems having NCO/OH 1:1.

systems synthesized by us. Diffusion process from the sorption kinetic study was found to be anomalous in nature. 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 an important role in controlling sorption and diffusion of solvents in PU networks.

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