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Sorption and diffusion of organic solvents through interpenetrating polymer networks (IPNs) based on polyurethane and unsaturated polyester

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Abstract

The equilibrium swelling experiments of interpenetrating polymer networks (IPNs) based on castor oil based polyurethanes (PU) and unsaturated polyester (UPE) were performed in various solvents, in order to calculate their solubility parameter. The kinetics of swelling and sorption have also been studied in chlorobenzene at 25°C. IPNs with various weight composition of PU and UPE (80:20, 50:50, 20:80), and also having various crosslink density (NCO/OH ratio) viz. 1.2, 1.5 and 2.0 were employed in the study. The results are found to vary with the weight composition of the components and crosslink density of the samples. The sorption behavior is also found to vary with the hydroxyl number (molecular weight) of the polyol employed in the preparation of PU. Studies revealed that, the sorption is anomalous in nature in all the cases. Diffusion coefficient (*D*) is found to increase with both increase in NCO/OH ratio and UPE content, whereas sorption coefficient (*S*) shows a reverse trend in all the samples studied. From the swelling studies, the molecular weight between two crosslinks (M_c) and hence the number of chains per unit volume (*N*) and degree of crosslinking (*v*) were also calculated. The results obtained were compared with that of the homopolymer networks. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Castor oil; Polyurethane; Unsaturated polyesters; Network; Sorption; Degree of crosslinking

1. 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 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. As a result, the dimensional network gets extended 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 polymers, which are used in various applications such as membranes, ion exchangers, etc. The transport properties of various engineering polymers like polyurethanes, crosslinked polystyrene, natural rubber and various synthetic rubbers have been extensively studied using organic solvents with various polarity and interacting groups, and also using aqueous salt solutions of various acids by many researchers [5–9]. However, the transport properties of interpenetrating polymer networks (IPNs) are rarely found in the literature [10,11] eventhough they are widely used in many applications such as membranes, gel permeation chromatography, control release of drugs and enzyme immobilization [12–15]. IPNs are materials containing two or more polymers in a network form, in which at least one of the components is synthesized or crosslinked in the immediate presence of the

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other [12]. They differ in their swelling from other crosslinked polymers as they consist of two components, one rubbery and the other glassy. 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 [6]. The aim of the present study is to investigate the sorption behavior of IPNs made of castor oil based polyurethane (PU) and unsaturated polyester (UPE) with changes in parameters such as: (a) crosslink density (NCO/OH ratio), (b) weight composition of components, PU and UPE in the IPN and (c) hydroxyl value of polyols (R60 and R92).

2. Experimental

2.1. Materials

The UPE used in the study was synthesized from orthophthalic acid (1 mol) and propylene glycol (2.2 mol) by a dry process. Maleic anhydride (1 mol) was used to provide unsaturation along the polymer chain. The acid value was determined by end group analysis and was found to be ~20. Styrene (35% w/w) was used as the crosslinker for the UPE phase. The detailed synthesis is beyond the scope of this article. The polyols, designated as R60 and R92, used in the study are castor oil modified resins and were supplied by H.K. Agencies, Ahmedabad, India. The specifications are given in Table 1.

The PU was formed in situ, during the IPN synthesis, by the reaction of toluene diisocyanate (TDI), an 80:20 mixture of 2,4 and 2,6 isomer, with polyols R60 and R92, respectively. IPNs were synthesized from the above mentioned PU and UPE by a simultaneous polymerization technique [12]. Thus, different sets of samples were prepared by changing various parameters, such as weight composition of PU and polyester viz. 80:20, 50:50 and 20:80; crosslink density (NCO/OH ratio) viz. 1.2, 1.5 and 2.0 and also by varying the type of polyol (R60 or R92) by a transfer molding technique. All the solvents used were of analytical grade and were further purified by distillation.

2.2. Swelling experiments

The solubility parameters of the IPNs having various crosslink densities and compositions were determined at 30°C by equilibrium swelling method. Swelling was carried out in various solvents ranging their solubility parameter value (δ) from 7.4 to 14.5 (cal/cm^3)$^{1/2}$, until an equilibrium weight was achieved. The equilibrium degree of swelling (Q), which is the reciprocal of the volume fraction of polymer in swollen state (V_p), was calculated from the swelling data using the relation $Q = 1/V_\mathrm{p}$ and was plotted against δ of various solvents. From the plots (Fig. 1), chlorobenzene ($\delta = 9.5$ (cal/cm^3)$^{1/2}$) gave the maximum value of Q for all the samples studied and hence was used for further sorption kinetic studies.

In the kinetic experiments, the so-called pat-and-weight technique was used for liquid sorption [16]. Circular samples (diameter of ~1.5 cm) of definite thickness, after taking the dry weight were placed in chlorobenzene in a standard joint test tube, which was maintained at a constant temperature of 25 ± 0.1°C. Specimens were taken out at regular intervals of time, solvent adhering to the surface is rubbed off, weighed immediately and replaced in the solvent. This procedure was continued till equilibrium swelling was achieved. This was repeated for at least three specimens from each network in order to ensure the reproducibility of results. The time taken for wiping out the solvent from sample surface and weighing was kept minimum in order to minimize the error due to solvent evaporation. Identical experiments were performed for homopolymer networks also.

Table 1
Specifications of polyols

Polyol	Hydroxyl groups/mol	Equivalent weight	Brookfield viscosity (cP)
R60	5.0	220	620 ± 6
R92	6.0	190	700 ± 10

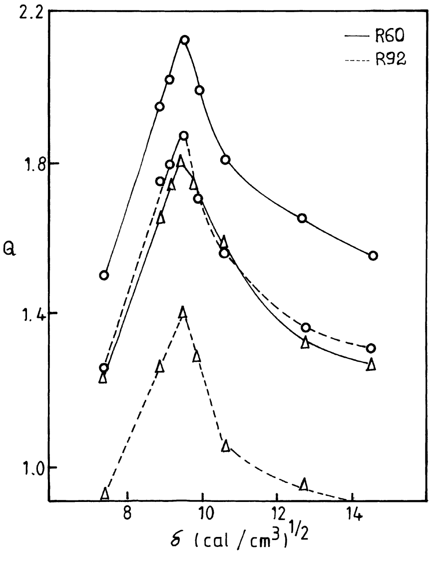

Fig. 1. The plot of volume equilibrium degree of swelling (Q) versus solubility parameter (δ) for IPNs based on R60 (—) and R92 (- - -) having NCO/OH ratio, 1.2 (○) 80:20 and (△) 20:80.

3. 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 the equation [7]

$$Q_t = \frac{m_e/m_r}{m_i} \times 100,$$

where m_e is the mass of solvent taken up at equilibrium, m_r is the relative molecular mass of solvent and m_i is the dry weight 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. Figs. 2 and 3 show the sorption curves of PU, UPE and various IPNs (NCO/OH = 1.2) obtained by plotting Q_t versus $(\text{time})^{1/2}$. From the curves it is clear that, the homopolymer networks 100% PU (100:00) and 100% UPE (00:100) show the maximum and minimum values of Q_t, respectively, at a particular time. The uptake capacity of IPNs was intermediate between that of the constituents. With increase in the UPE content and NCO/OH ratio, sorption decreases and reaches a minimum value irrespective of the type of PU used in all the samples. The values of Q_∞ also follow the same trend.

The whole phenomena can be explained on the basis of crosslink density and composition of network. As NCO/OH ratio increases, crosslink 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 of 1.2, the chains will have maximum flexibility due to less crosslink points, and thus, the sorption capacity will be maximum. With further increase in the NCO/OH ratio to 1.5 and 2.0, flexibility of chains gradually decreases resulting in less sorption and hence low values of Q_t and Q_∞. From Table 2, it is also clear that IPNs made of R60 based polyol show more solvent uptake capacity compared to that made of R92 based polyol. This could be due to more number of hydroxyl groups in the latter (Table 1) which leads to increase in crosslink density. The values of V_p and N (Table 4) also support the above reasoning.

To understand the mechanism of sorption, the values of Q_t and Q_∞ were substituted in the general equation for transport phenomena [17]

$$Q_t/Q_\infty = kt^n,$$

where Q_t is the mole percent uptake at time t and Q_∞ is the equilibrium mole percent uptake. k is a constant, which depends on the structural characteristics of the polymer and its interaction with solvent. The values of n determine the mode of transport. In the general equation for transport phenomena, when $n = 1/2$, diffusion

Table 2
Values of mole percent uptake at infinite time (Q_∞), n and k for all the samples studied

Polyol	NCO/OH	Q_∞ (mol%), PU:UPE (w/w%)					n, PU:UPE (w/w%)					$k \times 10^2$, PU:UPE (w/w%)				
		100:00	80:20	50:50	20:80	00:100	100:00	80:20	50:50	20:80	00:100	100:00	80:20	50:50	20:80	00:100
R60	1.2	2.01	1.89	1.56	1.23	0.80	0.53	0.54	0.59	0.62	0.64	3.94	4.21	3.66	5.42	4.79
	1.5	1.96	1.70	1.40	1.04	0.80	0.52	0.60	0.52	0.58	0.64	5.84	3.99	4.11	4.84	4.79
	2.0	–	1.49	1.29	0.95	0.80	–	0.56	0.51	0.63	0.64	–	4.63	4.44	3.82	4.79
R92	1.2	1.74	1.50	1.32	0.99	0.80	0.51	0.57	0.54	0.62	0.64	4.11	2.98	5.48	4.01	4.79
	1.5	1.67	1.37	1.17	0.82	0.80	0.51	0.55	0.63	0.56	0.64	6.10	3.62	4.23	5.33	4.79
	2.0	–	1.28	1.05	0.84	0.80	–	0.61	0.58	0.60	0.64	–	5.12	4.71	5.01	4.79

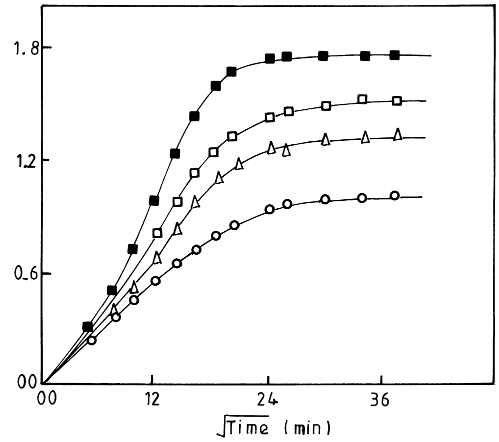

Fig. 2. The sorption curves showing the mole percent uptake of homopolymer networks and IPNs based on R60, (■) 100:00 (□) 80:20 (△) 50:50 (○) 20:80 and (▲) 00:100.

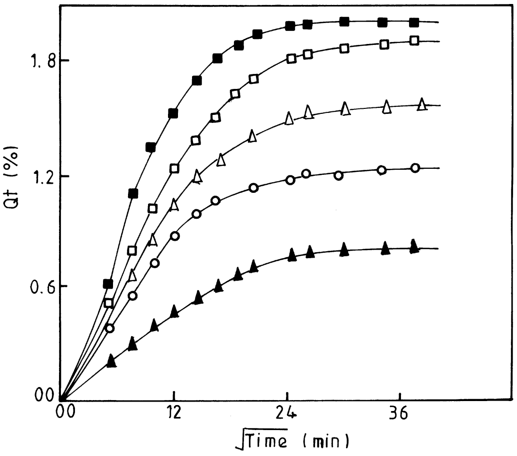

Fig. 3. The sorption curve showing the mole percent uptake of homopolymer networks and IPNs based on R92; symbols are as shown in Fig. 2.

obeys Fick's law, which occurs when segmental mobility of the polymer chains is faster than the rate of diffusion of penetrant molecules. When $n = 1$, the diffusion is said to be non-Fickian. In the present system, the values of k and n were obtained from the linear plot of $\log Q_t/Q_\infty$ versus $\log t$ (correlation coefficient > 0.95), and are represented in Table 2. In all the cases, the magnitude of n varies from 0.51 to a maximum of 0.64, which suggests that the diffusion process deviates slightly from the normal Fickian behavior and may be treated as anomalous in nature.

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 molecules to move among the polymer segment and the sorption coefficient S, which gives an idea about the equilibrium sorption, were calculated from the following equations [4,15].

$$D = \pi(h\theta/4Q_\infty)^2 \quad \text{and} \quad S = m_\infty/m_p,$$

where h is the thickness of the sample and θ is the slope of the linear portion of the sorption curve. m_∞ and m_p represent the mass of the solvent taken up at equilibrium and the initial mass of the sample, respectively. The permeability coefficient (P), which gives a combined effect of both D and S, was also calculated using the equation $P = D \times S$. The values of D, S and P for all the systems are summarized in Table 3.

For a given NCO/OH ratio, the diffusion coefficient increases and the sorption coefficient decreases with an increase in the polyester content. This signifies less affinity of solvent molecules with the polyester moiety, as can also be seen from their Q_∞ values. The PU network show high sorption in chlorobenzene compared to UPE network. This may be due to the specific interaction of solvent molecules with PU and more segmental mobility compared to the UPE network. The values of diffusion coefficient are slightly higher in PU and IPNs based on R92 compared to that based on R60 polyols. This is in contradiction with the general tendencies observed in the swelling studies [18]. This higher values of D in R92-based systems may be due to the formation of more number of polyurethane linkages, there by rendering it more susceptible to attack by chlorobenzene molecules. It is also observed that the sorption coefficient decreases with an increase in the NCO/OH ratio for a given composition. At low NCO/OH ratios, the network structure is more flexible and mainly forms urethane linkage, which may have specific interaction with chlorobenzene. However, as the NCO/OH ratio increases, more of allophanate linkages will be formed [19] along with urethane linkages having less interaction with solvent molecules and hence reducing the sorption values. The permeability coefficient did not show any particular trend with either change in the composition or the NCO/OH ratio in all the IPNs studied.

The average molecular weight between two crosslinks (M_c), which is a direct measure of the crosslink density, was measured from the well known Flory–Rehner equation [20].

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

where V_p is the volume fraction of the polymer in the swollen gel, V_1 is the molar volume of solvent, ρ is the density of the network, χ_{12} is the polymer solvent interaction parameter which is calculated by using the following equation [21]:

Table 3
Values of diffusion coefficient (D), sorption coefficient (S) and permeability coefficient (P) for various samples in chlorobenzene

Polyol	NCO/OH	$D\times10^6$ (cm^2/s), PU:UPE (w/w%)					S (g/g), PU:UPE (w/w%)					$P\times10^6$ (cm^2/s), PU:UPE (w/w%)				
		100:00	80:20	50:50	20:80	00:100	100:00	80:20	50:50	20:80	00:100	100:00	80:20	50:50	20:80	00:100
R60	1.2	3.51	3.84	4.42	5.88	8.63	2.30	2.10	1.58	1.09	0.78	8.07	8.06	6.98	6.40	6.73
	1.5	3.69	4.12	4.86	6.14	8.63	2.13	1.69	1.52	1.01	0.78	8.43	6.96	7.38	6.20	6.73
	2.0	–	5.03	6.01	7.22	8.63	–	1.56	1.26	0.94	0.78	–	7.84	7.57	6.78	6.73
R92	1.2	4.14	4.33	4.91	6.64	8.63	2.01	1.91	1.40	0.98	0.78	8.32	8.27	6.87	6.50	6.73
	1.5	4.51	4.81	5.93	7.04	8.63	1.90	1.70	1.19	0.94	0.78	8.56	8.17	7.05	6.61	6.73
	2.0	–	5.92	6.64	8.21	8.63	–	1.64	1.12	0.80	0.78	–	9.70	7.43	6.55	6.73

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

where δ_p and δ_s are the solubility parameters of the polymer and the solvent, respectively, and B, the lattice constant, which is taken as 0.34.

The degree of crosslinking (v) and the number of chains per unit volume (N) were also calculated for all the samples using the equations [7,22]:

$$v = 1/(2M_c) \quad \text{and} \quad N = \rho/M_c,$$

where ρ is the density of the network.

The values of V_p, N and v for all the systems are given in Table 4. From the table, it can be confirmed that the present system as a whole has got a high crosslink density. For a given NCO/OH ratio, V_p increases while M_c decreases with an increase in the UPE content, indicating that the swelling of IPNs in chlorobenzene is largely attributed to the PU content rather than to the UPE content. The values of M_c are maximum and minimum for the homopolymers, PU and UPE, respectively. Such low values of M_c in the UPE network seem to be the result of the formation of shorter chains between two crosslinks compared to that of the PU. The values of IPNs fall in between that of homopolymer networks depending on the contribution of PU and UPE.

The effect of the crosslink density on V_p and M_c follow the same trend as observed for compositional variations. As the NCO/OH ratio of PU increases, for a given composition, the number of crosslink points increases, and ultimately, the system becomes more rigid in nature with low values of M_c.

PU network and its IPNs based on R92 polyol show low values of M_c compared to those based on R60 polyol. This could be due to more number of hydroxyl groups present in the former, which lead to more number of crosslink points compared to the system based on R60.

The above data were also used to establish a relationship put forward by de Gennes [23] for swollen polymer networks, 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 $\gamma = 3/5$. These power laws are represented by straight line plots as shown in Fig. 4, for IPNs based on R60 having NCO/OH ratio 1.2. The exponent values of β for all the IPNs are nearly 1, which is agreeable with the foregoing theoretical prediction and other findings [24] within experimental errors. This means that chlorobenzene is a poor solvent for the present IPN system at 25°C. The γ values were found to be in the range of 0.35–0.48, which are rather small compared to the theoretical prediction. Incidentally Oikawa and Murakami [25] have investigated poly(dimethyl siloxane) gels in benzene by means of

Table 4
Values of volume fraction of polymer (V_p), number of chains per unit volume (N) and degree of crosslinking (ν) for the IPNs studied

Polyol	NCO/OH	V_p, PU:UPE (w/w%)					$N\times10^3$ (mol/ml), PU:UPE (w/w%)					$(\nu\times10^4$ (mol/g), PU:UPE (w/w%)				
		100:00	80:20	50:50	20:80	00:100	100:00	80:20	50:50	20:80	00:100	100:00	80:20	50:50	20:80	00:100
R60	1.2	0.394	0.479	0.526	0.688	0.848	0.86	1.18	1.52	3.48	8.16	4.05	5.36	6.58	14.32	32.67
	1.5	0.401	0.536	0.528	0.700	0.848	1.06	1.61	1.54	3.70	8.16	4.95	7.22	6.60	15.29	32.67
	2.0	–	0.549	0.594	0.701	0.848	–	1.72	2.25	3.63	8.16	–	7.70	6.93	15.01	32.67
R92	1.2	0.442	0.539	0.578	0.701	0.848	0.96	1.59	2.00	3.72	8.16	4.46	7.18	8.63	15.29	32.67
	1.5	0.484	0.564	0.580	0.720	0.848	1.21	1.86	2.02	4.10	8.16	5.63	8.33	8.66	16.83	32.67
	2.0	–	0.571	0.587	0.721	0.848	–	1.93	2.09	4.11	8.16	–	8.62	8.97	16.77	32.67

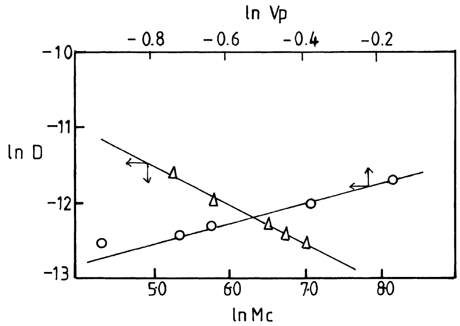

Fig. 4. The log–log plot of diffusion coefficient (D) against M_c (Δ) and V_p ($\bigcirc$) for IPNs based on R60 having an NCO/OH ratio of 1.2.

dynamic light scattering technique and obtained $\gamma = 0.29$. Chee [26] also observed low values of γ for the poly(ethyl methacrylate) crosslinked system.

4. Conclusions

All the IPNs studied show high crosslink densities and hence low diffusion and sorption values compared to the common crosslinked networks. For a given crosslink density, the sorption decreases with an increase in the polyester content. Increase in the crosslink density also reduces the sorption for a given composition. The diffusion process from the sorption kinetic study was found to be anomalous in nature.

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