Sorption Behavior of Biodegradable Polyurethanes with Carbohydrate Crosslinkers

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ABSTRACT: Polyether–polyurethanes (PUs) with a series of carbohydrate crosslinkers: monosaccharide (glucose), disaccharide (fructose) and polysaccharide (starch), were synthesized. The kinetics of swelling was studied in industrially important solvents like toluene, xylene and chlorobenzene. The R value and diol / triol ratio were varied to study the effect on crosslink density and sorption. It was observed that the swelling extent increased with increasing concentration of crosslinker in the polymer. Interestingly the effect of diisocyanate concentration on extent of sorption varied with the type of carbohydrate used for crosslinking. Considering the effect of diisocyanate con-

centration, the PUs containing disaccharide sucrose showed greater solvent uptake. Though the sorption behaviours were different, the solubility parameters of all PUs were the same irrespective of the type and concentration of the crosslinkers. All the PUs were observed to be biodegradable with glucose containing PUs exhibiting highest weight loss. Scanning electron microscope revealed absence of phase segregation in all the PU systems. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1296–1305, 2010

Key words: polyurethane; sorption; biodegradable; carbohydrates

INTRODUCTION

The study of structure–property relationship in segmented polyurethanes (PUs) has acquired importance because of their broad range of applications. The prediction of the swelling extent of crosslinked polymer network by a pure solvent has received considerable attention in past years, given the direct implication it offers in selecting a polymeric material for defined barrier or permeation properties.

The idea of swelling equilibrium was developed by Flory and Rehner,[1] and since then many scientists have extensively studied the sorption phenomenon. On the basis of the observed swelling process, parameters could be assessed, which were specific for the mass transfer process, i.e., diffusion coefficient, sorption coefficient, and permeability coefficient.

Aminabhavi and coworkers[2–7] have extensively studied the transport of organic solvents through various polymers like commercial PU membranes, PU/PBMA interpenetrating polymer network,[5] tetrafluoroethylene/propylene,[6] and PVA systems[7] at different temperatures. Their studies showed that molecular migration depends on membrane–solvent interactions, size of the penetrants, temperature, and availability of free volume within the membrane matrix.

Nair et al.[8] have carried out swelling experiments of block copolymers based on natural rubber as soft segment and PU derived from toluene diisocyanate and 1,3-butane diol (1,3-BDO) as hard segment in various solvents. Block copolymers with different NCO/OH ratio, viz., from 1.26 to 1.96 were employed in this study. The crosslink densities and sorption behavior was found to vary with the NCO/OH ratio.

The kinetics of swelling and the sorption performance were observed by Krol and Wojturska[9] for the interpenetrating polymer networks of PU and unsaturated polyester during their exposure to chlorobenzene at 25°C. It was found that the rates for solvent transport and solvent absorption processes were controlled by the chemical composition of the formulation studied. In the scanning electron microscope analysis of samples, which had been subjected to swelling, no leaching was observed for any phase present in the system, despite phase separation for both the components. Krishnaiah et al.[10] have applied the pervaporation method for dehydration of tetrahydrofuran by using crosslinked poly(vinyl alcohol)/poly(ether imide) (PVA/PEI) blend membranes.

Although PUs are technologically and industrially important products, nonbiodegradability is restricting their utility in commodity applications. Hence, the possibility of converting them into partially biodegradable products is investigated. Among carbohydrates, the use of starch in the synthesis of PUs has been reported in only a few publications.[11–16] Dosmann and Steel[11] added starch to urethane

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systems to yield shock-absorbing foams. Lu et al.[12] have studied the miscibility and physical properties of plasticized starch modified with PU. They observed that the occurrence of hydrogen bonding interaction between starch and PU plays a key role in the improvement of the performance of the material. A study of rheological properties of PU incorporated with starch granules was carried out by Ha and Broecker.[16]

Biodegradable PUs containing starch have been synthesized and characterized in our laboratory.[17] The sorption kinetics of various PUs has also been studied by us in the past.[18] As a further development, we synthesized biodegradable PUs using a series of carbohydrate like glucose (monosachharide), sucrose (disachharide), and starch (polysachharide) as crosslinkers by varying the NCO : OH and diol : triol ratios. The PUs synthesized were observed to swell in industrially important solvents—toluene, xylene, and chlorobenzene.

The data obtained from the sorption experiments were used to calculate molecular weight, degree of crosslinking, and sorption coefficient S. It is useful to select material for membrane and barrier applications. Moreover, an attempt was made to evaluate structural parameters that describe topology of the obtained networks. The morphology and biodegradation studies of PUs were also carried out.

EXPERIMENTAL

Materials

The polypropylene glycol (PPG), molecular weight 2000, and hexamethylene diisocyanate (HMDI) were purchased from Fluka AG, Switzerland. The crosslinkers—glucose, sucrose, and starch—were supplied by Qualigens, Bombay, India. The synthesis of PUs was carried out by a procedure already reported earlier.[17] The molar compositions of PUs synthesized are given in Table I. The PUs containing glucose, sucrose, and starch as crosslinkers are designated as Gl, Su, and St, respectively. The symbols A, B, and C denote R value 1, 1.25, 1.5, respectively, with a constant diol : crosslinker ratio 1. The system B was synthesized with two more diol : crosslinker ratios 0.66 and 1.2 designated as B (0.66) and B (1.2).

Sorption studies

The sorption studies were carried out by the reported procedure.[18] The possibility of an error introduced due to evaporation of solvent while weighing was minimized by weighing as quickly as possible within 30 s. The sorption was carried out at $(27 \pm 1)°C$. Sorption experiments were continued until attainment of equilibrium.

The results of the sorption process are expressed as moles of solvent sorbed by 100 g of the polymeric material (Q_t) at time t, because it is more convenient than the actual weight gain results and is the practice followed in literature. This was calculated by using equation[18]:

$$Q_t = \frac{M_s/M_{r(s)}}{M_p} \times 100 \qquad (1)$$

where M_s is the mass of the solvent absorbed at equilibrium, $M_{r(s)}$ is the relative molecular mass of the solvent, and M_p is the initial mass of the polymer sample. At equilibrium, Q_t is taken as Q_∞, i.e., the mole percent uptake at infinite time.

Soil degradation studies

Biodegradation of the PUs was studied by the soil burial method as per the procedure described elsewhere.[19]

Morphology

The surface morphology of the PUs before and after swelling was examined by means of Jeol Scanning Electron Microscope (model-JSM-5610 LV). An accelerating potential of 15 kV was used for the analysis of the sample. The photographs of representative areas of the samples were taken at different magnifications.

TABLE I
The Molar Composition of PUs Synthesized

| Code | Components | | | | |
	PPG-2000	HMDI	Crosslinkers (St/Su/Gl)	NCO/OH (R Value)	Diol/Crosslinker
A	1.0	2.0	1.0	1.0	1.0
B (0.66)[a]	0.8	2.5	1.2	1.25	0.66
B	1.0	2.5	1.0	1.25	1.0
B (1.5)[a]	1.2	2.5	0.8	1.25	1.5
C	1.0	3.0	1.0	1.5	1.0

In A, B, and C, diol : crosslinker ratio = 1.
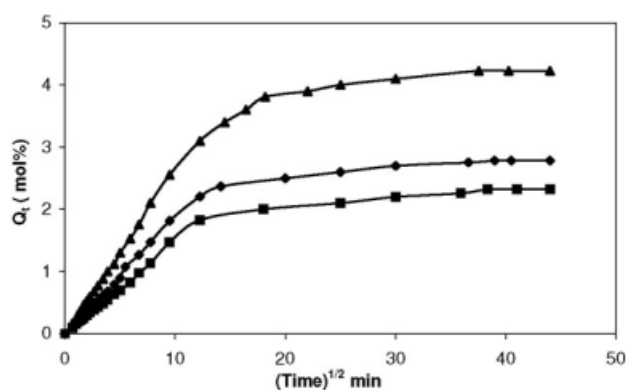[a] The figure in parentheses indicates diol : crosslinker ratio.

Figure 1 Sorption plots for Gl-B(1.5) PU in the three solvents (■) xylene (◆) toluene (▲) chlorobenzene.

RESULTS AND DISCUSSION

Sorption of solvents by a series of PUs under study is expressed as mole percentage uptake (Q_t) versus square root of time. From the representative plots for Gl B(1.5) PU (Fig. 1), with varying crosslinker concentration and isocyanate content, it is observed that the extent of sorption goes on increasing from xylene to toluene to chlorobenzene in all cases. Also the solvent intake is much higher in case of chlorobenzene, which can be attributed to the greater difference in solubility parameter between chlorobenzene and toluene. (The solubility parameters of toluene, xylene, and chlorobenzene are 8.8, 8.9, and 9.5 $(cal/cm^3)^{1/2}$ respectively.) The degree of swelling was found to be inversely proportional to the concentration of crosslinkers. As the diol to crosslinker ratio increases in the system from 0.66 to 1.5, the extent of swelling increases. This is clearly seen in Figure 2. Similarly, the samples having a higher content of isocyanate and thus higher crosslinking due to the formation of allophan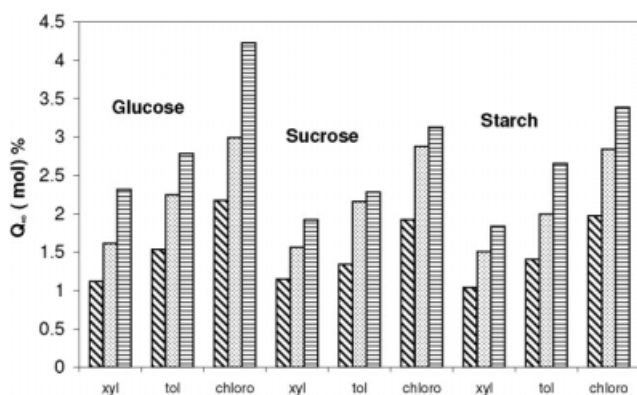ates are expected to show lower swelling in all the solvents.[18] But interestingly, this was the case only in PUs containing sucrose as crosslinker where order of solvent uptake was A > B > C (Fig. 3). Thus, for this set of PUs, the polymers with higher R values are efficiently crosslinked, less flexible, and hence have lower solvent uptake. The reason for this may be higher uptake capacity of this system.

In case of St-PUs and Gl-PUs, the order of maximum uptake was observed to be B > C > A. This anomaly in the trend can be explained on the basis of the structure of HMDI. It has a long chain of six methylene groups, which makes it a flexible molecule. Generally, increase in isocyanate content increases the crosslinking and hence the rigidity of the network. But an isocyanate like HMDI can also increase the flexibility of the polymer. The higher values of Q_∞ for samples B and C compared with A indicates that high isocyanate content increases the overall flexibility of the PU molecule. Again among B and C, greater swelling is observed in case of B, though the content of isocyanate is less. This suggests that the crosslinking effect of HMDI is more dominant at this concentration.

Considering the effect of isocyanate concentration, among the carbohydrate crosslinkers, the sorption was found to be maximum in case of PUs containing sucrose followed by those containing glucose and starch. The lowest swelling observed in case of St-PUs is attributed to multiple hydroxyls, which lead to formation of multiple isocyanate linkages and greater crosslinking. In addition, the polymeric structure of starch promotes formation of strong network. Similarly, Su-PUs should exhibit lower swelling than Gl-PUs because of more number of hydroxyls per molecule in sucrose than glucose. But the reverse is observed, which may be due to the plasticization effect of the disaccharide; sucrose also reflected in the normal trend observed in samples with different R values.

Figure 2 Variation of final solvent uptake with diol : crosslinker ratio for the three sets of PUs in toluene, xylene, and chlorobenzene. ▨ 0.66, ▥ 1, and ▤ 1.5.
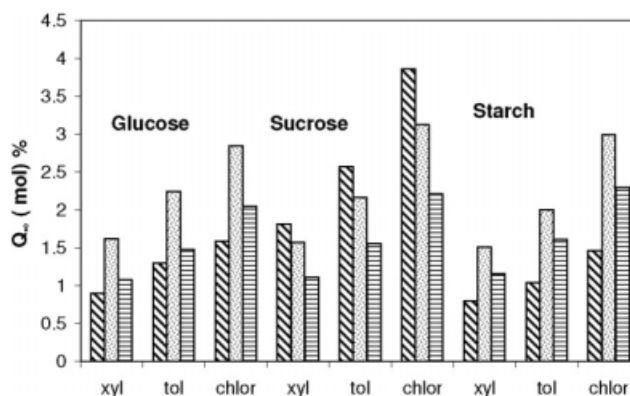

Figure 3 Variation of final solvent uptake with R value for the three sets of PUs in toluene, xylene, and chlorobenzene. ▨ A, ▥ B, and ▤ C.

TABLE II
Values of n and k (g/g min^2) for Diffusional Behavior

Code	Chlorobenzene		Toluene		Xylene	
	n	k	n	k	n	k
St A	0.79	0.26	0.36	0.17	0.25	0.17
St B (0.66)	0.99	0.06	0.47	0.05	0.44	0.06
St B	0.99	0.04	0.52	0.07	0.42	0.08
St B (1.5)	0.99	0.05	0.53	0.05	0.53	0.06
St C	0.45	0.05	0.49	0.05	0.45	0.04
Su A	0.65	0.06	0.43	0.04	0.40	0.04
Su B (0.66)	0.44	0.07	0.44	0.04	0.40	0.07
Su B	0.96	0.05	0.49	0.07	0.47	0.06
Su B (1.5)	0.30	0.11	0.48	0.08	0.45	0.08
Su C	0.98	0.18	0.50	0.05	0.48	0.06
Gl A	0.42	0.14	0.40	0.12	0.43	0.11
Gl B (0.66)	0.47	0.13	0.36	0.07	0.37	0.12
Gl B	0.52	0.12	0.35	0.06	0.47	0.06
Gl B (1.5)	0.51	0.06	0.50	0.06	0.40	0.08
Gl C	0.50	0.05	0.49	0.06	0.50	0.06

Diffusion process

Diffusion of a liquid in a polymer matrix is described by Fick's laws.[2] In a Fickian diffusion, the rate of diffusion is much less than that of relaxation due to mechanical and structural modes of the polymer–solvent interaction. Deviation from Fickian diffusion can occur for different reasons such as when sorption equilibrium is not achieved at a film surface due to an appreciable surface evaporation rate or when diffusion and relaxation rates are comparable. As a result, non-Fickian or anomalous sorption curves exhibit sigmoidal shapes.

The sorption curve in Figure 1 shows that the transport is very rapid in the beginning upto about 50% of equilibrium sorption and then levels off as equilibrium is approached.

To study the diffusion mechanism, the results were fitted into the equation[20]:

$$\log (Q_t / Q_\infty) = \log k + n \log t \qquad (2)$$

where k is a constant, which indicates the extent of polymer–solvent interaction, and is a property characteristic of the polymer. The value of n indicates the type of sorption phenomenon. For Fickian diffusion, n is upto 0.5, whereas for values of n between 0.5 and 1, the diffusion is said to be anomalous. The values of n and k are determined by linear regression analysis. The glucose containing PUs showed fickian diffusion almost entirely in all the solvents with n values between 0.1 and 0.5 (Table II), whereas sucrose and starch containing PUs exhibited non-Fickian diffusion in chlorobenzene. In the beginning, the curves seem to be showing a slight sigmoidal shape, which indicates the non-Fickian trend. Thus, the diffusion mechanism observed in the present study is mainly of Fickian type. Chlorobenzene causes a significant

amount of swelling of the polymers, which may result in greater surface vaporization and hence an anomalous type of diffusion. The values of k in all the solvents are almost same and are well below Flory's critical value of 0.5. A slightly higher value in chlorobenzene indicates greater interaction with the solvent.

The observed order of sorption of the solvents under study can be explained on the basis of solubility parameter theory. Maximum swelling of a crosslinked polymer can take place in the solvent whose solubility parameter is close to that of the polymer. The solubility parameter of the polymers was calculated by allowing them to swell in a series of solvent of varying solubility parameter viz. acetone, dichloroethane, dichloromethane, glacial acetic acid, and isoamylalcohol. The extent of sorption at equilibrium was noted in each case. The swelling coefficient α was calculated by using the equation[18]:

$$\alpha = \{M_s/M_p\} \times \{1/\rho_s\} \qquad (3)$$

where M_s is the mass of the solvent at equilibrium, ρ_s is density of the solvent, and M_p is the initial mass of the polymer sample; α is indicative of the volume of solvent per unit mass of the polymer. The representative plots of swelling coefficient α versus solubility parameters of solvents for PUs containing highest amount of carbohydrate are shown in Figure 4. It is observed that maximum swelling takes place in glacial acetic acid. Hence, the solubility parameter of the PUs under study was considered to be 10.1 $(cal/cm^3)^{1/2}$ irrespective of the type of crosslinker used in the present systems. This may be because the three crosslinkers are chemically very similar and are expected to have same effect on the solubility parameters. It was observed from the swelling data of other PUs that the solubility parameter also does not depend on the concentration of diisocyanate or crosslinker. This is because the polyol has
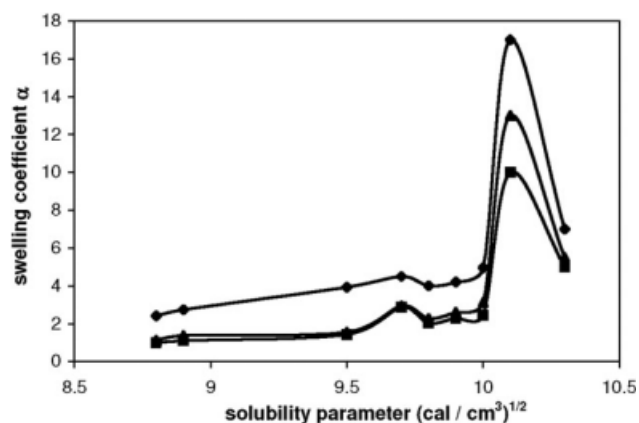
Figure 4 Swelling coefficient of PUs (system A) with different crosslinkers versus solubility parameters of solvents, (■) starch, (◆) sucrose, and (▲) glucose.

TABLE III
Values of the Swelling Coefficient α

Code	Chlorobenzene	Toluene	Xylene
St A	1.43	1.10	0.99
St B (0.66)	1.98	1.52	1.30
St B	2.94	2.13	1.79
St B (1.5)	3.38	2.82	2.31
St C	2.25	1.71	1.46
Su A	3.93	2.74	2.42
Su B (0.66)	1.96	1.43	1.39
Su B	2.87	2.31	1.95
Su B (1.5)	3.20	2.42	2.38
Su C	2.27	1.65	1.37
Gl A	1.55	1.38	1.12
Gl B (0.66)	2.13	1.68	1.38
Gl B	2.85	2.30	2.01
Gl B (1.5)	4.15	2.96	2.86
Gl C	2.01	1.58	1.36

high equivalent weight and is the component with high weight percentage. Hence, the contribution of other components to the total weight of the polymers is less and does not affect the properties like solubility parameter. For the solvents under study, it is observed that chlorobenzene has the closest solubility parameter to the polymers, and hence shows highest swelling coefficient (Table III).

Solubility parameter was also calculated from the following equation[8] representing Gee's theory.[21]

$$Q/Q_{max} = \exp[-a\,Q(\delta_S - \delta_P)]^2] \qquad (4)$$

where Q is the swelling ratio of the polymer reaching swelling equilibrium, a is a constant, and δ_P and δ_s are the solubility parameters of the polymer and the solvent, respectively. Q_{max} can be calculated for the following equation where w is taken as the weight fraction of the maximally swollen sample.

$$Q_{max} = [1 + \rho/\rho_S\,(W^{-1} - 1)] \qquad (5)$$

The maxima in the plot of Q_{max} against solubility parameter of solvents correspond to the solubility
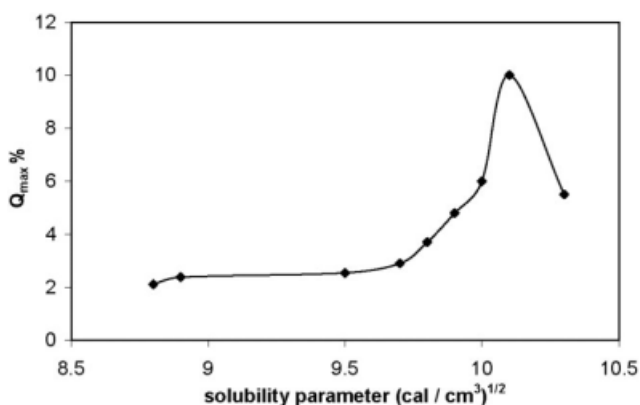
Figure 5 Plot of Q_{max} versus solubility parameters of solvents for Gl-A PU.
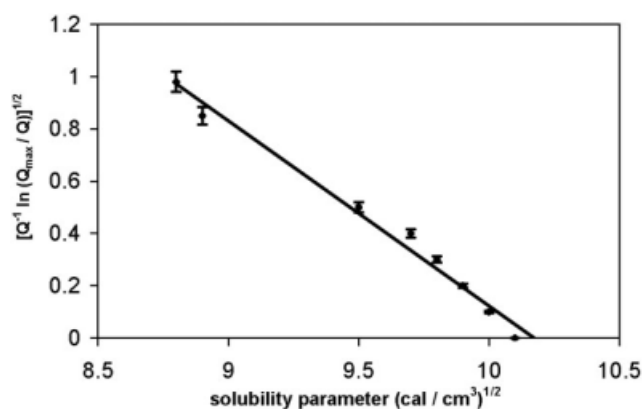
Figure 6 Plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ versus solubility parameters of solvents for Gl-A PU.

parameter of the polymer (Fig. 5). However, sometimes the exact position of maxima is ill defined. Hence eq. (4) was rearranged as follows.

$$[Q^{-1}\ln(Q_{max}/Q)]^{1/2} = [a^{1/2}(\delta_S - \delta_P)] \qquad (6)$$

A plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ versus δ_S was found to be linear, and the slope and intercept at horizontal axis gave the values of a and δ_P, respectively. A representative plot for Gl-PU is shown in Figure 6. The values of solubility parameter obtained from these plots were close to 10.1 $(cal/cm^3)^{1/2}$ for all the PU systems as seen earlier.

The volume fraction of polymer ϕ in the solvent swollen sample was calculated by using the equation[17]

$$\phi = \frac{M_p/\rho_p}{M_s/\rho_s + M_p/\rho_p} \qquad (7)$$

where M_p is the initial weight of the polymer sample, ρ_p is its density, M_s the weight of the solvent in the fully swollen sample, and ρ_s is the density of the solvent. From the results in Table IV, it is observed that

TABLE IV
Volume Fraction of Polymer ϕ

Code	Chlorobenzene	Toluene	Xylene
St A	0.412	0.476	0.501
St B (0.66)	0.335	0.416	0.434
St B	0.254	0.320	0.359
St B (1.5)	0.228	0.261	0.302
St C	0.307	0.369	0.406
Su A	0.203	0.268	0.293
Su B (0.66)	0.338	0.412	0.419
Su B	0.259	0.302	0.339
Su B (1.5)	0.238	0.293	0.296
Su C	0.306	0.377	0.421
Gl A	0.391	0.420	0.471
Gl B (0.66)	0.319	0.373	0.421
Gl B	0.260	0.304	0.332
Gl B (1.5)	0.194	0.253	0.259
Gl C	0.333	0.387	0.423

TABLE V
Volume Equilibrium Degree of Swelling q

Code	Chlorobenzene	Toluene	Xylene
St A	2.427	2.101	1.996
St B (0.66)	2.985	2.404	2.304
St B	3.937	3.125	2.785
St B (1.5)	4.386	3.831	3.311
St C	3.257	2.710	2.463
Su A	4.926	3.731	3.413
Su B (0.66)	2.958	2.427	2.386
Su B	3.861	3.311	2.950
Su B (1.5)	4.202	3.413	3.378
Su C	3.268	2.652	2.375
Gl A	2.557	2.381	2.123
Gl B (0.66)	3.135	2.681	2.375
Gl B	3.846	3.289	3.012
Gl B (1.5)	5.155	3.953	3.861
Gl C	3.003	2.584	2.364

Figure 8 Variation of q and ϕ with R value for St-PUs in the three solvents. (◆) (◇) chlorobenzene, (▲) (△) toluene, and (■) (□) xylene.

the volume fraction ϕ of the polymer is directly proportional to crosslink density of the polymer and inversely proportional to the sorption extent of the solvents. Hence the volume equilibrium degree of swelling q was calculated as the reciprocal of the volume fraction of the polymer. The results are given in Table V. The effect of crosslinker and diisocyanate concentrations on ϕ and q is seen in Figures 7 and 8.

To calculate the degree of crosslinking and molecular weight between crosslinks, the polymer solvent interaction parameter χ was calculated using the solubility parameter obtained and the equation[17]:

$$\chi = \beta + V_s\{(\delta_p - \delta_s)^2/RT\} \tag{8}$$

where β is the lattice constant whose value is about 0.34,[17,20] V_s is the molar volume of the solvent, and δ_p and δ_s are the solubility parameters of the polymer and the solvent, respectively. The polymer–solvent interaction parameter (χ) values for chlorobenzene, toluene, and xylene were found to be 0.4010, 0.5952, and 0.6857, respectively. Lower χ
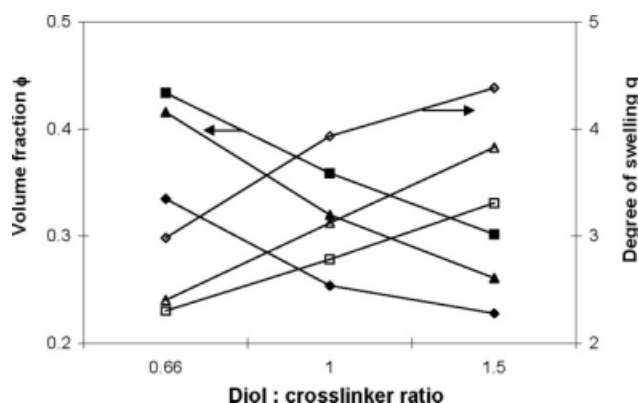

Figure 7 Variation of q and ϕ with diol : crosslinker ratio for St-PUs in the three solvents. (◆) (◇) chlorobenzene, (▲) (△) toluene, and (■) (□) xylene.
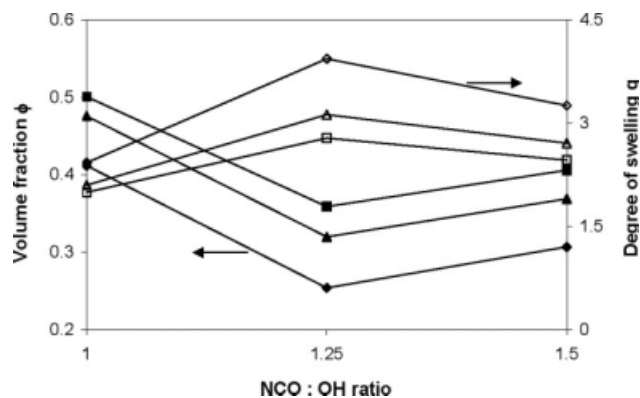
value indicates higher interaction of the polymer with chlorobenzene, resulting in greater sorption, as observed in the sorption studies.

When the polymer sample is immersed in a solvent medium, its molecules diffuse into the polymer until the elastic retraction of the network balances the osmotic pressure driving the solvent into the swollen polymer.[18] Because the retraction of the network depends upon the molecular weight between crosslinks M_c was calculated from the Flory-Rehner equation[1]:

$$M_c = \frac{\rho_p V_s \phi^{1/3}}{\ln(1 - \phi) + \phi + \chi\phi^2} \tag{9}$$

where ρ_p is the density of the polymer.

The degree of crosslinking is inversely proportional to the molecular weight between crosslinks and is given by the equation

$$v = 1/2M_c \tag{10}$$

The values for M_c and v are given in Tables VI and VII, respectively. Theoretical values for M_c were calculated using the knowledge of the mole fractions of the various components of the PUs.[18] In case of St-PUs, molecular weight of the repeat unit of starch is considered for calculations, because unlike PPG, the functionalities of starch are not end groups. The effect of crosslinker and diisocyanate concentrations on M_c and v is seen in Figures 9 and 10.

The results obtained show considerable deviation from the theoretically calculated values. The deviations were also observed within the different solvents and the extent of deviation was more for the solvents with which the polymer has lesser interaction. Similar results have been reported earlier[2,8,18] and may be because of limitations of the Flory–Rhener theory for heterogeneous system like PU comprising of hard and soft segments. The complexity of polymer–solvent interaction affects the

TABLE VI
Molecular Weight Between Crosslinks (M_c)

Code	Theoretical	Chlorobenzene	Toluene	Xylene
St A	669[a]	1481	2339	4443
St B (0.66)	450[a]	2524	4178	15576
St B	552[a]	4948	15450	23049
St B (1.5)	707[a]	6283	75555	26574
St C	474[a]	3117	7326	9358
Su A	669	8063	57008	22615
Su B (0.66)	450	2464	4387	15606
Su B	552	4684	22262	21689
Su B (1.5)	707	5724	26768	26077
Su C	474	3112	6613	15880
Gl A	629	1703	4036	7050
Gl B (0.66)	414	2890	6941	15126
Gl B	519	4632	11002	22025
Gl B (1.5)	644	8922	21396	23071
Gl C	447	2560	5951	20817

[a] Molecular weight of the repeat unit of starch is considered for calculations.

microdomain structure of PU to different extents. Chlorobenzene being a polar solvent has good interaction with the soft as well as the hard segment of the polar PU. Such a factor encourages the diffusion of solvents into the polymer matrix, which enhances the macromolecular chain relaxation process responsible for the non-Fickian transport mentioned earlier. The nonpolar toluene and xylene have minimum interaction with the polymer, so that they are unable to interact with both the segments. Hence, the values of M_c calculated on the basis of swelling in these solvents show much higher deviation from theoretical values. Since the values of M_c are different in different solvents they can be regarded as the segment length between two consecutive physical crosslinks rather than chemical crosslinks. Physical crosslinks are the entanglements and also the point of secondary bond interactions.[8]

TABLE VII
Degree of Crosslinking v

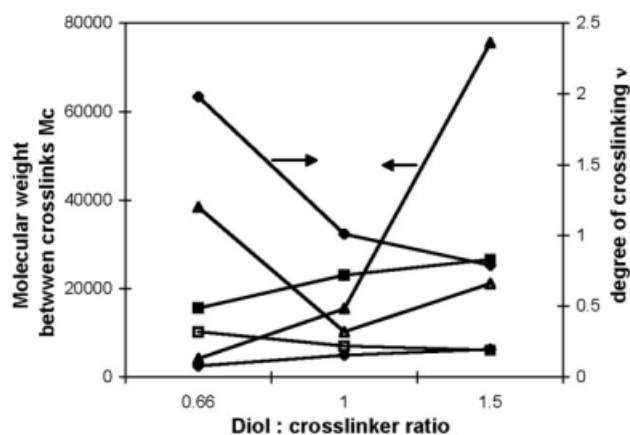| | v (10^4) | | |
Code	Theoretical	Chlorobenzene	Toluene	Xylene
St A	7.47	3.38	2.14	1.13
St B (0.66)	11.11	1.98	1.20	0.32
St B	9.06	1.01	0.32	0.22
St B (1.5)	7.07	0.79	0.66	0.19
St C	10.55	1.6	0.68	0.53
Su A	7.47	0.62	.09	0.22
Su B (0.66)	11.11	2.03	1.14	0.32
Su B	9.06	1.07	2.25	0.23
Su B (1.5)	7.07	0.87	0.19	0.19
Su C	10.55	1.61	0.76	0.31
Gl A	7.95	2.94	1.24	0.71
Gl B (0.66)	12.08	1.73	0.72	0.33
Gl B	9.63	1.08	0.45	0.23
Gl B (1.5)	7.76	0.56	0.23	0.22
Gl C	11.19	1.95	0.84	0.24

Figure 9 Variation of M_c and v with diol : crosslinker ratio for St-PUs in the three solvents. (◆) (◇) chlorobenzene, (▲) (△) toluene, and (■) (□) xylene.

The trend observed in the experimentally calculated M_c is in agreement with the trend observed in theoretically obtained values to some extent. As the diol/crosslinker ratio increases, M_c increases in both cases. However, the anomalous swelling behavior exhibited by St-PU and Gl-PU with respect to variation in NCO : OH ratio was also reflected in the values of M_c. Theoretically in all the cases M_c decreases as the degree of crosslinking increases with increasing isocyanate content. But experimental data of all solvents exhibits a different trend. This further supports the argument that HMDI imparts flexibility to the PU molecule.

The degree of crosslinking data shows that though increase in concentration of either crosslinker or HMDI affects crosslink density, the crosslinker has much more pronounced effect on the properties.

The sorption coefficient, which is related to the maximum sorption of the penetrant, can be obtained
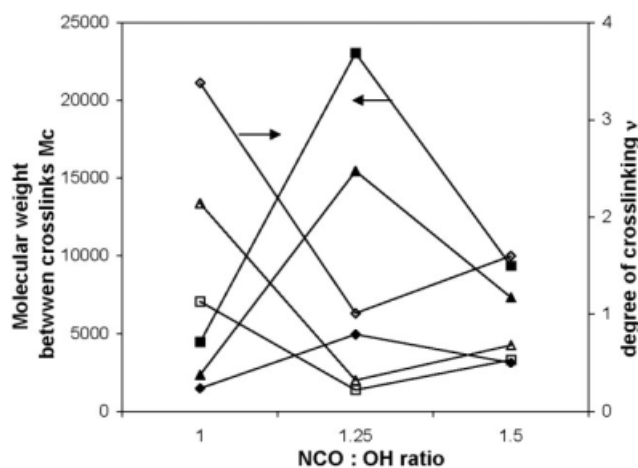

Figure 10 Variation of M_c and v with R value for St-PUs in the three solvents. (◆) (◇) chlorobenzene, (▲) (△) toluene (■) (□) xylene.

TABLE VIII
Sorption Coefficient (S) (g/g)

Code	Chlorobenzene	Toluene	Xylene
St A	1.58	0.95	0.86
St B (0.66)	2.19	1.32	1.12
St B	3.16	1.84	1.54
St B (1.5)	3.74	2.44	1.98
St C	2.22	1.48	1.25
Su A	4.35	2.37	2.08
Su B (0.66)	2.17	1.23	1.19
Su B	3.18	2.00	1.68
Su B (1.5)	3.53	2.09	2.05
Su C	2.51	1.43	1.18
Gl A	1.72	1.20	0.97
Gl B (0.66)	2.36	1.45	1.18
Gl B (1)	3.25	1.98	1.73
Gl B (1.5)	4.59	2.56	2.46
Gl C	2.49	1.37	1.17

from the ratio of weight of the solvent taken up at equilibrium to the initial weight of the polymer.

$$S = M_s/M_p \qquad (11)$$

As evident from Table VIII, the sorption coefficient follows the same trend as that of swelling coefficient. As the crosslinker concentration decreases, the sorption coefficient increases.

The diffusion coefficient characterizes the ability of the solvent molecules to move along the polymer segments. It can be calculated from the equation

$$D = \pi(h\theta/2Q_\infty)^2 \qquad (12)$$

where h is the initial thickness of the sample, and θ is the slope of the linear portion of the sorption curves. The trend observed in the case of diffusion coefficient is quite opposite to that observed in the case of sorption coefficient. The data in Table IX indicates that sample Gl B 1.5 is the material with lowest value of diffusion coefficient because of high-

TABLE IX
Diffusion Coefficient D (10^3 cm^2 s)

Code	Chlorobenzene	Toluene	Xylene
St A	4.54	7.17	41.71
St B (0.66)	4.05	15.42	59.49
St B	1.84	4.27	13.26
St B (1.5)	1.32	3.24	10.44
St C	4.67	7.28	14.57
Su A	1.79	4.1	4.53
Su B (0.66)	3.09	6.4	7.2
Su B (1)	2.39	6.44	8.19
Su B (1.5)	1.75	1.15	4.78
Su C	2.49	8.99	18.71
Gl A	6.67	11.76	12.8
Gl B (0.66)	3.66	5.35	10.25
Gl B	1.84	4.32	5.92
Gl B (1.5)	0.86	1.31	1.53
Gl C	2.43	8.18	13.71

TABLE X
Permeability Coefficient P (10^3 cm^2 s^{-1})

Code	Chlorobenzene	Toluene	Xylene
St A	7.17	6.81	35.87
St B (0.66)	8.87	20.35	66.63
St B	5.81	7.86	20.42
St B (1.5)	4.94	7.91	20.67
St C	10.37	10.77	18.21
Su A	7.79	9.72	9.42
Su B (0.66)	6.71	7.87	8.57
Su B	7.60	12.88	13.76
Su B (1.5)	6.18	2.40	9.80
Su C	6.25	12.86	22.08
Gl A	11.47	14.11	12.42
Gl B (0.66)	8.64	7.76	12.10
Gl B	5.98	2.61	10.24
Gl B (1.5)	3.95	3.35	3.76
Gl C	6.05	11.21	16.04

est diol/triol ratio and additional flexibility due to suitable concentration of HMDI. Therefore, it is best suitable as barrier material.

The permeability coefficient, product of diffusion coefficient and sorption coefficient, implies net effect of diffusion and sorption. Its values are given in Table X.

Gel content

The gel content[22] (the fraction of uncrosslinked material) of the PUs used for swelling studies was found to be in the range of 4–6%. This is somewhat higher than the PU systems that we have studied in the past where the crosslinker was 1,1,1- trimethylolpropane.[22] This may be due to the lower reactivity and poor solubility of the highly hydrophilic carbohydrates in the reaction medium.

Biodegradation studies

The biodegradation in terms of percentage weight loss with time, given in Figure 11 for the samples A,
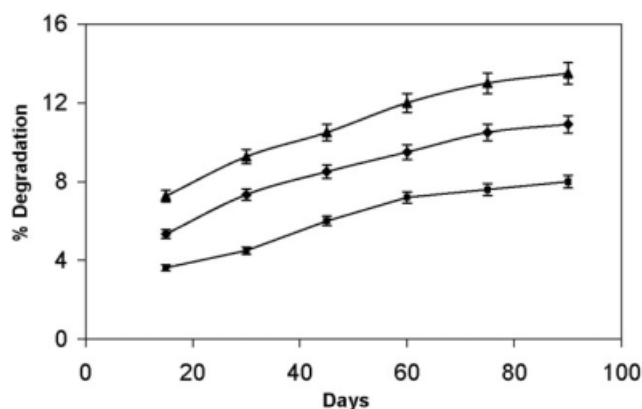
Figure 11 Plot of percentage weight loss versus time for PUs containing highest amount of carbohydrates (B 1.5). (■) Starch, (◆) sucrose, and (▲) glucose.
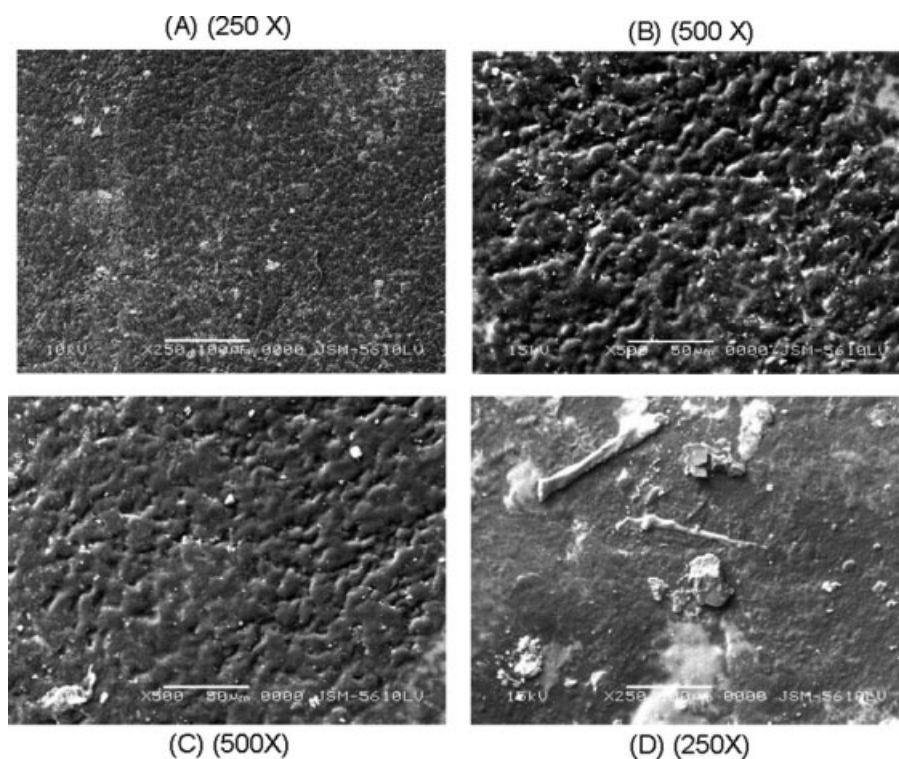
Figure 12 Scanning electron micrographs of PUs containing different crosslinkers. (a) Gl B, (b) Su B, (c) St B, and (d) postswollen St B.

indicates that the PUs under study exhibit high rate of degradation. The observed weight loss was much higher in the case of glucose containing PU. The percentage degradation decreases as monosaccharide is replaced by disaccharide followed by polysaccharide.

Morphology

The scanning electron micrographs of the PUs [Fig. 12(a–d)] indicate monophasic structure with no phase segregation because of presence of hard and soft segments.[22] Development of wrinkles observed may be due to solvent evaporation at the time of curing. The micrograph of the St-PU taken after swelling and drying shows disappearance of the wrinkles. The particles seen on the surface may be the gel fraction that may have dissolved during swelling and redeposited on drying. The micrographs of other postswollen PUs exhibited similar morphology.

CONCLUSIONS

From the series of PUs containing carbohydrate crosslinkers it was observed that the sorption of solvents under study followed the sequence sucrose > glucose > starch. The sorption was inversely proportional to the crosslink density and hence crosslinker concentration of the PUs. An interesting trend was observed in the samples with different R values in

case of St and Gl PUs. The sample A with lowest isocyanate content exhibited minimum swelling, which was attributed to relatively flexible structure of HMDI. Sorption was observed to be mostly of Fickian nature. The sucrose and starch systems exhibited non-Fickian diffusion in chlorobenzene because of a greater diffusion rate and smaller relaxation rate, as maximum swelling occurred in this solvent followed by nonpolar toluene and xylene. This fact was reflected in the value of interaction parameters, χ and k. The solubility parameter for all the PUs was found to be 10.1 $(cal/cm^3)^{1/2}$, which was closer to that of chlorobenzene which among solvents under study. It was observed that molecular weights between crosslinks and the swelling coefficient are inversely proportional to the concentration of crosslinker. The trend observed for diffusion coefficient is quite opposite to that observed in the case of sorption coefficient. According to the diffusivity data, the sample Gl B 1.5 with highest diol/triol ratio and additional flexibility due to suitable concentration of HMDI is best suitable as barrier material. The scanning electron micrographs of the PUs indicate monophasic structure. PUs under study exhibit high rate of degradation, which decreases as monosaccharide is replaced by disachharide followed by polysaccharide.

Finally, it can be concluded that, although increase in concentration of either crosslinker or HMDI

affects crosslink density, the carbohydrate has much more pronounced effect on the transport properties.

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