The Swelling Behavior of Interpenetrating Polymer Networks Composed of Polyurethane and Unsaturated Polyester

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ABSTRACT: The kinetics of swelling and the sorption performance were observed for the polymer compositions with interpenetrating polymer networks made up of polyurethane 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. 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. Moreover, an attempt was made to evaluate structural parameters that describe topology of the obtained networks. It was found that the increasing share of polyurethane in the composition reduced crosslinking density in the polyester network that resulted in faster diffusion of the solvent and higher sorption capacity for the solvent. The higher the styrene content in the composition, the higher the crosslinking density in the system, and hence the diffusion of solvent and its sorption inside the polymer network was much more difficult. 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. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3511–3519, 2006

Key words: polyurethanes; polyester; interpenetrating networks (IPN); swelling; electron microscopy

INTRODUCTION

The interpenetrating networks (IPN) polymeric systems result from interpenetration of a few polymer networks, when one of them is formed by polymerization or crosslinking in the presence of the other. In most cases, the processes that form the polymer systems follow different polymerization mechanisms, e.g., free-radical chain polymerization, typical for vinyl monomers, and step-growth polymerization—polyaddition or polycondensation in the case of polyurethanes or epoxy resins. The polymer systems produced in that way form separate but interpenetrating spatial structures, with basically no chemical bonds observed between them.[1–5]

Chemical composition of the network, degree of interpenetration of system components, and possible physical interactions between functional groups affect morphology of IPN-forming polymers, scope of phase separation within an IPN, as well as size, shape, and arrangement of microregions. Those factors influence the physical–mechanical properties of such systems and create new possibilities for employing them as a modern organic material in many applications like membranes, gel permeation chromatography, drug release control, etc.[6–9]

Quite valuable may be investigation of kinetics and equilibrium of sorption and diffusion phenomena, which take place when a liquid inert substance penetrates through the complex system of polymer networks. It will make it possible to find more detailed relations between the structural features and properties of the produced IPN systems.

The ability of a low-molecular-weight substance to diffuse through the matrix of amorphous polymer is closely related to not only the nature and type of interactions between that substance (which plays the role of solvent for example) and the polymer, but also the shape and size of voids among polymer chains.[10] The swelling process of the IPN compositions in the presence of a properly selected solvent can be carefully analyzed to provide valuable information on the structure existing on the macromolecular level, i.e., on degree of crosslinking, on distribution of chain length, on presence of network defects (free ends, loops), on chains having got tangled, on chain rigidity, etc.[11]

As the study of the kinetics of swelling and evaluation of the transport properties were found to be useful to the structural analysis of various engineering polymers like polyurethanes, polystyrene, natural

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rubber, or synthetic rubbers,[12–16] and the transport properties of interpenetrating polymer networks can hardly be found in the literature, we consider that it is advisable to show possibilities for getting by this way complementary information about structure of polyurethane/unsaturated polyester (UP) IPN which were obtained by us.[2–5] The sorption behavior under swelling for IPN compositions based on UPs and polyurethanes is complicated and completely different from that of other crosslinked polymers because IPNs consist of two components, one rubbery and the other glassy. The behavior of rubbery polymers toward solvents would be different from that of glassy polymer as there are differences in their free volumes and in their molecular mobility specifications.[17]

EXPERIMENTAL

Preparation of IPN compositions

The detailed descriptions of raw materials used, conditions adopted for the synthesis of intermediates, and method applicable in producing IPN compositions have been presented in our earlier reports. [2–5] Hence, only the most important information will be supplemented in this article.

A number of IPN formulations were prepared, which were different from each other in their chemical compositions, yet each of them was made of two components: UP resin and polyurethane (PUR) with various levels of branching.

Unsaturated polyester resins were employed as the second component in IPN compositions; they were obtained by dilution with styrene (ST) of UP derived from the reaction of maleic and phthalic anhydrides with 1,2-propane diol and di(ethylene glycol) in equimolar proportion. This type of polyester is used in Zakłady Chemiczne "Nowa Sarzyna" (Poland) to produce the UP resin with the trade name of *Polimal 103* (acid value, 32 mg KOH/g).

The polyurethane component was obtained in a two-stage polyaddition process that involved 2,4- and 2,6-tolylene diisocyanate, a selected polyetherol: oligo(oxypropylene)diol (Rokopol D2002 available from Zakłady Chemiczne "Organika-Rokita" in Brzeg Dolny, Poland) or oligo(oxyetylene–propylene)triol (Rokopol 330 available from the same producer) and ST as a solvent. So obtained isocyanate prepolymer was then extended with 1,4-butanediol or trimethylolopropane. Depending on the type of polyol and chain extender employed, styrenic solutions of polyurethanes with linear or slightly branched structures were obtained.

The polyurethane components of the IPN composition derived from Rokopol D2002 and butane-1,2-diol were denoted with the symbol **d2b,** those in compositions synthesized from Rokopol D2002 and trimethyloolopropane with the symbol **d2t,** those in compositions produced from Rokopol R330 and butane-1,2-diol as **r3b,** and those in PUR compositions obtained from Rokopol R330 and trimethyloolopropane with the symbol **r3t**

The polyester–polyurethane IPNs studied in this work were designated as:

$$x\text{-}PUR\text{-}y \qquad (1)$$

where PUR is the type of used polyurethane, according to notation in the frame; x is the weight % of PUR in IPN composition; y is the weight % of ST in UP resin used for preparing the IPN composition, for example:

$$10\text{-}\boldsymbol{r3t}\text{-}40 \qquad (2)$$

which refers to the IPN composition containing 10% of PUR type **r3t** and 90% of UP resin with 40% of ST inside.

Kinetics for swelling of polymer networks

The kinetics of the swelling process was found by means of the weight method at 25°C. Cylindrical samples were measured by means of a micrometer (precision ± 0.01 cm), weighed on an electronic balance (precision ±0.001 g), and then kept immersed in chlorobenzene as nonsolvent, in test bottles. Two parallel tests were run for every type of IPN system, with different densities and chemical compositions. The difference between them was less than 3%. The samples were taken out of the liquid at regular time intervals, the nonsolvent adhering to the surface was rubbed off, and the samples were weighed and replaced in the test bottles. The time for each weighing was kept to a minimum (at most 1 min). This procedure was continued till equilibrium swelling was achieved. The swelling experiments were conducted at 25°C.

The mol percent uptake Q_t, [%mol/g] is defined as:[17]

$$Q_t = \frac{(m_1 - m_0)M}{m_0} \times 100 \qquad (3)$$

where m_t is the weight of swollen sample after time interval t, [g]; m_o is the initial weight of dry sample, [g]; M is the molecular weight of chlorobenzene, [g/mol]. The average molecular weight between crosslinks (M_c) was calculated from the Flory-Rhener equation:[18]

$$M_c = -\frac{\rho_{\text{IPN}} V \phi^{173}}{ln(1 - \phi) + \phi + \chi\phi^2} \qquad (4)$$

where ρ_{IPN} is the density of IPN composition, [g/cm³]; V is the molar volume of solvent, [cm³/mol]; ϕ is the volume fraction of polymer in the swollen gel and χ is the polymer–solvent interaction parameter calculated by the following equation:[19]

$$\chi = 0.34 + \frac{V(\delta_{IPN} - \delta_r)^2}{RT} \tag{5}$$

where V is the molar volume of solvent, [cm³/mol]; δ_{IPN} is the solubility parameter of IPN composition, [(kJ/m³)$^{1/2}$]; δ_r is the solubility parameter of solvent, [(kJ/m³)$^{1/2}$]; R is the gas constant, [J/K(mol) and T is the temperature, [K].

The volume fraction of rubber in the solvent-swollen sample (ϕ) was calculated from:

$$\phi = \frac{m_0/\rho_{IPN}}{m_0/\rho_{IPN} + m_r/\rho_r} \tag{6}$$

where m_o is the initial weight of the IPN sample, [g]; ρ_{IPN} is the density of IPN composition determined by the immersion method in accordance with ISO 1183 : 1987, [g/cm³]; m_r is the weight of chlorobenzene in the swollen IPN sample, [g] and ρ_r is the density of the solvent, [g/cm³].

The solubility parameters of IPN compositions were calculated based on experimentally determined solubility parameter of pure solvents via Small's tables.[20] The degree of crosslinking (ν) was also calculated with the use of equation:

$$v = \frac{1}{2M_c} \tag{7}$$

Relative changes of average molecular weight between crosslinks ($\delta M_{c\ IPN}$) and degree of crosslinking ($\delta \nu_{IPN}$) in relation to equal parameters characteristic for pure UP resin with adequate concentrations were calculated using the following equations:

$$\delta M_{cIPN} = \frac{M_{cIPN} - M_{cUP}}{M_{cUP}} \times 100 \tag{8}$$

$$\delta v_{IPN} = \frac{v_{IPN} - v_{UP}}{v_{UP}} \times 100 \tag{9}$$

Thus, defined quantities can assume both positive and negative values when the crosslinking degree in the IPN system is lower than that for neat reference polyester resin. Then, the diffusion coefficient D [cm²/s], sorption coefficient S [g/g], and permeability coefficient P [cm²/s] were calculated:

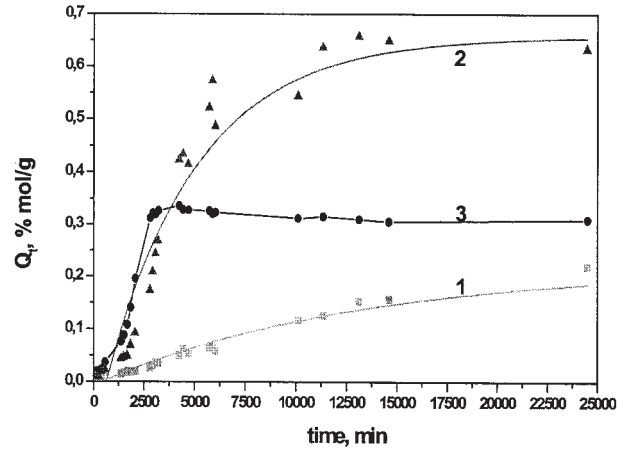$$D = \pi \left(\frac{h\theta}{4Q_\infty} \right)^2 \tag{10}$$

Figure 1 Sorption curve showing the mole percent uptake of IPN compositions containing different amounts of PUR r3b with 10% of styrene in UP: 1–10%, 2–20%, 3–30%.

$$S = \frac{m_{r,\infty}}{m_0} \tag{11}$$

$$P = DS \tag{12}$$

where h is the thickness of test piece, [cm]; θ is the slope of the straight line that describes the swelling process $Q_t = f(t^{1/2})$, [% mol/g·(s$^{1/2}$)]; $m_{r,\infty}$ is the amount of solvent absorbed to reach the condition of equilibrium, [g] and m_o is the initial weight of a test piece, [g].

Scanning electron microscopy

After reaching the swelling equilibrium degree Q_∞, the chosen IPN samples were drained at room temperature during 14 days. The pictures of the produced IPN samples were taken with the use of a scanning electron microscope (SEM) NOVASCAN 3.0—the fractures were observed after a layer of gold had been deposited on them by sputtering.

RESULTS AND DISCUSSION

The findings from the swelling process obtained for IPN compositions were interpreted from the viewpoint of search for explanation of structural questions connected with crosslinking and interpenetration of PUR chains and UP resin which had been crosslinked with ST. These two form a complex supermolecular structure, as will be presented later.

For that purpose, Figure 1 presents swelling profiles for IPN composition obtained from branched PUR type r3b. The swelling process proceeds initially at the constant and considerable rate, which results from active penetration of the solvent molecules into the network. That process, however, undergoes stabiliza-

TABLE I
Values of Mol Percent Uptake at Infinite Time for IPN Compositions

Chemical composition		Polyurethane components used for IPN compositions			
Amount of ST in UP [wt %]	Amount of PUR in IPN [wt %]	d2b	d2t	r3b	r3t
		$Q_{\infty,ch}$ [% mol/g]			
	10	0	0.2552	0.2824	0.2750
10	20	0.6715	0.6915	0.6710	0.6148
	30	–	–	0.3239	0.3067
	10	0.1305	0.1974	0.1687	0.1786
20	20	0.6659	0.6795	0.3155	1.0010
	30	–	–	0.2903	–
	10	0.1023	0.1191	0.1034	0.0771
30	20	0.3619	0.6582	0.3142	0.3405
	30	–	–	0.2466	–
	10	0.0357	0.0366	0.0974	0.0801
40	20	0.3047	0.3659	0.3341	0.1772
	30	–	–	–	–

–, Some IPN samples underwent decomposition under measurement conditions. No measurement could be taken in those cases.

tion and equilibrium is finally reached. The linear profile for that relation suggests that initial sorption of solvent into the polymeric sample is based on the relaxation capacity of the polymeric network to expand its free volume which is then filled with a solvent.

Gentle curving can be observed in initial sections of sorption lines for some *solvent-IPN composition* systems, which makes the indication of small deviations from the Fick's laws diffusion.

Table I shows the swelling degrees for synthesized IPN compositions as found at equilibrium. The figures speak unequivocally that the equilibrium sorption of solvent inside the polymeric network is strongly affected by chemical composition of IPN.

When analyzing the progress of the swelling process in chlorobenzene as in formally "nonsolvent," the amount of PUR incorporated into the IPN network was found to have a definite effect on the swelling rate and the $Q_{\infty,ch}$ value. The swelling kinetics curves were compared for the systems that contained 10 and 20% PUR: faster swelling and higher values of equilibrium swelling degree $Q_{\infty,ch}$ (Fig. 1) were observed for higher contents of polyurethane components, both linear and branched.

On the other hand, the structure of PUR itself was of minor significance in that case (Fig. 2). When the PUR share was increased in the composition up to 30 wt %, two types of sorption performance could be observed for IPN compositions, which resulted directly from the type of supermolecular structure. Figure 1 reveals that IPNs synthesized from branched PURs have the initial period of fast swelling, and then, the diffusion slows down or even the adverse process can be observed. Thus, the swelling degree Q_t can be reduced and the equilibrium is reached at a lower value of

$Q_{\infty,ch}$. That behavior of IPN compositions results most probably from a slight solubility of polyurethane–polyester phase in chlorobenzene and leaching that phase out of the sample. The leaching process involves probably only low-molecular-weight fractions, which can be dissolved in chlorobenzene with more ease.

No typical swelling is observed for IPN compositions where the content of linear PUR (d2b, d2t) reaches 30%. The samples contacted with the solvent quickly lose their weight which ends up with their decomposition (Fig. 3).

That type of behavior is specific solely for the systems that contain 30% PUR and only the specific type(s) of matrices can supposedly be prone to leaching. As we correlate the present results with our ear-
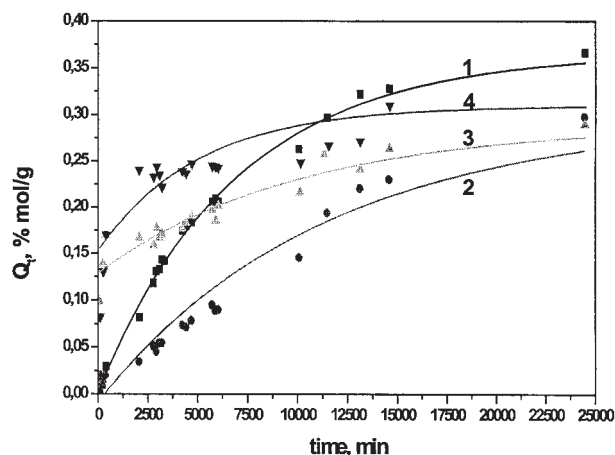

Figure 2 Sorption curve showing the mole percent uptake of IPN compositions containing 20% PUR with different chemical structures and 40% of styrene in UP: 1-d2b, 2-d2t, 3-r3b, 4-r3t.
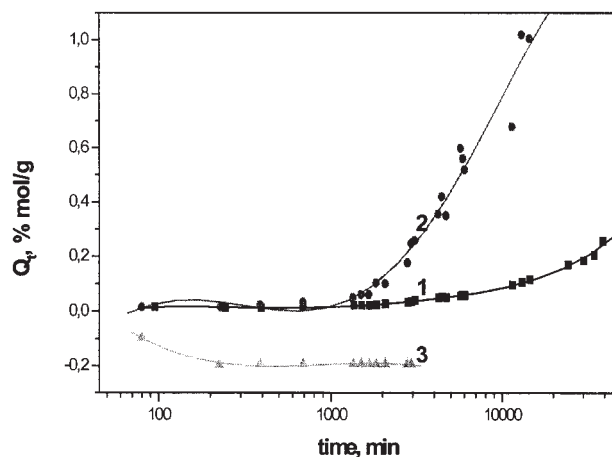
Figure 3 Sorption curve showing the mole percent uptake of IPN compositions containing different amounts of PUR d2t with 10% of styrene in UP: 1–10%, 2–20%, 3–30%.

Figure 5 Time dependence of the mole percent uptake of IPN compositions containing 30% PUR d2t with various amounts of styrene in UP: 1–10%, 2–20%, 3–30%, 4–40%.

lier observations made by SEM analysis,[4] we could find that it happens only for the systems with two-component and discontinuous matrices, formed by clearly separated small-diameter globular structures, which join together and thus create the dispersion medium. When the two-component matrix is continuous—which is the case for IPN systems with low PUR and ST contents—typical swelling is observed.

The kinetics and equilibrium of the swelling process of the synthesized IPN compositions are strongly affected by the content of the crosslinking monomer, too. The increasing amount of ST results in decline of $Q_{\infty,ch}$, which is attributable to increasing density of crosslinking in the composition (Fig. 4). That manner of changes is observed for IPNs which contain 10 ÷ 30% ST, irrespective of PUR contents.

A nontypical profile was recorded for IPN compositions with 40% ST and 10% PUR which were sub-
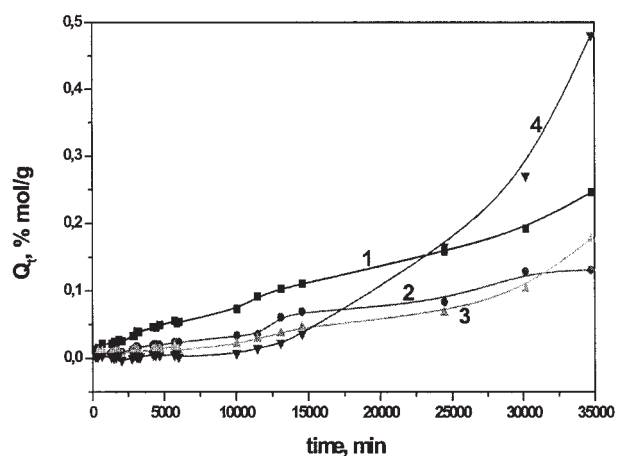

Figure 4 Sorption curve showing the mole percent uptake of IPN compositions containing 10% PUR d2b with various amounts of styrene in UP: 1–10%, 2–20%, 3–30%, 4–40%.
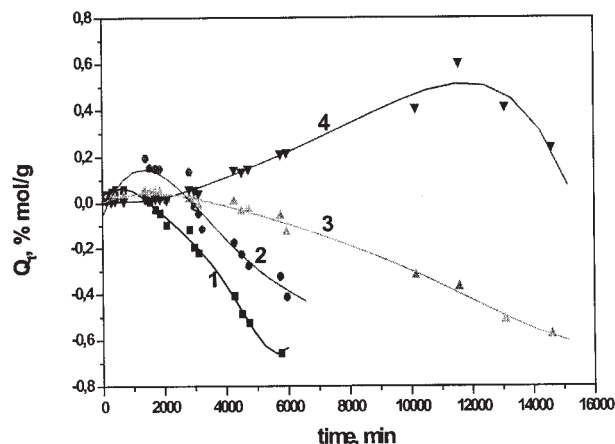
jected to swelling in chlorobenzene. Exactly as expected, the process was very sluggish over the first 10 days because of high density of crosslinking in the system and low PUR content at the same time. The swelling process became more intense afterwards: considerable growth of Q_t and then quick sample decomposition were observed (Fig. 4). That can be explained by differences in chemical affinity of chlorobenzene to structures that are formally crosslinked and only physically tangled up, just as present in IPN-type materials. Destruction of such a network leads to inferior cohesion of the material. Thus, the shear stresses between two layers, swollen gel coating and glassy (rigid) core, result in cracks of the sample surface layer.[16] That type of behavior is specific for the systems, in which 2nd type diffusion takes place. That diffusion is responsible for the so-called anomalous swelling.[21] When the cracks arrive, they can speed up the swelling process within the glassy core since the solvent finds it easier to migrate inside the core through the cracks in the outer shell. The equilibrium degree of swelling in those cases was assumed to be equal to the value Q_t just before the scratches and cracks appeared on the sample surface since any further diffusion of solvent took place under conditions which were no longer the same—the solvent-sample contact surface was increased considerably.

In case of IPN compositions, which suffered from partial elution of polyurethane–polyester fraction, their high ST contents caused the process to take place over a longer period of time, which proves higher density of crosslinking in those compositions. That, however, can be expected to result not only from the system of covalent bonds but from physical tangling of molecular chains as well, wherein polystyrene fragments are involved, too (Fig. 5).

On the basis of the data obtained from the measurements taken for chlorobenzene swelling, the joint-to-

TABLE II
Values of Average Molecular Weight Between Crosslinks ($M_{c\ IPN}$) and Degree of Crosslinking (ν_{IPN}) for IPN Systems With Different Chemical Compositions

Chemical composition		Polyurethane components used for IPN compositions							
		d2b		d2t		r3b		r3t	
Amount of ST in UP [wt %]	Amount of PUR in IPN [wt %t]	$M_{c\ IPN}$ [g/mol]	$\nu_{IPN}10^4$ [mol/g]	$M_{c\ IPN}$ [g/mol]	$\nu_{IPN}10^4$ [mol/g]	$M_{c\ IPN}$ [g/mol]	$\nu_{IPN}10^4$ [mol/g]	$M_{c\ IPN}$ [g/mol]	$\nu_{IPN}10^4$ [mol/g]
10	10	924.3	5.41	1620.0	3.09	1648.6	3.03	2118.8	2.36
	20	2089.0	2.39	2520.1	1.98	1996.9	2.50	4848.0	1.03
20	10	310.2	16.12	560.6	8.92	304.6	16.42	460.5	10.86
	20	1697.4	2.95	1439.3	3.47	439.2	11.38	2237.6	2.23
30	10	218.3	22.90	260.0	19.23	175.0	28.57	172.3	29.02
	20	580.3	8.62	705.6	7.09	392.5	12.47	438.0	11.42
40	10	107.3	46.59	108.0	45.95	118.4	42.24	124.0	40.32
	20	185.8	26.91	286.0	17.48	280.3	17.84	278.7	17.94

Unsaturated polyester resin								
Chemical composition of UP/ST, [g/g]		60/40		70/30		80/20		90/10
$M_{c\ UP}$ [g/mol]	$\nu_{UP}10^4$ [mol/g]	87.7	57.04	154.7	32.31	278.6	17.94	384.0	13.02

joint molar weight values[4] and degree of crosslinking values[7] were evaluated, i.e., the parameters were assessed which are specific for the spatial structures of obtained IPN compositions.

To evaluate the molecular weight values for the polymer sections between crosslinks ($M_{c\ IPN}$) and the crosslinking density values (ν_{IPN}), it was necessary to calculate the content of polymer fraction (ϕ) in the swollen gel beforehand. IPN compositions with high ST contents showed higher ϕ values which is synonymous to higher density of crosslinking and hence lower ability to absorb solvent molecules. Lower ϕ values were characteristic for IPN compositions with lower ST contents of with higher PUR shares, which could absorb more solvent.

The calculated molecular weights for joint-to-joint sections and crosslinking degrees were presented in Table II. Comparatively, the same method was employed to calculate the values of corresponding parameters for "neat" UP resins with various ST contents as reference samples.

In case of a perfect copolymer structure of alternately organized maleic anhydride, phthalic anhydride, 2,2'-oxydiethanol and propane-1,2-diol segments, which makes the model for the polyester resin used, the molecular weight of the joint-to-joint units equals to 392 g/mol. Hence, the values of $M_{c\ UP}$ and $M_{c\ IPN}$ (Table II) obtained from measurements taken for swelling of "neat" UP resins are underrated. The reason for those deviations can be the values of solubility parameters δ, which have been calculated theoretically and assumed too low. In that case, the values provided in Table II for our IPN systems can be incorrect. Thus, our further analysis was confined and it covered

only relative changes in δM_c and $\delta \nu$, in relation to the parameters for "neat" UP resins with corresponding chemical compositions, as shown in Table III.

Our calculations demonstrate that the increasing share of ST in IPN compositions is responsible for higher and higher density of crosslinking (joint-to-joint molecular weight is lower and lower in those cases). However, none of IPN systems can offer such a high density of crosslinking as "neat" UP resins can. The less ST is present in the system, the clearer the differences become between $M_{c\ IPN}$ and $M_{c\ UP}$ values for a given resin.

On the other hand, increasing the PUR content results in the opposite effect. The joint-to-joint molecular weight increases and it climbs up to follow the growing PUR content in the composition.

Confirmation for the conclusions drawn can be found in the calculated values of the parameters, which characterize solvent transport into the network—diffusion coefficient,[10] sorption coefficient,[11] and permeability coefficient.[12] These values have been supported by the observational findings for the swelling process (Table IV).

The volume of nonsolvent absorbed by the compositions is closely related to the chemical constitution of samples. The higher the crosslinking density, the slower the nonsolvent diffusion is. Increased ST content in the system will reduce the absorbed volumes of nonsolvent, and finally it will bring them down to the minimum values specific for neat polyester resins. That makes the evidence for the absorption and diffusion of chlorobenzene inside the sample becoming harder and harder. The similar nature of changes in

TABLE III
Relative Change of Average Molecular Weight Between Crosslinks (δMc IPN) and Degree of Crosslinking (δνIPN) for IPN Systems With Different Chemical Compositions

Chemical composition		Polyurethane components used for IPN compositions							
		d2b		d2t		r3b		r3t	
Amount of ST in UP [wt %]	Amount of PUR in IPN [wt %]	$\delta M_{c\ IPN}$ [%]	$\delta \nu_{\ IPN}$ [%]	$\delta M_{c\ IPN}$ [%]	$\delta \nu_{\ IPN}$ [%]	$\delta M_{c\ IPN}$ [%]	$\delta \nu_{\ IPN}$ [%]	$\delta M_{c\ IPN}$ [%]	$\delta \nu_{\ IPN}$ [%]
10	10	140.7	−58.4	321.9	−76.3	329.3	−76.7	451.8	−81.9
	20	444.0	−81.6	556.3	−84.8	420.0	−80.8	1162.5	−92.1
20	10	11.3	−10.1	101.2	−50.3	9.3	−8.5	65.3	−39.5
	20	509.3	−83.6	416.6	−80.7	57.6	−36.6	703.2	−87.6
30	10	41.1	−29.1	68.1	−40.5	13.1	−11.6	11.4	−10.2
	20	275.1	−73.3	356.1	−78.1	153.7	−61.4	183.1	−64.7
40	10	22.3	−18.3	23.1	−19.4	35.0	−25.9	41.4	−29.3
	20	111.9	−52.8	226.1	−69.4	219.6	−68.7	217.8	−68.5

diffusion and sorption coefficients is observed when the amount of PUR in the system is reduced.

Diffusion of solvent into the polymer network can become even the opposite process in time, i.e., some condensed phases can undergo leaching out of the composition and the polymer fractions that are soluble under given conditions will be just dissolved. That is in particular probable in case of IPN compositions, which have been produced from linear PURs type d2b. The obtained SEM micrograms present two types of behavior for IPN composition samples under the

influence of chlorobenzene. These result directly from the type of sample morphology, and in particular its continuous phase.

The compositions with one-component matrices perform like polymers in glossy condition. The SEM microgram presented in Figure 6 shows that the penetrating solvent splits the sample into two layers: the swollen superficial layer and the core.

Chlorobenzene clearly increases the volume of the superficial layer that can result in gradual breaking away of the fragment located at the sample edges.

TABLE IV
Values of Diffusion Coefficient (D), Sorption Coefficient (S), and Permeability Coefficient (P) for IPN Systems With Different Chemical Compositions, Subjected to Swelling in Chlorobenzene

Chemical composition		Polyurethane components used for IPN compositions											
		d2b	d2t	r3b	r3t	d2b	d2t	r3b	r3t	d2b	d2t	r3b	r3t
Amount of ST in UP [wt %]	Amount of PUR in IPN [wt %]	$D \times 10^{-9}$ [cm^{2}s^{-1}]				S [g/g]				$P \times 10^{-10}$ [cm^{2}s^{-1}]			
10	10	2.191	3.338	2.755	4.666	0.318	0.287	0.318	0.309	6.97	9.58	8.76	14.42
	20	2.366	3.815	3.126	6.701	0.755	0.778	0.755	0.692	17.86	29.68	23.60	46.37
	30	–	–	6.193	9.225	–	–	0.359	0.345	–	–	22.23	31.83
20	10	1.372	1.802	1.665	4.046	0.147	0.222	0.190	0.201	2.02	4.00	3.16	8.13
	20	1.736	3.395	1.941	4.046	0.749	0.764	0.355	1.127	13.00	25.94	6.89	51.91
	30	–	–	4.436	–	–	–	0.327	–	–	–	14.51	–
30	10	0.618	0.665	1.303	3.625	0.115	0.134	0.116	0.087	0.72	0.892	1.51	3.15
	20	1.274	1.218	2.638	3.909	0.407	0.730	0.353	0.383	5.19	8.89	9.31	14.97
	30	–	–	3.211	–	–	–	0.278	–	–	–	8.911	–
40	10	0.355	0.255	0.449	2.311	0.040	0.041	0.110	0.090	0.14	0.10	0.494	2.08
	20	0.855	1.369	1.935	3.212	0.343	0.412	0.376	0.348	2.94	5.64	7.27	11.18
	30	–	–	–	–	–	–	–	–	–	–	–	–

Unsaturated polyester resin			
Chemical composition of UP/ST, [g/g]	$D \times 10^{-9}$ [cm^{2}s^{-1}]	S [g/g]	$P \times 10^{-10}$ [cm^{2}s^{-1}]
60/40	0.184	0.032	0.059
70/30	0.755	0.071	0.539
80/20	1.490	0.118	1.761
90/10	2.754	0.139	3.820

Figure 6 SEM micrograph of fracture surfaces of IPN 20**d2b**20 after reaching equilibrium (t = 580 h).
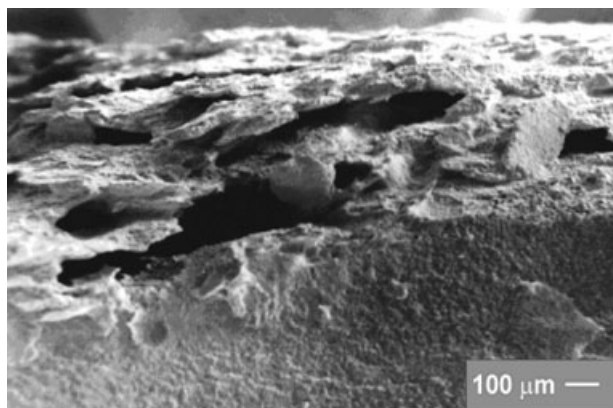

Figure 8 SEM micrograph of fracture surfaces of IPN 10**r3b**40 after reaching equilibrium (t = 170 h).

Similar behavior can be observed in case of "neat" UP resin that has been crosslinked with ST (Fig. 7). No changes have been observed in the structure of sample core (Fig. 8).

One can conclude from Figure 9 that the solvent is swelling the whole sample volume in case of IPN samples with two-component matrices. After a time needed to reach equilibrium, changes in the appearance of the matrix become apparent, but there are no differences visible in the morphology of condensed phases located deep inside, away from the surface.

Although the two-component matrix is not leached out completely, the matrix becomes less compact and numerous voids are present. The structure is formed which is nearly openwork.

CONCLUSIONS

The study of the kinetics of swelling and the sorption performance was found to be helpful for interpreting the supramolecular structure, which was observed by
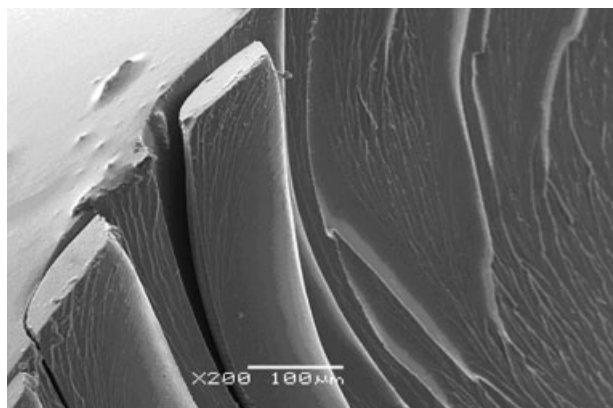
SEM technique. The experimental findings have confirmed that the studied polyurethane–polyester mixtures are typical IPN compositions. They form a structurally complex system composed of polyester resin crosslinked by covalence bonds and occluded macromolecules of linear or branched PUR. Despite limited miscibility of components in the studied IPN systems, which produces samples with heterogeneous phases, chlorobenzene basically does not leach out any separate phase. Hence, the phases must be interconnected, most probably through tangling of their chains and considerable physical interactions supported by dispersion phenomena.

It was found that the increasing share of ST in the IPN composition caused achieving the greater crosslinking density in the system while the higher the polyurethane content in the composition the larger molecular weight between crosslinks. The more compact the spatial structure of the formed IPNs is, the slower the solvent diffusion is, and the achieved levels of equilibrium swelling are lower. Increasing amounts of ST in IPN compositions slow down the sample

Figure 7 SEM micrograph of fracture surfaces of pure UP containing 40% styrene after reaching equilibrium (t = 320 h).

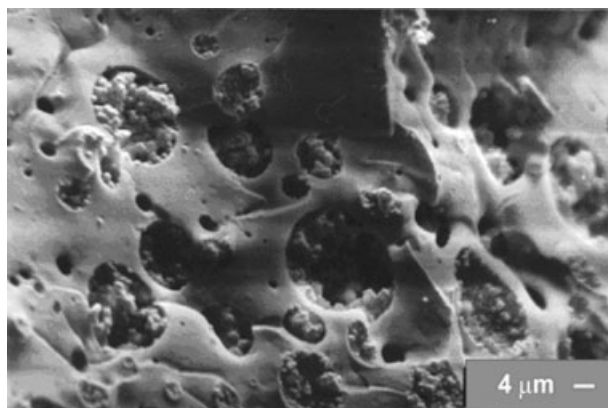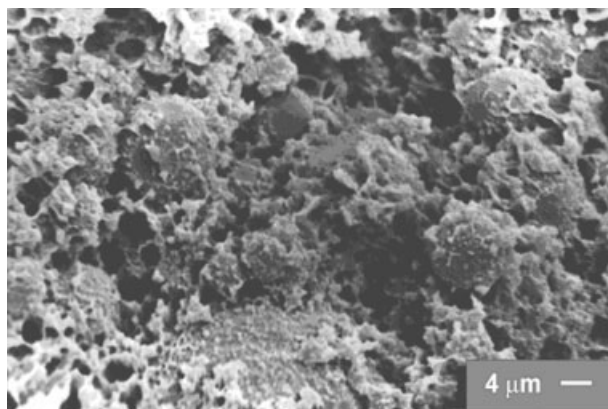**Figure 9** SEM micrograph of fracture surfaces of IPN 30**r3b**40 after reaching equilibrium (t = 408 h).

swelling process. The opposite effect is exhibited by the presence of PUR in the system.

It should be pointed out that the method of analysis of IPN, which was described above, is universal research procedure and it could be successfully use to appoint the structure of other multiphase crosslinked polymer materials. This tactics might be used as an auxiliary method for interpreting SEM micrograms.

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